Electronic Supplementary Material (ESI) for Dalton Transactions.

Donor-substituted phosphanes – surprisingly weak Lewis donors for phosphenium cation stabilisation

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Electronic Supporting Information

Synthetic Work

Solvents were purchased from Fisher Scientific. DCM was dried using an Innovation Technologies Benchtop Solvent Purification System and stored over activated molecular sieves. ^{n}Hexane and Diethyl ether were dried by reflux over sodium/benzophenone and stored over potassium mirrors. Anisole and ^{n}BuLi were purchased from Acros, N,N-dimethylaniline from Sigma Aldrich, and N,N-dimethylbenzylamine, Ph_2PCl, $PhPCl_2$ purchased from Alfa Aesar; Ph_2PCl and $PhPCl_2$ were distilled prior to use, the remainder were used without further purification. Sodium tetrakis(3,5-trifluoromethylphenyl)borate ($NaBAr^F$) was sourced from Matrix Scientific and washed with DCM prior to use. d2-DCM and $CDCl_3$ were purchased from Goss Scientific and distilled from CaH_2 and stored over activated 4 Å molecular sieves prior to use. Ortholithiation of anisole, N,N-dimethylaniline, and N,N-dimethylbenzylamine were performed according to literature methods.[1]

NMR spectra were recorded on a JEOL 400MHz NMR Spectrometer. Where deutro-solvent insert capillaries were used, the spectra were referenced to the appropriate residual solvent peaks.

Synthetic Work:

Donor Phosphine synthesis:

The donor substituted phosphanes below are well established in the literature as chelating ligands. In recent examples, **1a** has been shown to coordinate in a chelating mode to Ni[2], Rh[3] and Cu[4]; **1b** to Fe,[5] Ni,[6] Ru,[7] and Rh[8,9]; **1c** to Fe,[10] and Pd and Cu[11]; and **1d** to Ru[7] and Rh[9].

1a, **1b**, **1c** and **1d** were prepared according to the same general method *via* unoptimised syntheses using the appropriate aryl lithium and halophosphanes. The synthesis of **1b** is given as exemplar.
1b: Ph_2PCl (1.3 cm^3, 7.8 mmol) was dissolved in THF (10 cm^3) and cooled in a liquid nitrogen/acetone slurry. Ortho-lithiated N,N-dimethylaniline (1 g, 7.8 mmol) in THF (10cm^3) was added dropwise to the reaction mixture, and the whole was allowed to warm gradually to room temperature and stirred for a further hour, giving a straw coloured solution. The solvent was removed *in vacuo* and then the residue exhausted with DCM (2x5 cm^3). The yellow solution was filtered through a short silica plug to remove fine LiCl solids and the solvent removed *in vacuo.* The crude product was recrystallized from the minimum boiling ethanol – once cool, the ethanolic solution was stored at 4 °C. After five days, yellow crystals were isolated, washed with hexanes (5 cm^3) and dried *in vacuo* to give 1a as yellow needles (1.175 g, 50% yield)
1a, **1b** and **1d** were purified by recrystallization from boiling ethanol. **1c** was cleaned by heating into solution in ^{n}Hexane (3cm^3 per gram) and filtered before removal of solvent under prolonged vacuum – this was found to remove any polar or ionic impurities as well as trace benzylamine residues. The ^1H and ^{31}P NMR spectra were found to match literature values and they were used without further purification.

1a (66% yield)
^1H NMR (400MHz, DCM,20.2°C): δ = 7.38-7.23 (m, aromatic C-**H**, 11 H), 6.92 (dd, J=8.2Hz, 4.6Hz, aromatic C-**H**, 1H), 6.85 (t, J=7.3Hz, aromatic C-**H**, 1H), 6.66 (m, aromatic C-**H**, 1H), 3.73 (s, O**Me**, 3H)
^{31}P NMR(161.8MHz, DCM,20.2°C) : δ = 16.6

1b (50% yield)

^{1}H NMR (400MHz, DCM,20.1°C): δ = 7.37-7.19 (m, aromatic C-**H**, 12H), 6.99 (t, J=7.8Hz, aromatic C-**H,** 1H), 6.76 (ddd, J=7.3Hz, 3.7Hz, 1Hz, aromatic C-**H**, 1H), 2.60 (s, N**Me$_2$**, 6H)
^{31}P NMR(161.8MHz, DCM,20.1°C) : δ = -13.7

1c (73% yield)

^{1}H NMR (400MHz, DCM,20.5°C): δ = 7.44 (dd, J = 7.3Hz, 4.6Hz, aromatic C-**H**, 1H), 7.35-7.22 (m, aromatic C-**H**, 11H), 7.15 (t, J=7.3Hz, aromatic C-**H**, 1H), 6.92 (dd, J= 7.8Hz, 4.6Hz, aromatic C-**H**,1H), 3.60 (s, 2H, C**H2**-NMe$_2$), 2.01 (s, 6H, N**Me$_2$**)
^{31}P NMR(161.8MHz, DCM,20.5°C) : δ = -15.7

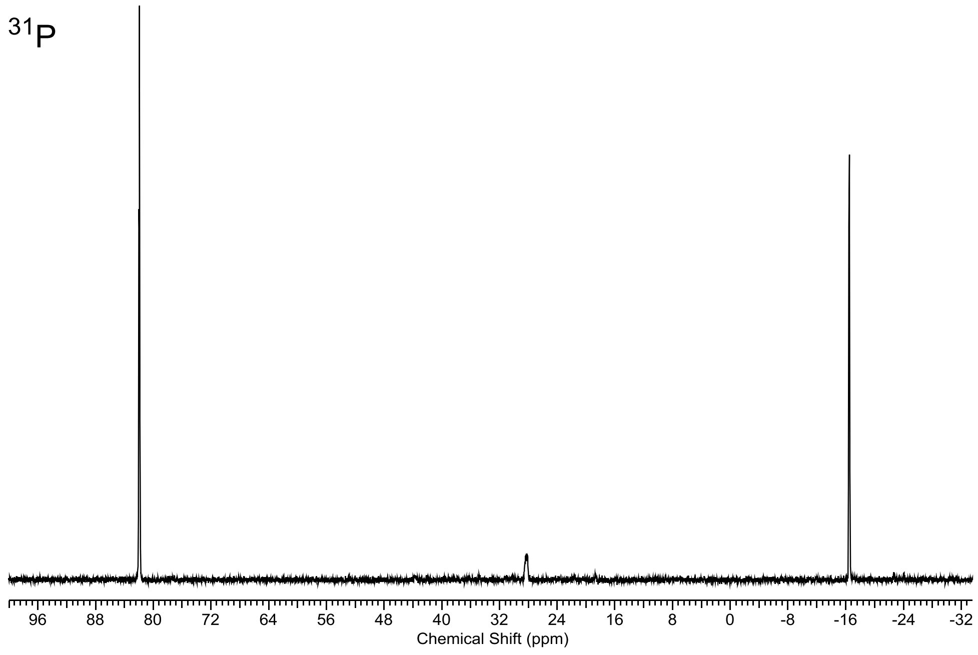
1d (29% yield)

^{1}H NMR (400MHz, DCM,20.1°C): δ = 7.34-7.26 (m, aromatic C-**H**, 5H), 7.22-7.12 (m, aromatic C-**H**, 4H), 6.96 (t, J=7.3Hz, aromatic C-**H**, 2H), 6.75 (ddd, J=7.8Hz, 3.2Hz, 1.8Hz, aromatic C-**H**, 2H), 2.65 (s, N**Me$_2$**, 12H)
^{31}P NMR(161.8MHz, DCM,20.1°C) : $\delta = -21.8$

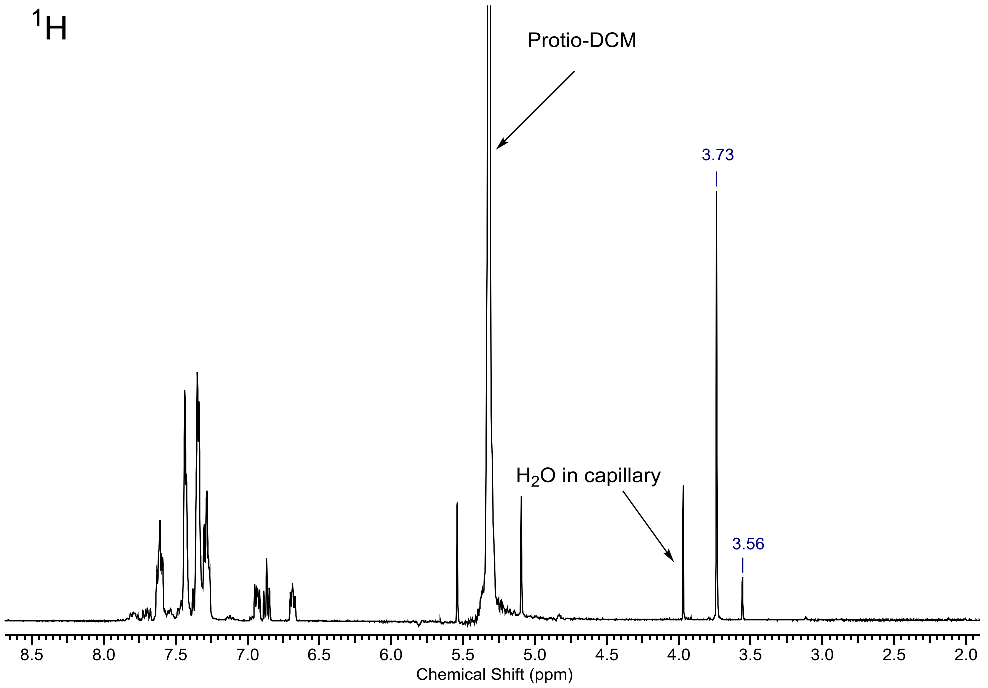
Direct reaction of donor phosphines with Ph_2PCl.

Reaction of 1a with Ph_2PCl, Formation of [2a]BAr^F

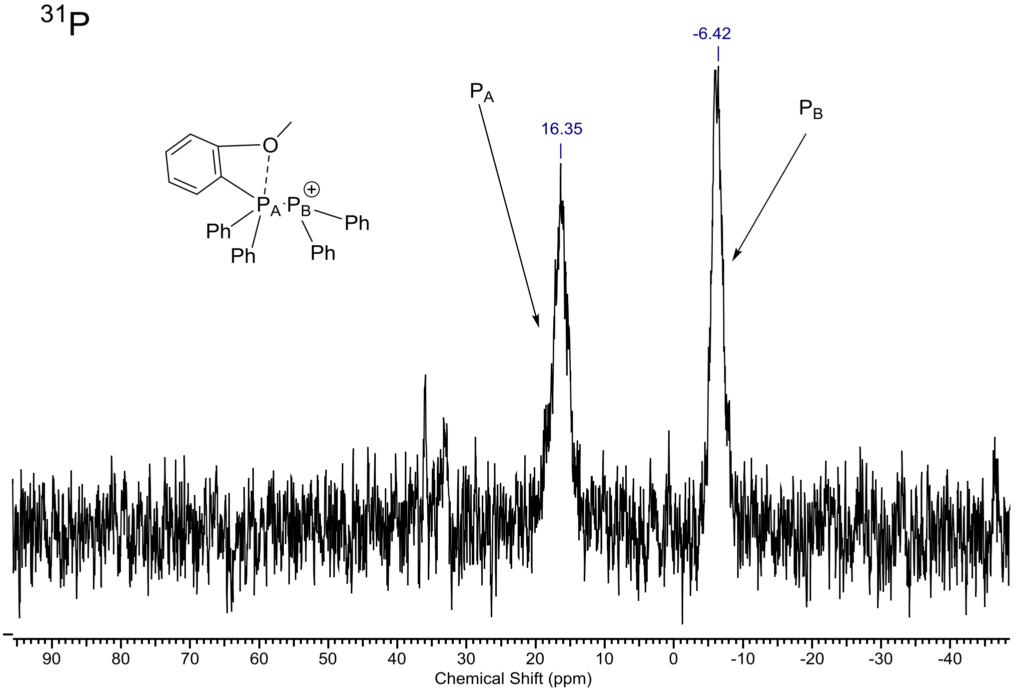
1a (29mg, 0.1mmol) was dissolved in DCM (0.8cm^3) in a J. Young's NMR tube fitted with a d6-DMSO capillary. Ph_2PCl (17µl, 0.1mmol) was added and the ^{1}H and ^{31}P NMR recorded. No new ^{31}P resonances can be unambiguously identified above the baseline (there is potential evidence for a doublet at approximately -23 ppm but no corresponding doublet can be located).



The ^{1}H NMR shows no shift in the OMe resonance for the phosphine.



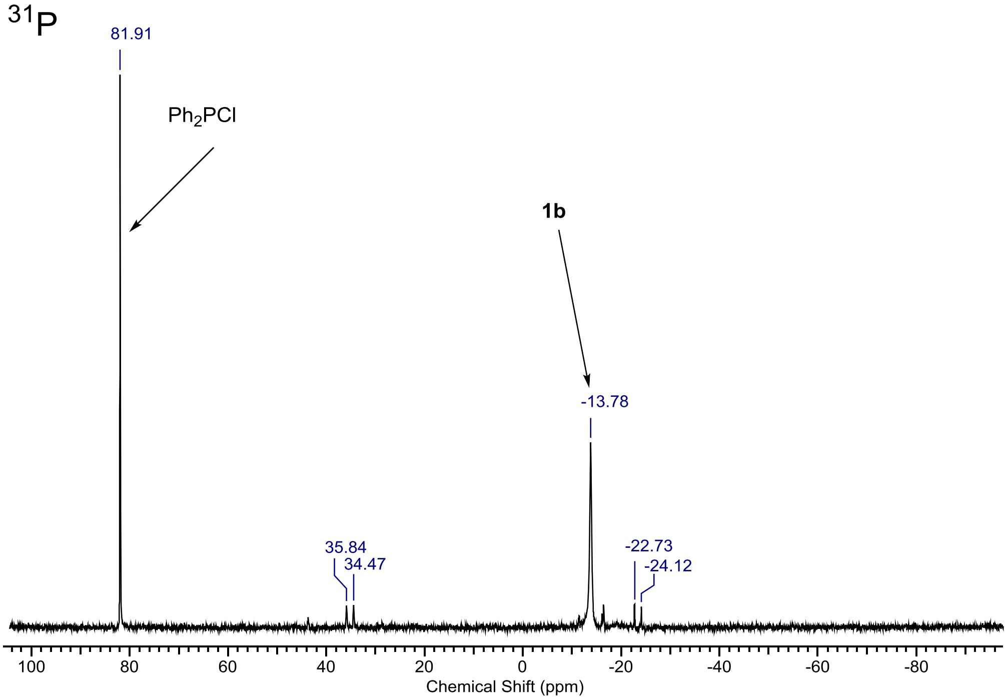
Upon addition of NaBAr^F, a pale precipitate formed immediately. The ^{31}P NMR spectrum shows only two major signals again corresponding to a phosphinophosphenium species, but no P-P coupling can be resolved, with two broad peaks at 16.4 ppm (fwhh = 380 Hz)and -6.4ppm (fwhh = 300 Hz).

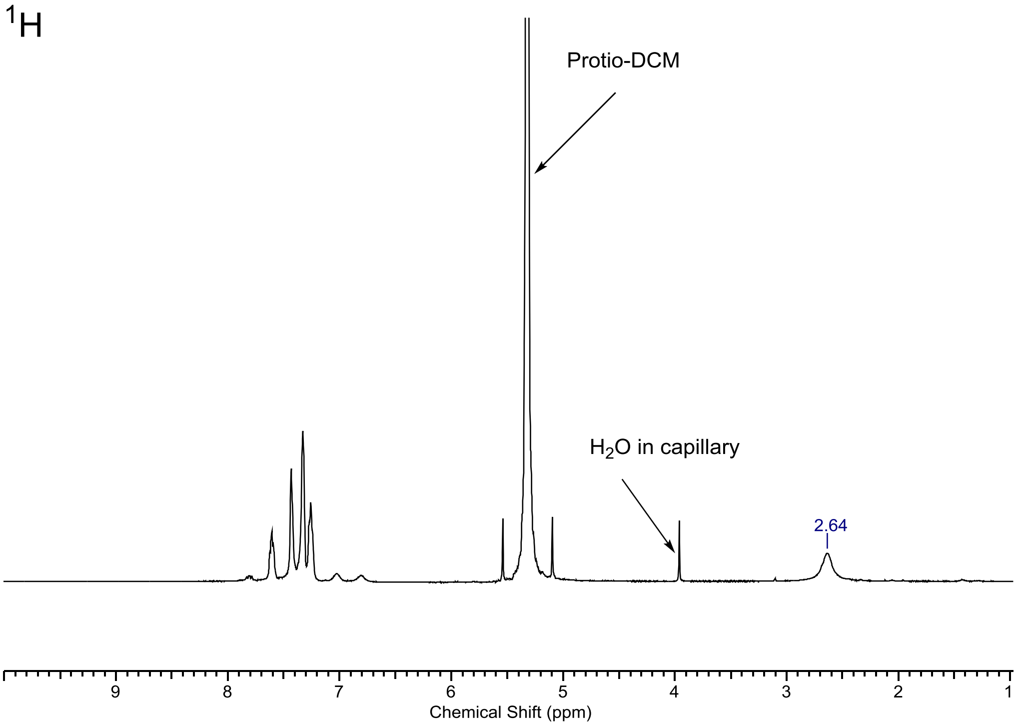


The reaction mixture was filtered and crystal growth attempted by slow diffusion of Et_2O or ^{n}hexane into the reaction mixture, but no solid products were isolated.

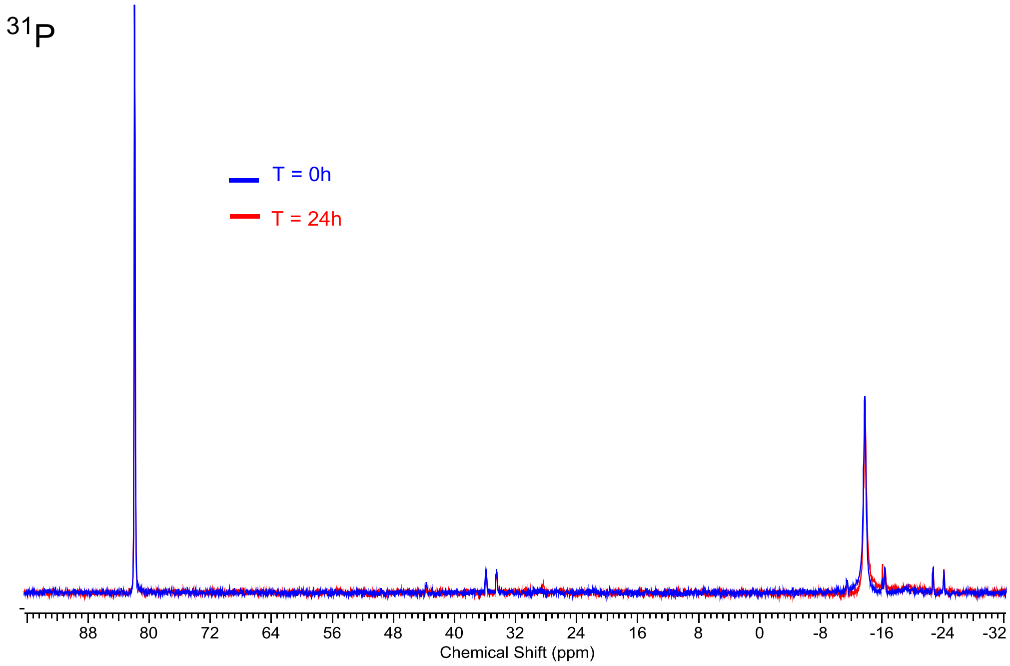
Reaction of 1b with Ph_2PCl, formation of [2b]BAr^F

1b (31 mg, 0.1 mmol) was placed in a J. Young's NMR tube charged with a d6-DMSO capillary and dissolved in DCM (0.8 cm^3). Ph_2PCl (17 µl, 0.1 mmol) was added, leading to a slight turbidity of the solution. ^{31}P NMR showed the formation of a pair of doublets at 35.2 and -23.4 ppm ($^1J_{P-P}$= 225 Hz) as trace impurities, indicating the formation of $Ph_2P(O)PPh_2$[12] due to trace H_2O presumably remaining from recrystalisation of the phosphane. The ^1H NMR shows that the signals for the NMe_2 peak broadened and shifted slightly downfield from 2.60 ppm in the free phosphane to 2.64 ppm.

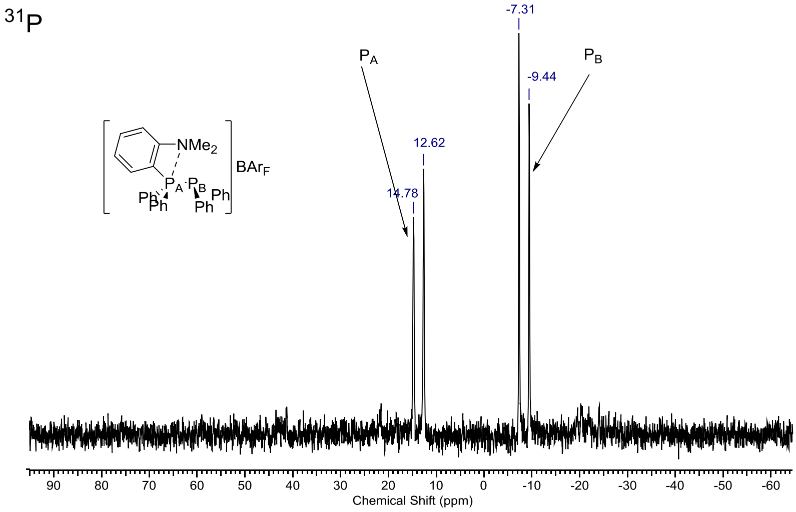




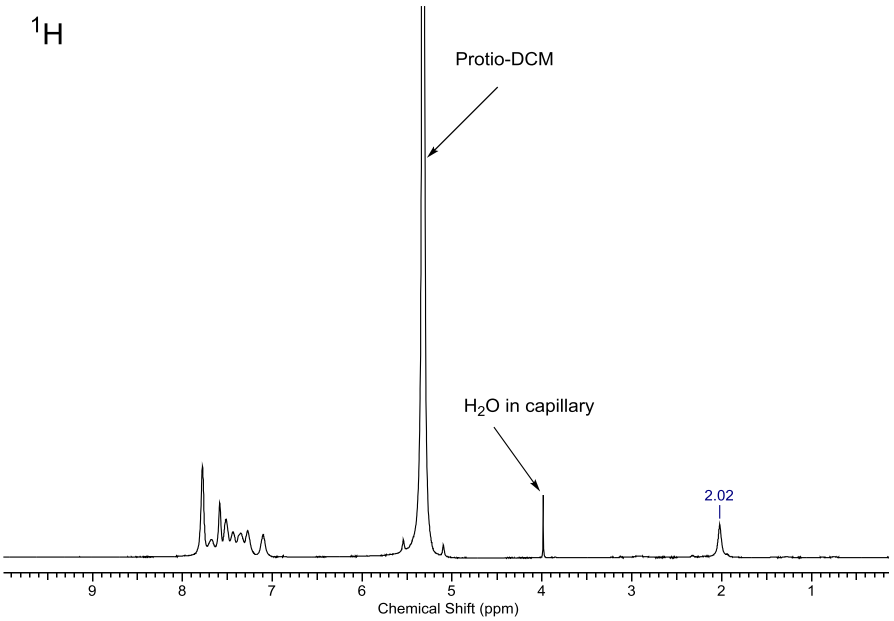
The reaction mixture was allowed to stand for 24 hours, and the spectra rerecorded – the ^{31}P is included to show that no further reaction occurred, although a small quantity of white solid (presumably poorly soluble $Ph_2P(O)PPh_2$) did settle out at the bottom of the NMR tube.



Upon addition of 1 equivalent of NaBAr^{F}, a fine precipitate developed (NaCl) and the ^{31}P spectrum changed significantly to show complete consumption of the starting materials and new P-P coupled species, giving a single product containing two coupled phosphorus environments in quantitative yield. ^{31}P NMR shows the formation of a pair of doublets at 13.7 and -8.4ppm ($^{1}J_{P\text{-}P}$=345Hz)



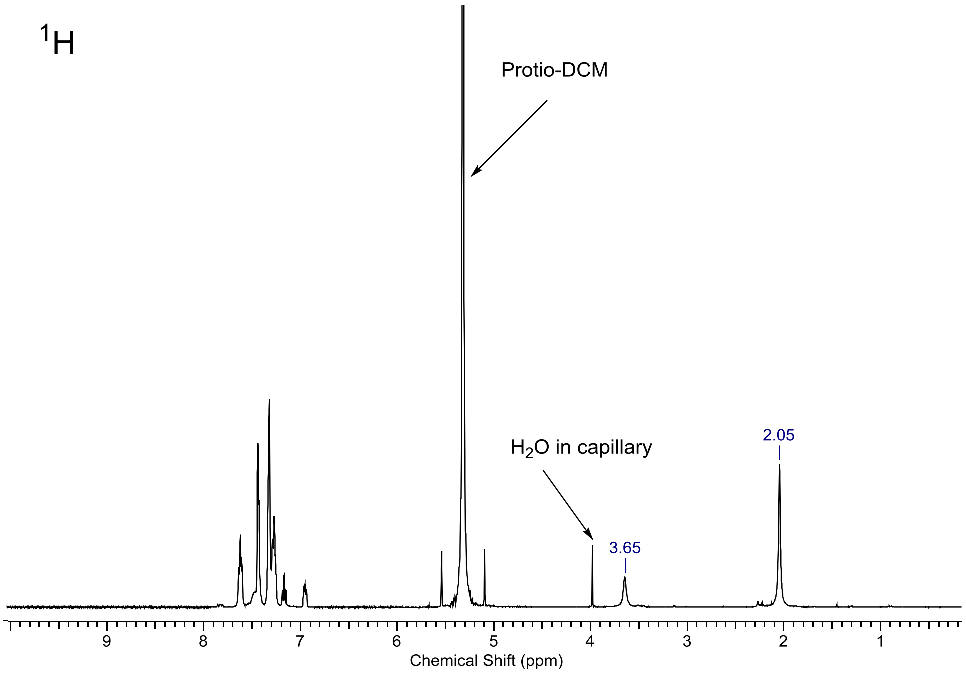
A similar change is visible in the ^{1}H where the NMe$_2$ resonance shifts upfield to 2.02ppm.

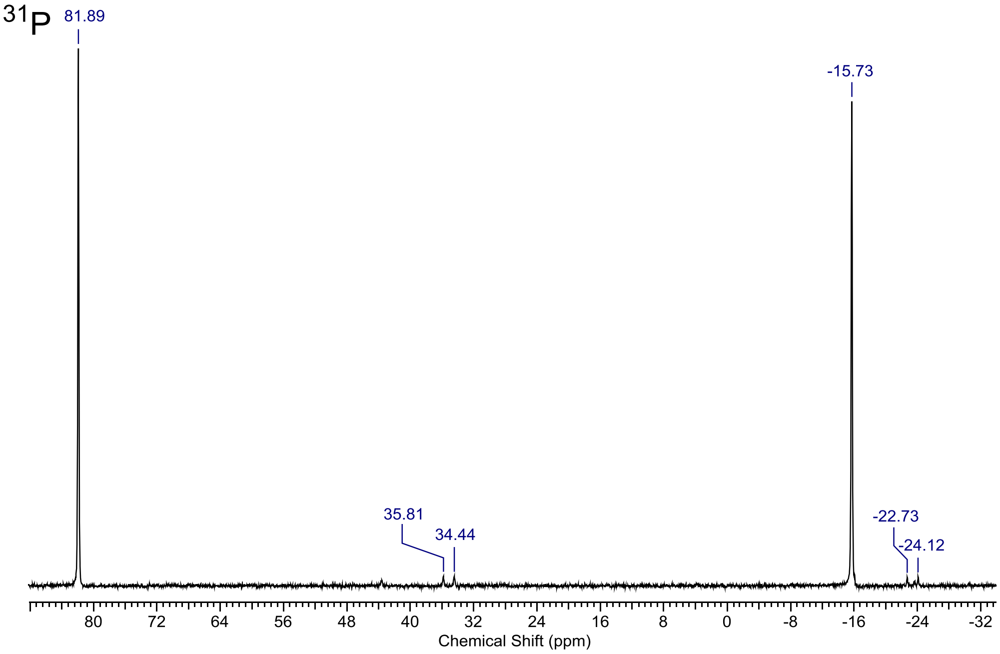


The reaction mixture was allowed to settle and the supernatant decanted into a J. Young's Schlenk. Crystal growth was attempted by slow diffusion of ^{n}Hexane or diethyl ether into DCM. No crystals were obtained, only decomposition products and a sticky oil.

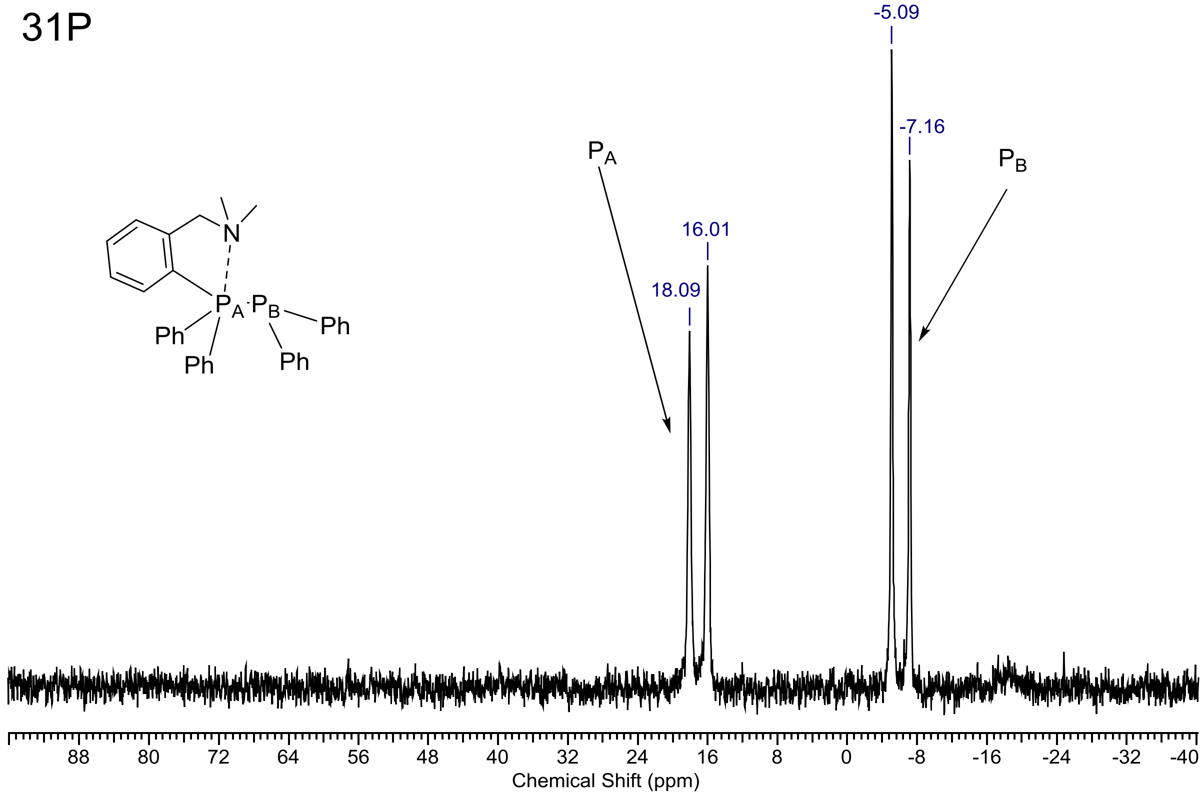
Reaction of 1c with Ph_2PCl, formation of [2c]BAr^F

1c (42mg, 0.14mmol N.B. **1c** is a viscous oil and so chosen as the limiting reagent in determining scale) was introduced to a J. Young's NMR tube fitted with a d6-DMSO capillary. Ph_2PCl (23µl, 0.014mmol) was added and the NMR spectra recorded. The ^1H NMR shows distinct changes in the benzylic and NMe_2 signals, both broadening. The benzylic peak shifts downfield to 3.65 ppm whilst the NMe_2 signals are downfield shifted to 2.05 ppm.

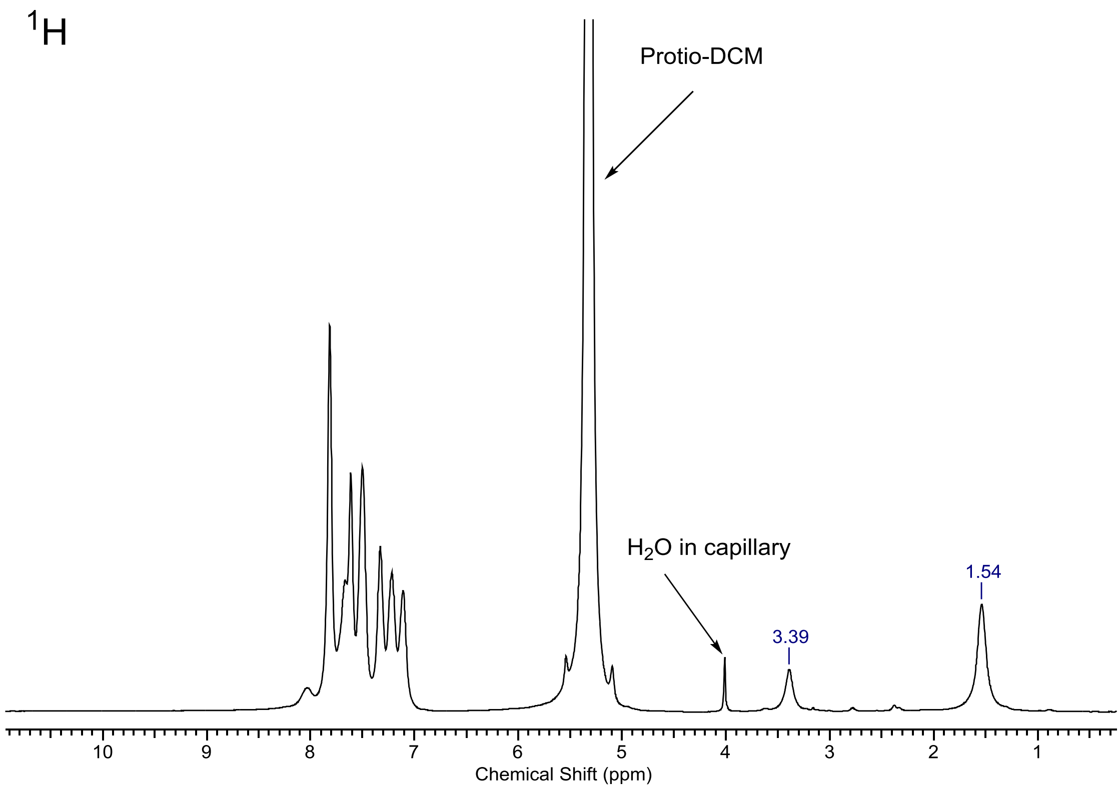




The formation of trace $Ph_2P(O)PPh_2$ is again visible. The nature of the trace impurities at 44ppm and 23ppm are unknown. Upon addition of 1 equivalent of $NaBAr^F$, a fine precipitate formed and once again total consumption of starting materials was observed; the ^{31}P NMR contains only two major resonances, corresponding to the desired phosphinophosphenium cation, with doublets at 17.0 ppm and -6.1 ppm, , $^1J_{P\text{-}P}$ = 335 Hz.



The reaction is reflected in the ^{1}H NMR by the benzylic protons shifting upfield to 3.39 ppm and the NMe_2 resonances shifting further upfield to 1.54 ppm.



The solution was allowed to settle and the supernatant decanted into a J. Young's tube. Crystals suitable for single crystal diffraction were grown by slow diffusion of ^{n}Hexane into the reaction mixture.

Targeted synthesis of [2c]BAr^F

A larger scale synthesis of [**2c**]BAr^F was performed to permit further analysis. **1c** (0.131 g, 0.41 mmol) and NaBAr^F (0.364 g, 0.41 mmol) were dissolved/suspended in DCM (10 cm^3). Ph$_2$PCl (73 µl, 0.41mmol) was added, resulting in rapid dissolution and formation of a fine precipitate. The reaction mixture was stirred for 20 minutes and then filtered through celite to remove insoluble ionic solids. The solution was concentrated under vacuum until solid began to appear and then warmed back to room temperature and all the solid had redissolved. ^{n}Hexane was then layered onto the reaction mixture, and large crystals grew by slow diffusion over 5 days. The crystals were isolated, washed with ^{n}Hexane (5cm^3) and dried *in vacuo* to give [**2c**]BAr^F (164mg, 0.12mmol, 29% isolated yield.)

^{1}H NMR (400MHz, CDCl$_3$,19.6°C) δ= 7.95ppm (m, aromatic C-**H**, 1H), 7.74 (s, BAr^F aromatic C-H, 8H), 7.71-7.60 (m, aromatic C-**H**, 4H), 7.53 (s, BAr^F aromatic C-**H**, 4H), 7.51-7.41 (m, aromatic C-**H**, 7H), 7.29 (t, J = 7.8 Hz, aromatic C-**H**, 4H), 7.13 (dd, J=12.4Hz, 8.2Hz , aromatic C-**H**, 4H), 7.03 (t, J=8.2Hz, aromatic C-**H**, 4H), 3.33 (s, C**H$_2$**-NMe$_2$, 2H), 1.51 (s, N**Me$_2$**, 6H).

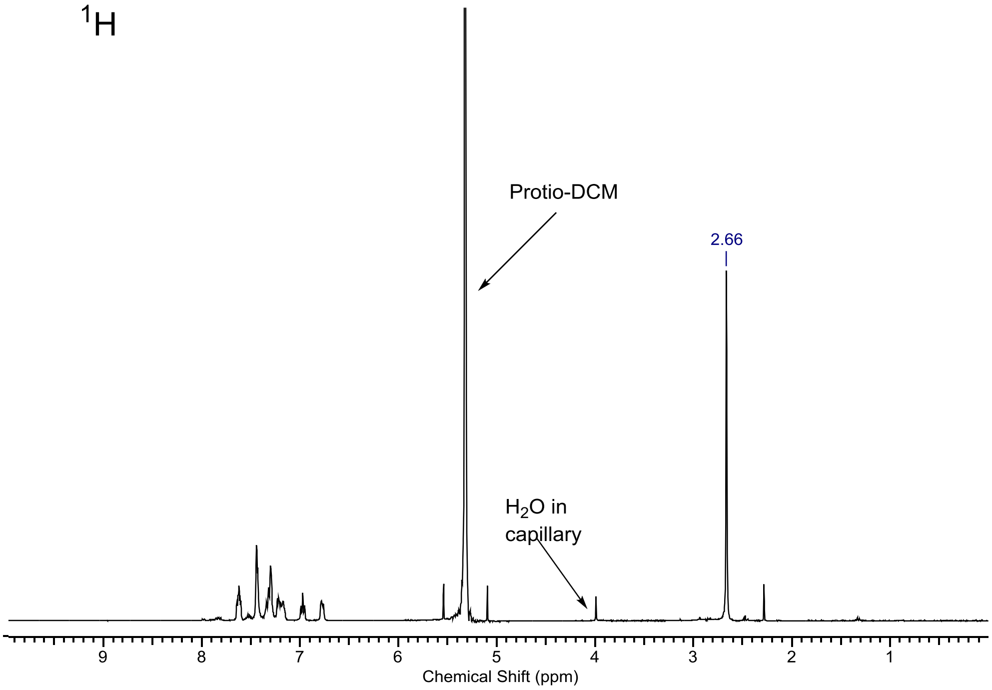
^{13}C NMR(100.5MHz, CDCl$_3$,19.7°C) δ=161.8 (1:1:1:1 q, $^1J_{C\text{-}B}$=50Hz, BAr^F), 136.8 (s), 135.2 (dd, $J_{C\text{-}P}$=23.3, 5.5Hz), 134.9 (s, BAr^F), 134.4 (s), 133.3 (s), 133.1 (d, $J_{C\text{-}P}$=10.0Hz), 132.6 (s), 129.9 (d, $J_{C\text{-}P}$6.8Hz), 129.8 (d, $J_{C\text{-}P}$=11Hz), 129.0 (q, $^1J_{C\text{-}F}$=30.1Hz, BAr^F),126.0(s), 123.2 (s, BAr^F), 120.6 (s), 120.2 (s), 117.6 (s), 63.1 (s, **C**H$_2$NMe$_2$), 44.0 (s, N**Me$_2$**)

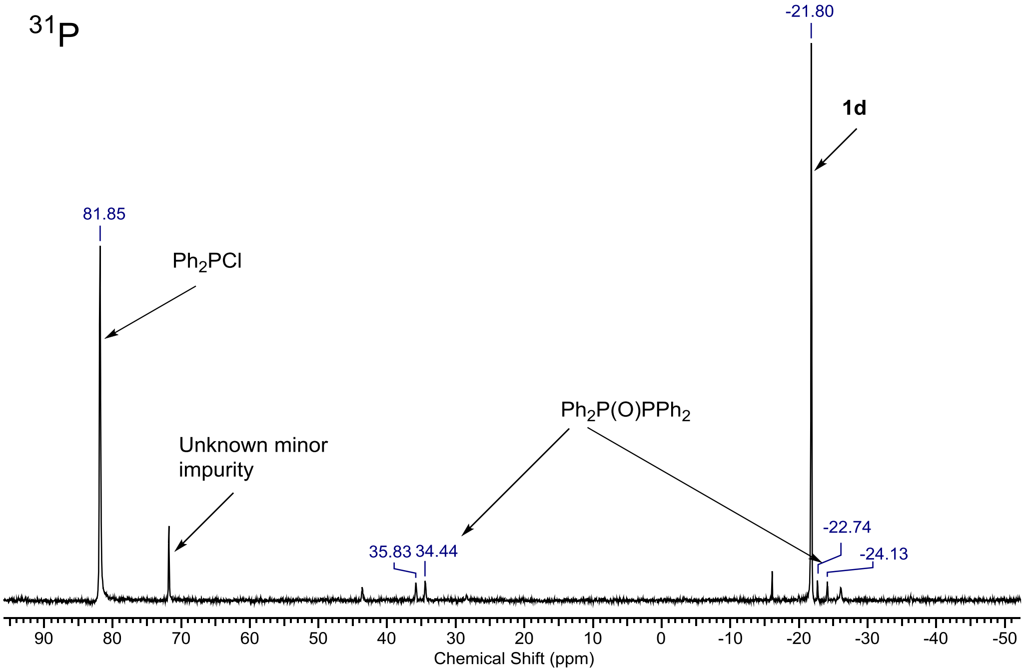
^{31}P NMR(161.8MHz, CDCl$_3$,19.4°C) δ=17.5 (d, $^1J_{P\text{-}P}$ = 335Hz), -5.3(d, $^1J_{P\text{-}P}$ = 335Hz).

Elemental Analysis: For $C_{65}H_{44}BF_{24}NP_2$, Calculated C 57.1, H3.24, N1.02. Found C56.9 H3.32 N1.04.

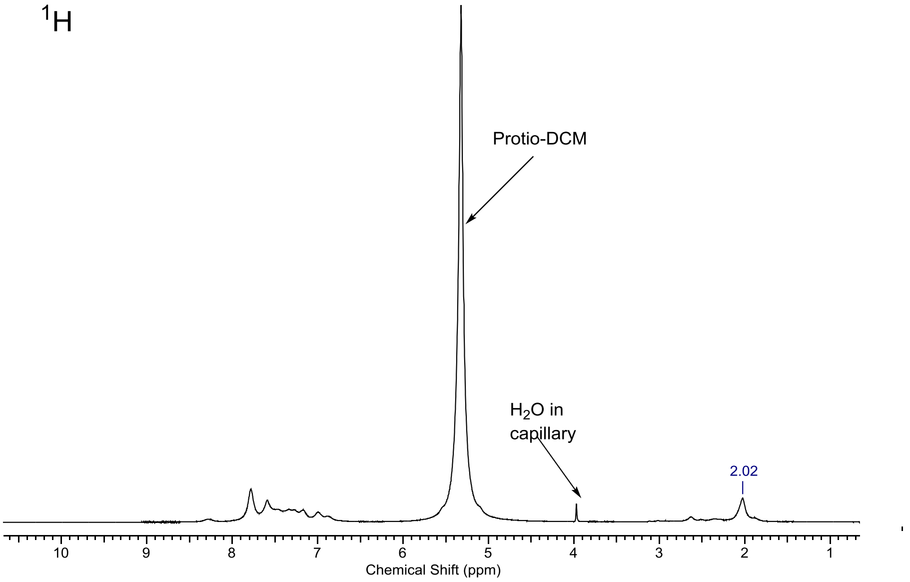
Reaction of 1d with Ph_2PCl, formation of [2d]BAr^F

1d (49mg, 0.14mmol) was dissolved in DCM ($0.8cm^3$) in a J. Young's NMR tube fitted with a d6-DMSO capillary, and Ph_2PCl (24µl, 0.14mmol) added. The ^1H NMR shows minimal significant change from that of the free phosphine.

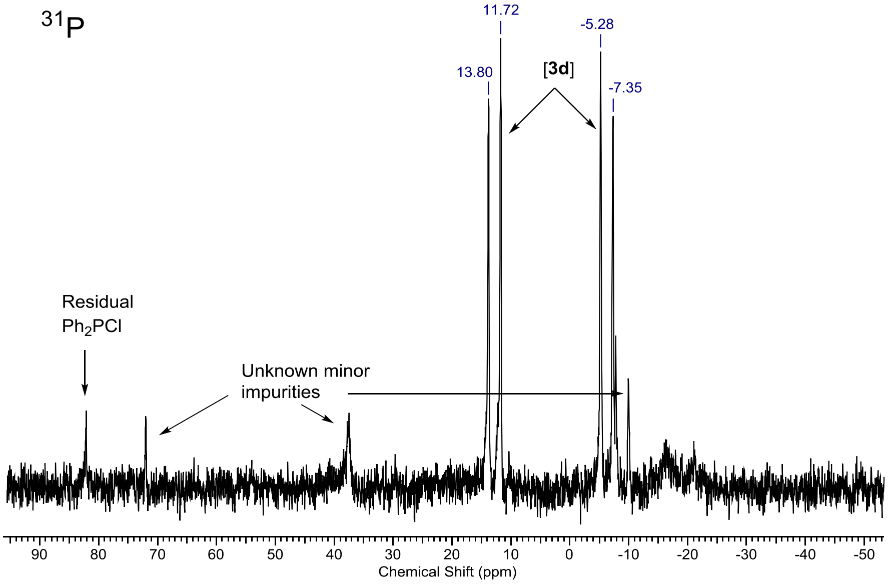




Upon addition of 1 equivalent of $NaBAr^F$, a small quantity of pale precipitate formed and began to settle out (NaCl). The solid resulted in very poor shimming for the ^1H NMR, so only broad peaks can be resolved, but the NMe_2 resonance clearly shifts to shift upfield to 2.02ppm, analogous to **1b**. Interestingly, only a single NMe_2 resonance is seen, indicating that either the structure adopted is symmetrical or, more likely, rapid dynamic exchange occurs between apical bound and equatorial NMe_2. This latter process might also contribute to the broad lineshapes observed.

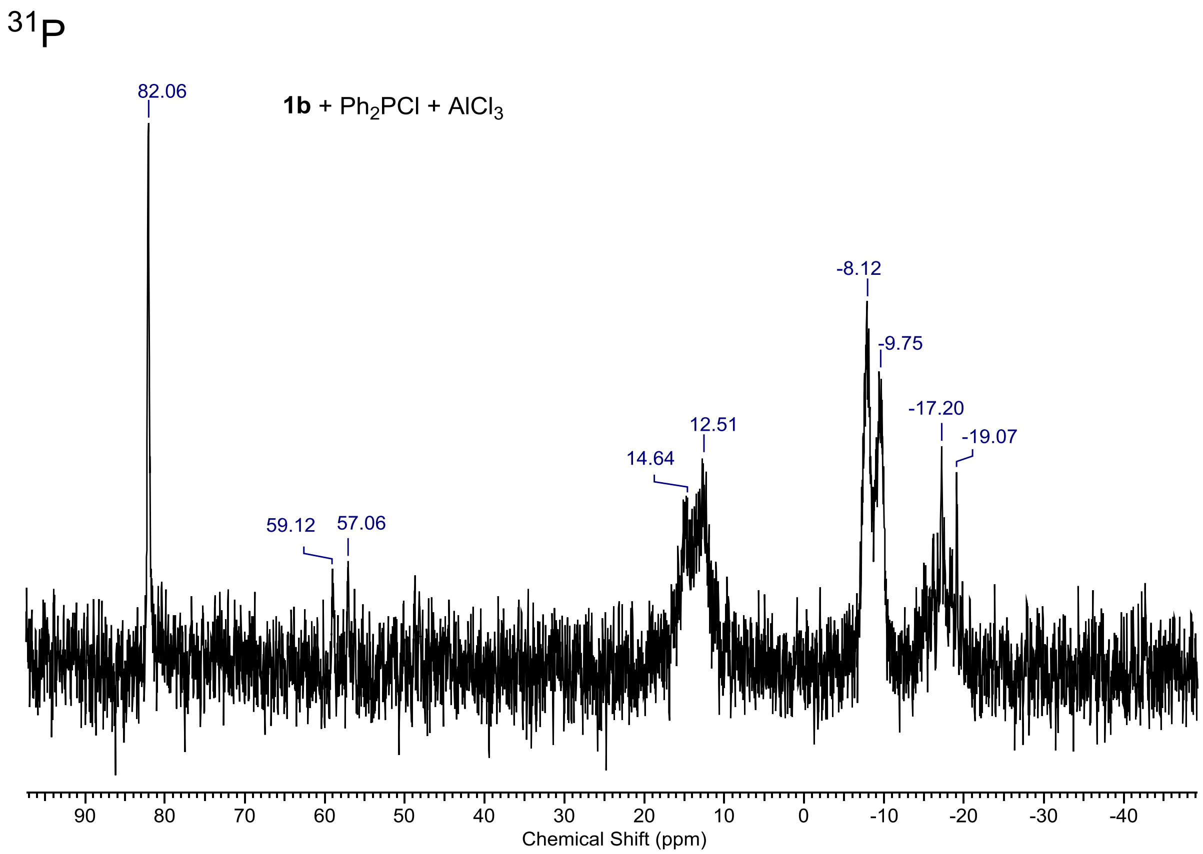


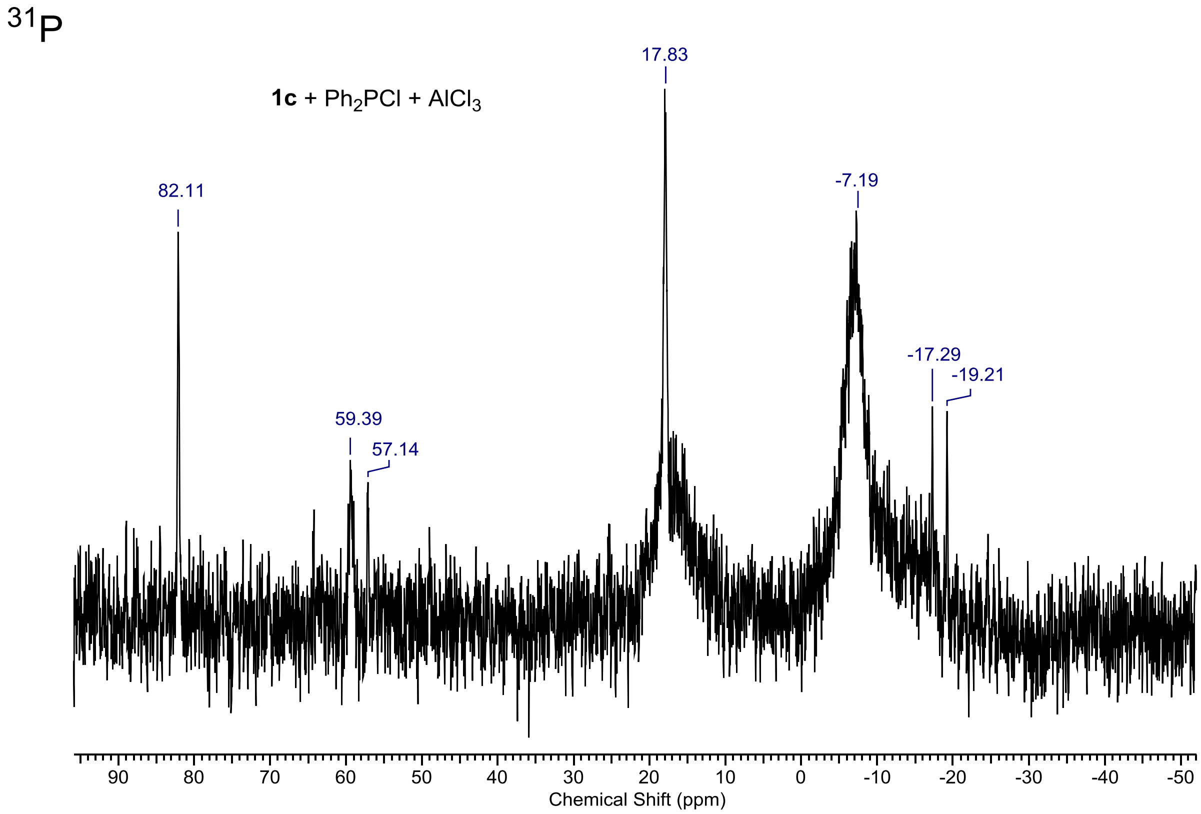
The ^{31}P NMR shows once more complete consumption of starting materials and two doublets indicative of the formation of [**3d**]BAr^F, centred at 12.8 ppm and -6.3 ppm, $^1J_{P-P}$ = 335 Hz. The supernatant was decanted and slow diffusion of hexane attempted to grow crystals, but only degradation products were isolated. Attempts with Et_2O diffusion were also unsuccessful.



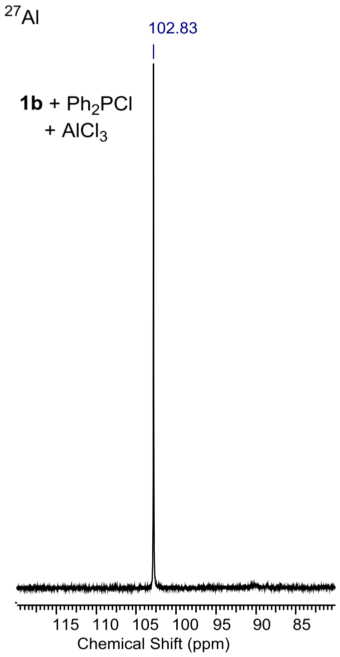
Attempted synthesis of $AlCl_4$ salts, [2b]$AlCl_4$ and [2c]$AlCl_4$

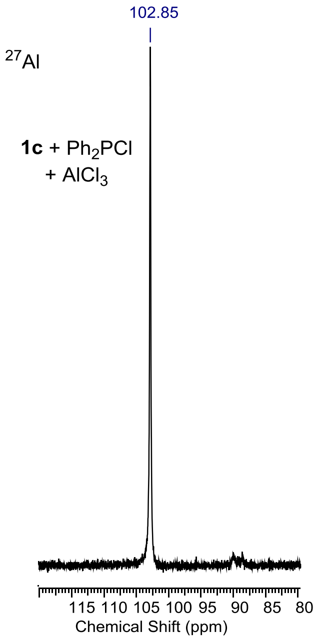
Reaction in a J. Young's NMR tube fitted with a d6-DMSO capillary of one equivalent each of either **1b**, Ph_2PCl and $AlCl_3$ (0.1 mmol scale) or **1c**, Ph_2PCl and $AlCl_3$ (0.51 mmol scale, triarylphosphane the limiting reagent) in DCM (0.8 cm^3) lead to complex mixtures as evidenced by the ^{31}P NMR.





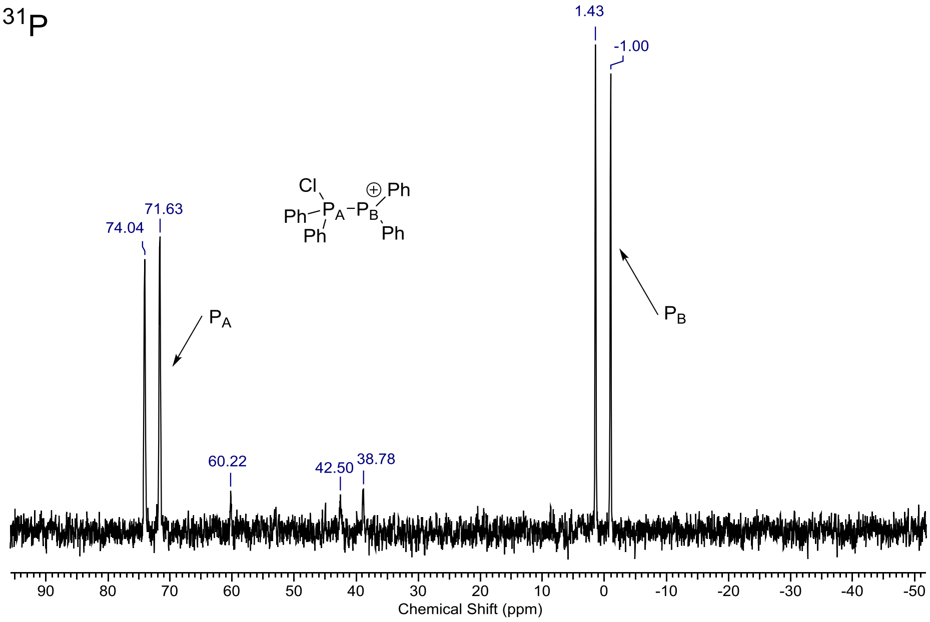
In both cases, the ^{27}Al NMR shows formation of $[AlCl_4]^-$ - the slight upfield shift from 104ppm indicative of equilibrium with $[Al_2Cl_7]^-$ arising from effective excess $AlCl_3$, explaining the residual Ph_2PCl visible in the ^{31}P despite initial 1:1 stoichiometries.

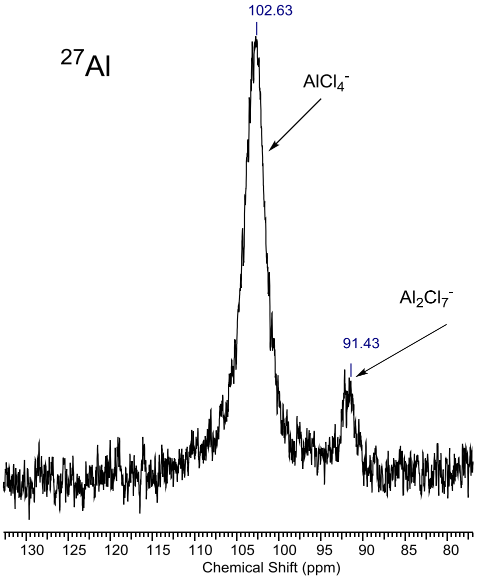




In neither case can clean signals corresponding to the expected tetrachloroaluminate salts be resolved, and despite careful stoichiometric control, there remain appreciable quantities of free Ph_2PCl. Nevertheless, broad signals can be seen where, for the BAr^F salts, well resolved doublets were previously obtained, as well as other minor features. We considered the possibility that, given equilibrium populations of free Ph_2PCl and $AlCl_3$, the homo-salt arising from Ph_2PCl acting as nucleophile might form, and performed an independent synthesis.

Ph_2PCl (17µl, 0.1mmol) was dissolved in DCM (0.8cm^3) in a J. Young's NMR tube charged with a d6-DMSO capillary and $AlCl_3$ (14mg, 0.1mmol) added, giving a clear solution. The ^{31}P shows clean formation of the desired phosphinophosphenium cation, with doublets at 72.8 ppm and and 0.2 ppm with $^1J_{P-P}$ = 390 Hz. The origin and nature of the minor impurities are not known. The ^{27}Al NMR spectrum shows broad singlets at 102.6ppm and 91.4ppm, indicative of exchange broadening between $[AlCl_4]^-$ and $[Al_2Cl_7]^-$.





Crucially, none of these doublets correspond to the signals seen in the attempted reactions with **1b** and **1c**. In the absence of any dynamic behaviour apparent in the ^{27}Al for the complex reaction mixtures, we conclude that a complex equilibrium must be in place. Attempts to crystallise [**2b**]$AlCl_4$ and [**2c**]$AlCl_4$ by slow diffusion of hexanes into the reaction mixtures produced only oily residues and no crystals were forthcoming.

in situ Synthesis of [2]OTf and [2]$GaCl_4$ salts

In light of the difficulty in isolating clean BAr^F salts for all but [**2c**]BAr^F despite the crystalline nature of the salts reported by Burford, the synthesis of the undertaken of the triflate and tetrachlorogallate derivatives. Once again, only degradation products could be isolated for the donor-functionalised systems despite the desired salts clearly forming in solution, despite [**2e**]OTf being isolated cleanly as a colourless crystalline solid.

General Synthesis of the Triflate Salts

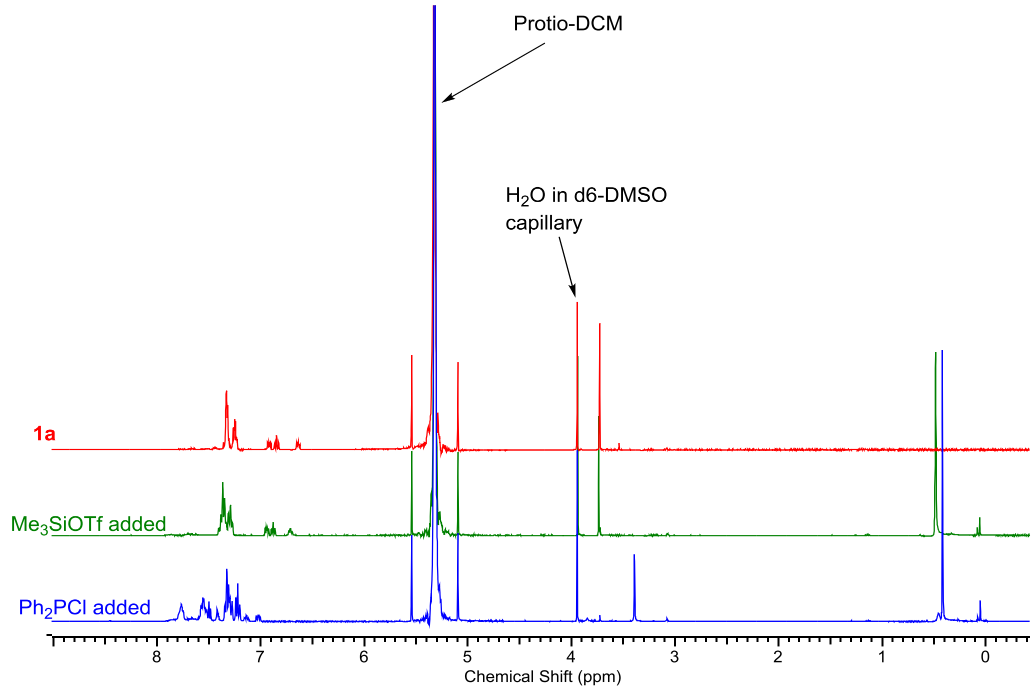
Phosphine **1** (1mmol) was dissolved in DCM (0.8 cm^3) in a J. Young's NMR tube fitted with a d-6 DMSO capillary. To this was added Me_3SiOTf (18 µl, 1mmol) followed by Ph_2PCl (18 µl, 1 mmol), with NMR spectra recorded at each stage. No colour change was observed but formation of [**2**]OTf was confirmed by ^{1}H and ^{31}P NMR (below), with concomitant formation of Me_3SiCl (δ0.43 ppm in the ^{1}H NMR). For the donor-functionalised systems, removal of solvent produced oily residues from which only degradation products could be found and no desired crystalline products could be isolated. Removal of solvent from [**2e**]OTf produced the literature compound as a colourless solid (see below).

Formation of 2aOTf

Upon addition of Me_3SiOTf to the solution of **1a**, the **1a**'s methyl resonance shows a very slight downfield shift (from δ 3.73 ppm to 3.74 ppm) and broaden, indicating a weak interaction. Upon addition of the Ph_2PCl, complete consumption of Me_3SiOTf is evident with formation of Me_3SiCl

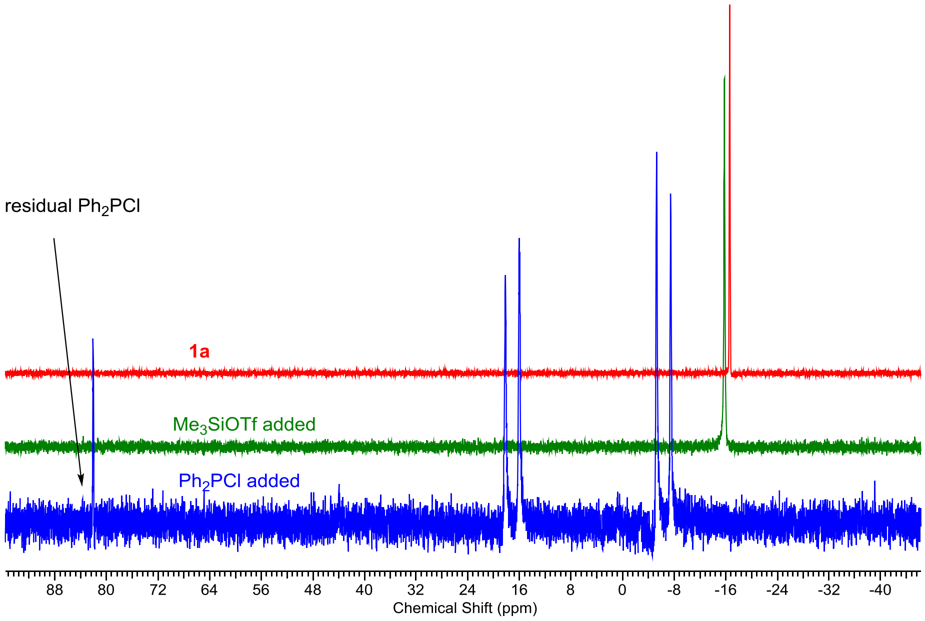
(0.42 ppm), and the methyl resonance moves upfield to δ3.39 ppm (*cf.* [**2a**]BAr^F, δ3.42 ppm)

^{1}H NMR for the formation of [**2a**]OTf



These changes are mirrored in the ^{31}P NMR spectra – on addition of the Me$_3$SiOTf, the phosphane resonance shifts downfield slightly (δ-16.6 ppm to δ-15.8 ppm). On addition of the Ph$_2$PCl, the formation of [**2a**]OTf is clearly seen by the two P-P coupled peaks (δ17.1 ppm and δ-6.4 ppm, $^1J_{P\text{-}P}$ = 355 Hz) (cf. [**2a**]BAr^F, δ16.4 ppm and δ-6.4 ppm). Interestingly, the P-P coupling can be clearly resolved for this system, but not for the equivalent BAr^F salt.

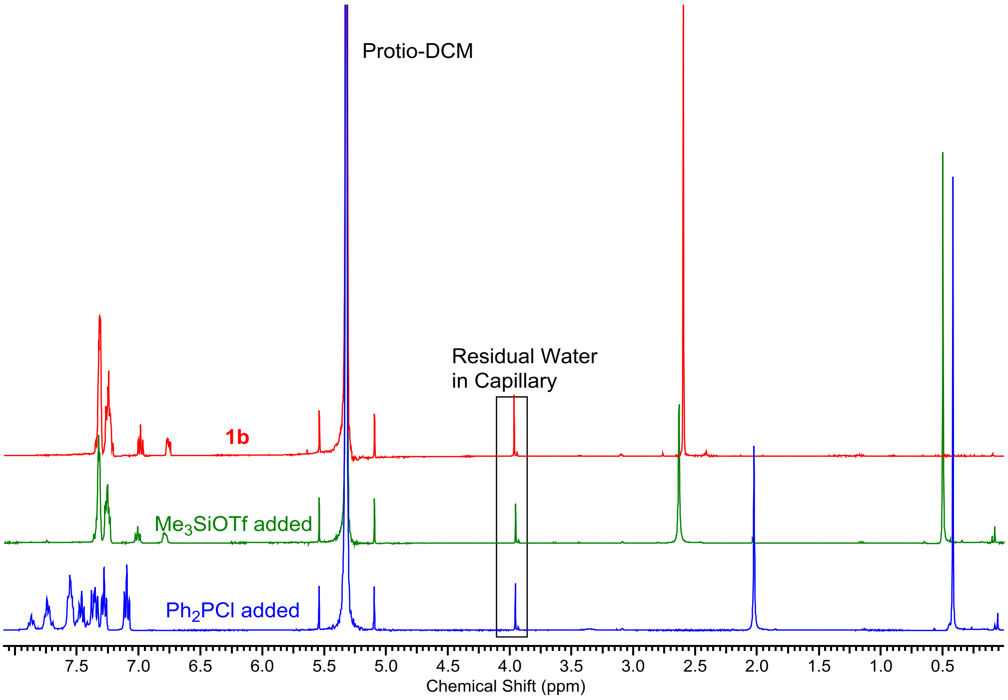
^{31}P NMR for the formation of [**2a**]OTf



Formation of [2b]OTf

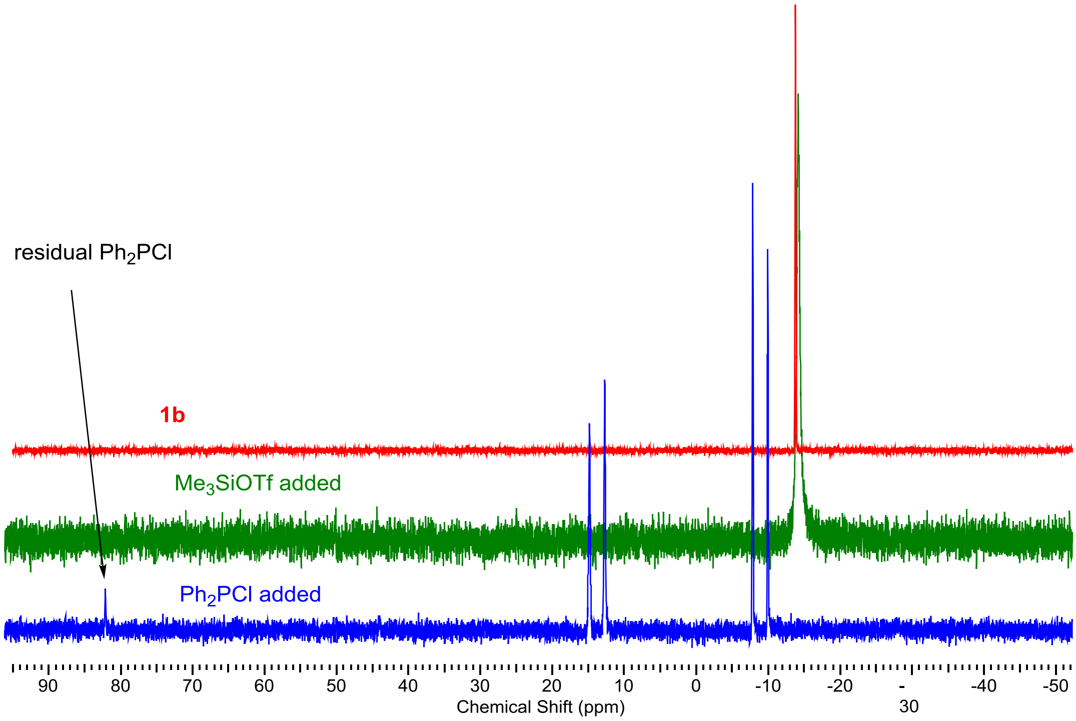
Upon addition of Me$_3$SiOTf to the solution of **1b**, the methyl resonances of **1b** also show a slight downfield shift (from δ 2.60 ppm to 2.63 ppm, larger than for **1a**)and broaden, indicating a weak interaction. Upon addition of the Ph_2PCl, complete consumption of Me_3SiOTf is evident with formation of Me_3SiCl (0.42 ppm), and the methyl resonances move upfield to δ2.02 ppm (*cf.* [**2b**]BAr^F, δ2.02 ppm)

^{1}H NMR Formation of [**2b**]OTf



Similar behaviour is observed by the 31P NMR. Upon addition of the Me3SiOTf, the signal for **1b** moves slightly upfield (from δ-13.8 ppm to δ -14.1ppm) and broadens. Upon addition of the Ph_2PCl (trace remaining in the spectrum), complete consumption of 1b occurs and the doublets of [**2b**]OTf clearly form at δ13.8ppm and δ-8.9 ppm ($^1J_{P-P}$ = 344 Hz), effectively identical to the BAr^F salt.

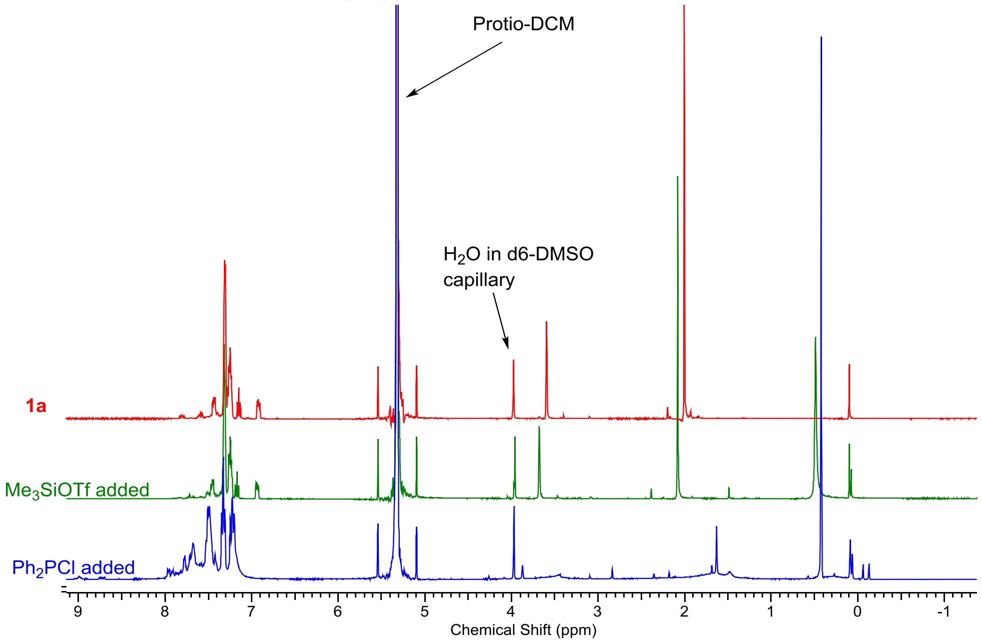
^{31}P NMR for the formation of [**2b**]OTf



in situ formation of [2c]OTf

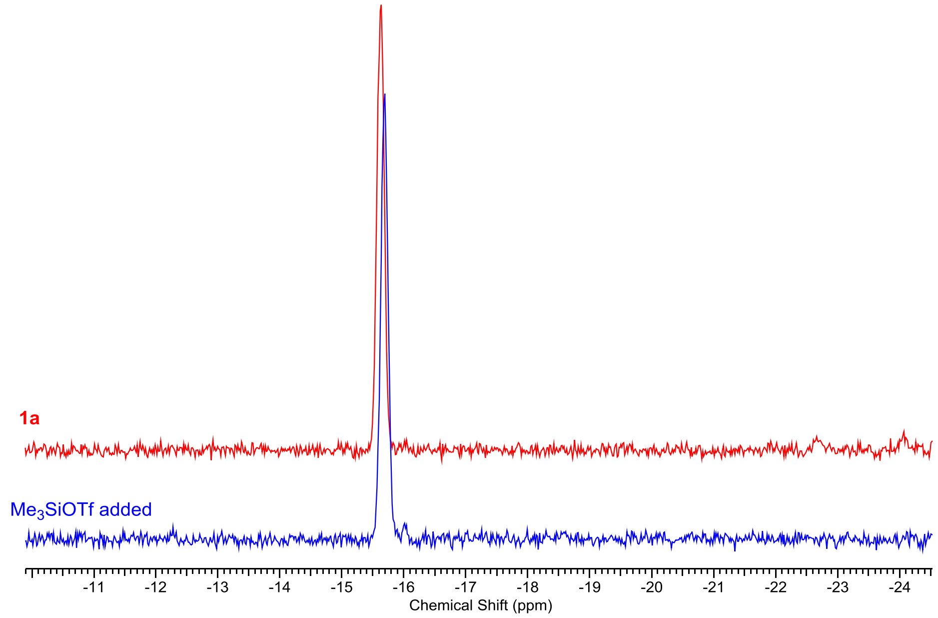
Somewhat surprisingly, given the facility with which [**2c**]BAr^F is formed and isolated, the equivalent triflate salt does not form cleanly or easily. On addition of Me_3SiOTf to **1c**, similar behaviour to **1a** and **1b** is seen, with downfield shifts of both the benzylic peak (δ3.59 ppm to δ3.68 ppm) and the methyl resonance (δ2.00 ppm to δ2.08 ppm). However, on addition of Ph_2PCl, the formation of Me_3SiCl is accompanied by almost total loss of sharp benzylic and methyl signals, and the formation of broad assymetric peaks visible as distortions of the baseline at approximately δ3.3 ppm and δ1.5 ppm, the expected peak positions of the [**2c**] cation, as well as multiple minor new unknown products

^{1}H NMR for the formation of [**2c**]OTf

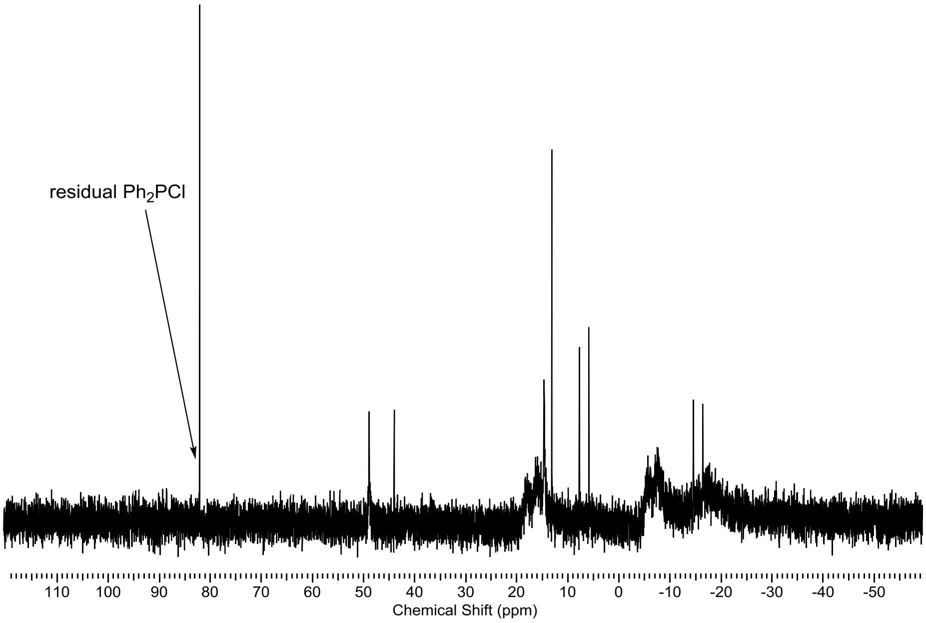


The ^{31}P NMR shows the same phenomenon, with tiny upfield shift of the phosphane resonance on addition of Me_3SiOTf (δ-15.7 ppm to δ-15.8 ppm), but broad unresolved signals after the addition of Ph_2PCl. Collecting many transients of the $^{31}P\{^1H\}$ NMR improved the signal to noise ratio sufficiently to show the formation of multiple unknown species. It must therefore be concluded that in this case, the triflate anion cannot be regarded as weakly coordinating, and that some subsequent reactivity must be being observed – the ^{19}F NMR of the reaction mixture shows only the expected singlet at δ-79.2 for the triflate anion, which implicates some rearrangement of the donor phosphane.

^{31}P NMR for the formation of [**2c**]OTf



^{31}P{1H} NMR of the reaction mixture to form [**2c**]OTf after addtition of Ph2PCl

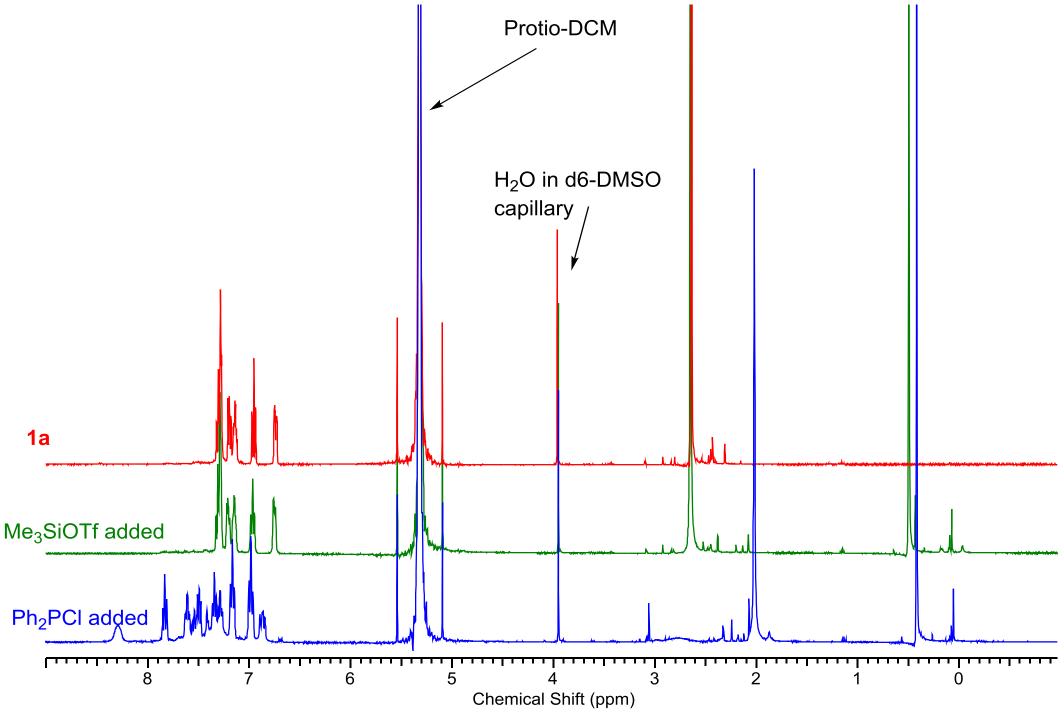


The broad doublets at δ~17 ppm and δ~-8 ppm are probably [**2c**]OTf in exchange with some other species such as the broad signal at δ~-18 ppm, but no pure solid materials could be isolated to allow definitive characterisation of the products.

in situ **Formation of [2d]OTf**

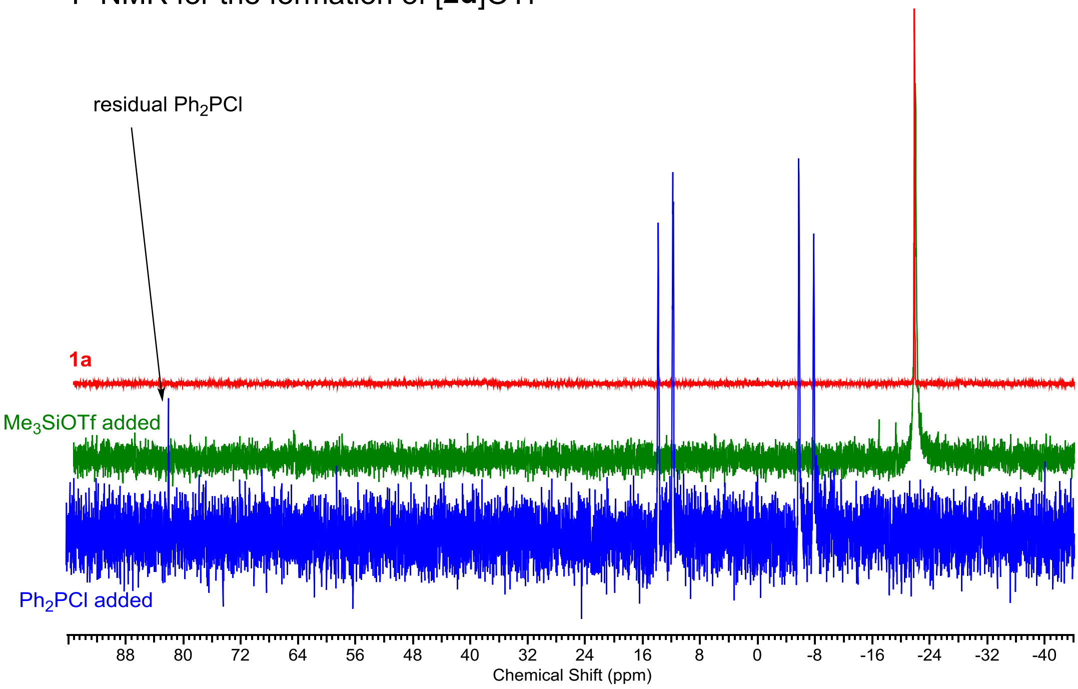
[**2d**]OTf forms in a manner analogous to [**2b**]OTf – the ^{1}H NMR shows a small downfield shift of the NMe_2 resonances (δ2.64 ppm to δ2.65 ppm) on addition of Me_3SiOTf, followed by an upfield shift to δ2.02 ppm (*cf.* δ2.02 ppm for [**2d**]BAr^{F}). No inequivalence of the methyl groups is observed, indicating either symmetrical binding or, more probably, rapid exchange on the NMR timescale.

^1H NMR for the formation of [**2d**]OTf



Similarly, the ^{31}P spectra shows the clear formation of two P-P coupled peaks following complete mixing of the three components, with signals at δ12.8 ppm and δ-6.8 ppm, $^1J_{P-P}$=331 Hz (*cf.* [**2d**]BAr^F at δ12.8 ppm and δ-6.3 ppm, $^1J_{P-P}$=335 Hz).

^{31}P NMR for the formation of [**2d**]OTf



Synthesis and isolation of [2e]OTf

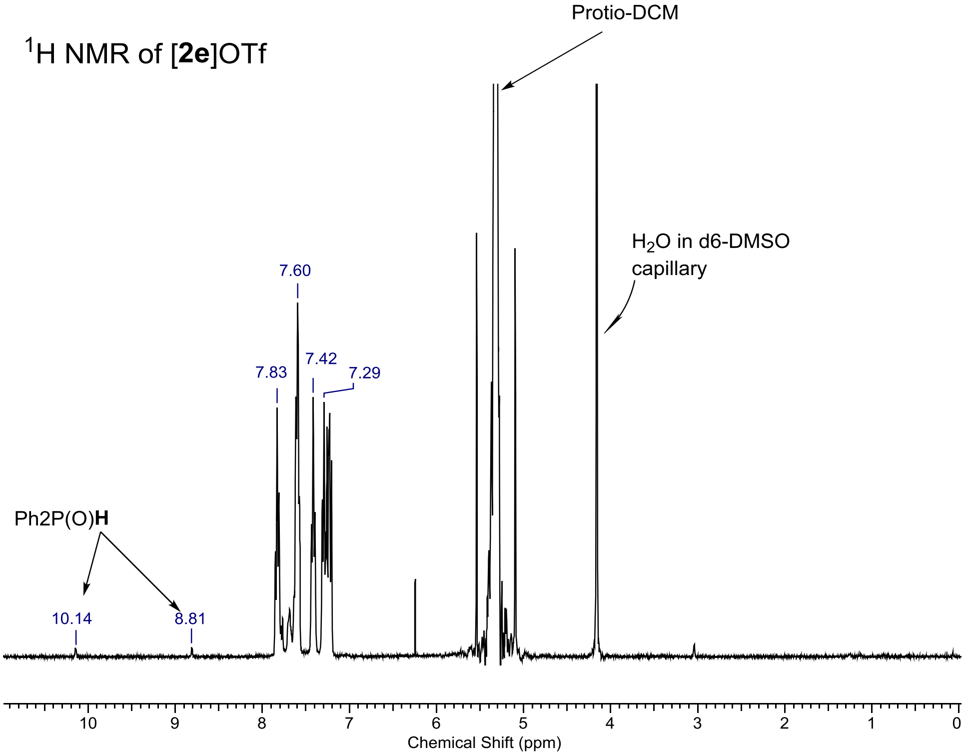
To a stirred solution of PPh_3 (140 mg, 0.55 mmol) in DCM (7.5 cm^3) was added Me_3SiOTf (97µl, 0.55 mmol) and Ph_2PCl (98 µl, 0.54 mmol). Hexane (15 cm^3) was then added forming a fine colourless precipitate that was isolated by filtration, washed with hexane (5 cm^3) and dried *in vacuo* to give [**2e**]OTf as a colourless solid (282 mg, 0.473 mmol, 88.5%). The NMR parameters were in good agreement with the literature, with broad peaks in the ^{31}P NMR which could nevertheless be resolved into broad doublets with an approximately 340 Hz coupling constant.[13] A small impurity of of $Ph_2P(O)H$ can be seen arising from *in situ* hydrolysis during sample preparation.

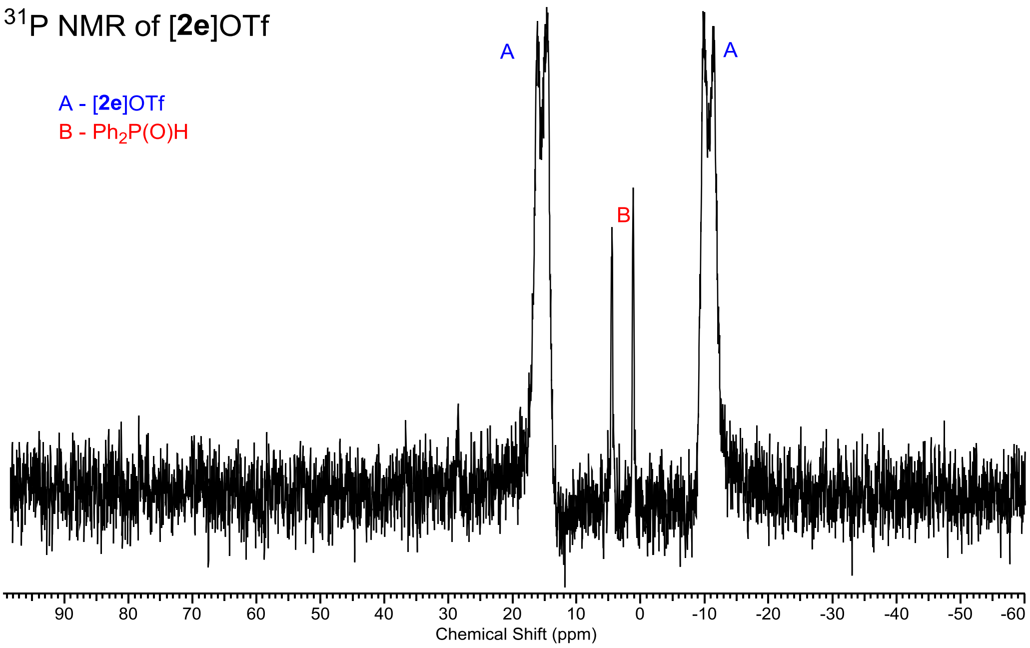
^1H NMR (400MHz, DCM, 18.7°C): δ = 7.83 (t, J = 7.5Hz, 4H), 7.60 (m, 8H), 7.42 (t, J=7.4Hz, 4H), 7.34-7.20 (m, 9H)

$^{31}P\{^1H\}$ NMR (161.83MHz, DCM, 18.7°C) : δ = 15.3 and -10.6 ($^1J_{P\text{-}P}$ ~ 340 Hz).

^{19}F (376MHz, DCM, 18.6°C) : δ =-79.3 ($[OTf]^-$).

Elemental Analysis: For $C_{31}H_{25}F_3O_3P_2S$, Calculated C 62.42, H, 4.22. Found C 60.45 H 4.23.



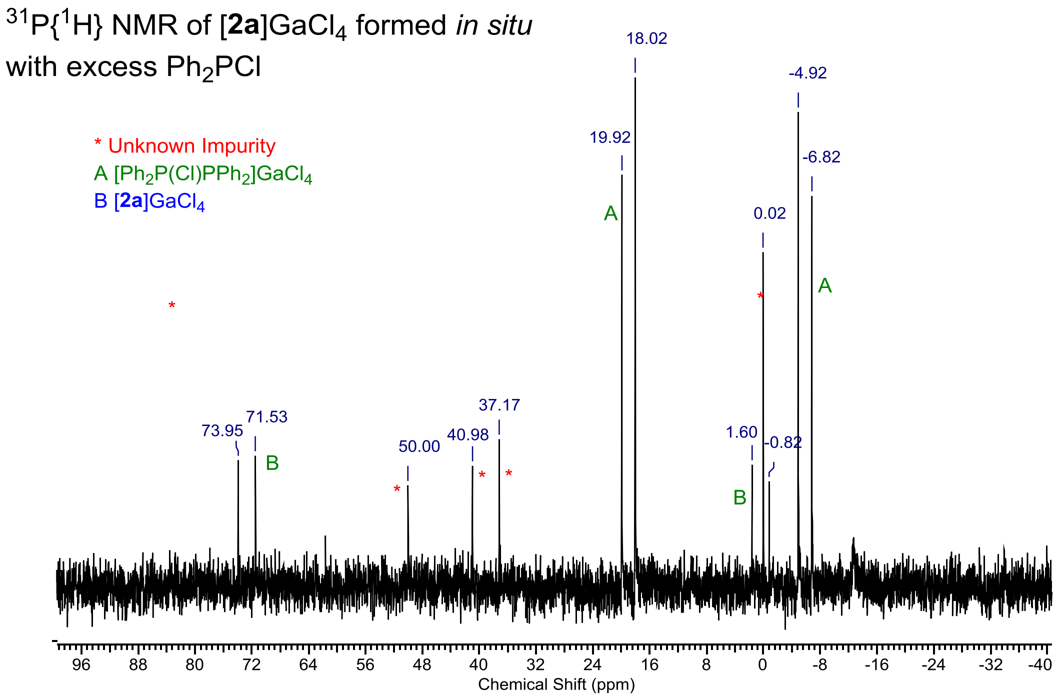


General Synthesis of the [GaCl4]⁻ Salts

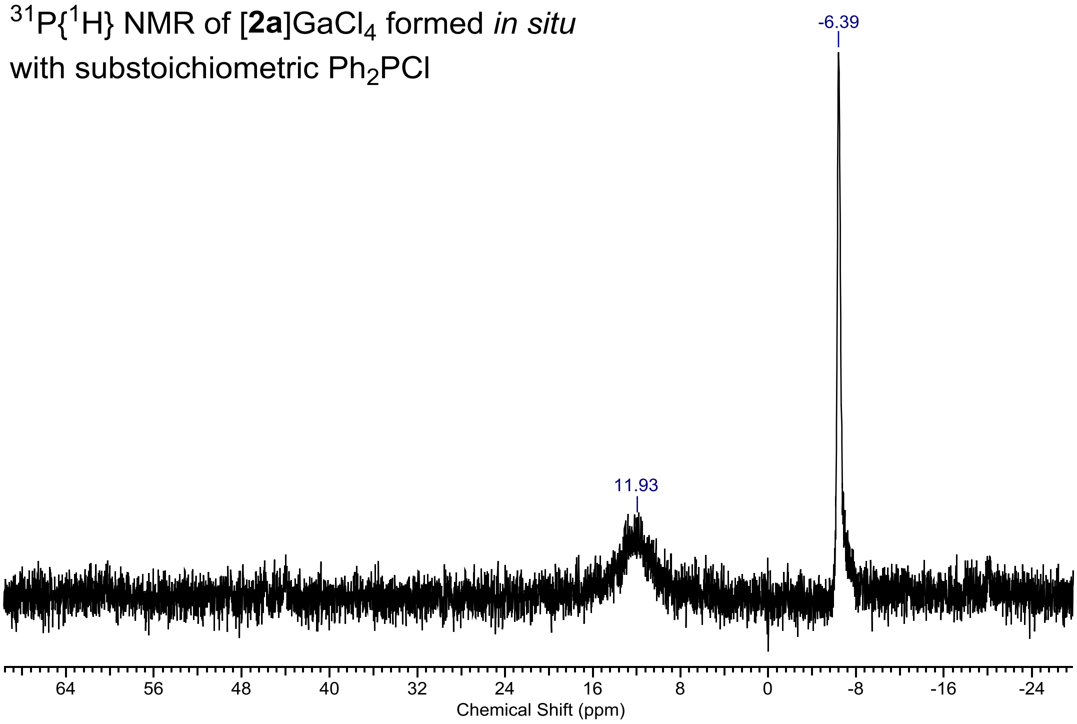
The tetrachlorogallate salts were all synthesised by the same generic method. Phosphane 1 (1 mmol) was dissolved in DCM (0.8 cm^3) in a J. Young's NMR tube fitted with a d6-DMSO capillary. To this was then added Ph_2PCl (18 µl, 1 mmol) followed by $GaCl_3$ (18 mg, 1 mmol) and the NMR spectra recorded. The reaction mixture was then layered with ^{n}Hexane and crystal growth attempted by slow diffusion. In no cases were solid materials isolated, with oily residues depositing from the reaction mixture.

in situ formation of [2a]$GaCl_4$

[**2a**]$GaCl_4$ forms under the described reaction conditions, with ^{1}H and ^{31}P NMR in broad agreement with the BAr^F and triflate salts. However, the formation is apparently extremely sensitive to changes in stoichiometry, with a reaction with an inadvertent slight excess Ph_2PCl showing the formation of of both [**2a**]$GaCl_4$ and $[Ph_2P(Cl)PPh_2]GaCl_4$ as well resolved pairs of doublets ([**2a**]$GaCl_4$: δ18.9 ppm, δ-5.8 ppm, $^1J_{P-P}$=307 Hz) and $[Ph_2P(Cl)PPh_2]GaCl_4$: δ72.7 ppm, δ0.4 ppm, $^1J_{P-P}$=391 Hz. Literature values[13] δ78 and δ3 ppm, with unresolved coupling emphasising the sensitivity to equilibrium phenomena), whilst limiting the addition of Ph_2PCl to 0.95 equivalents lead instead to the formation of two broad singlets.



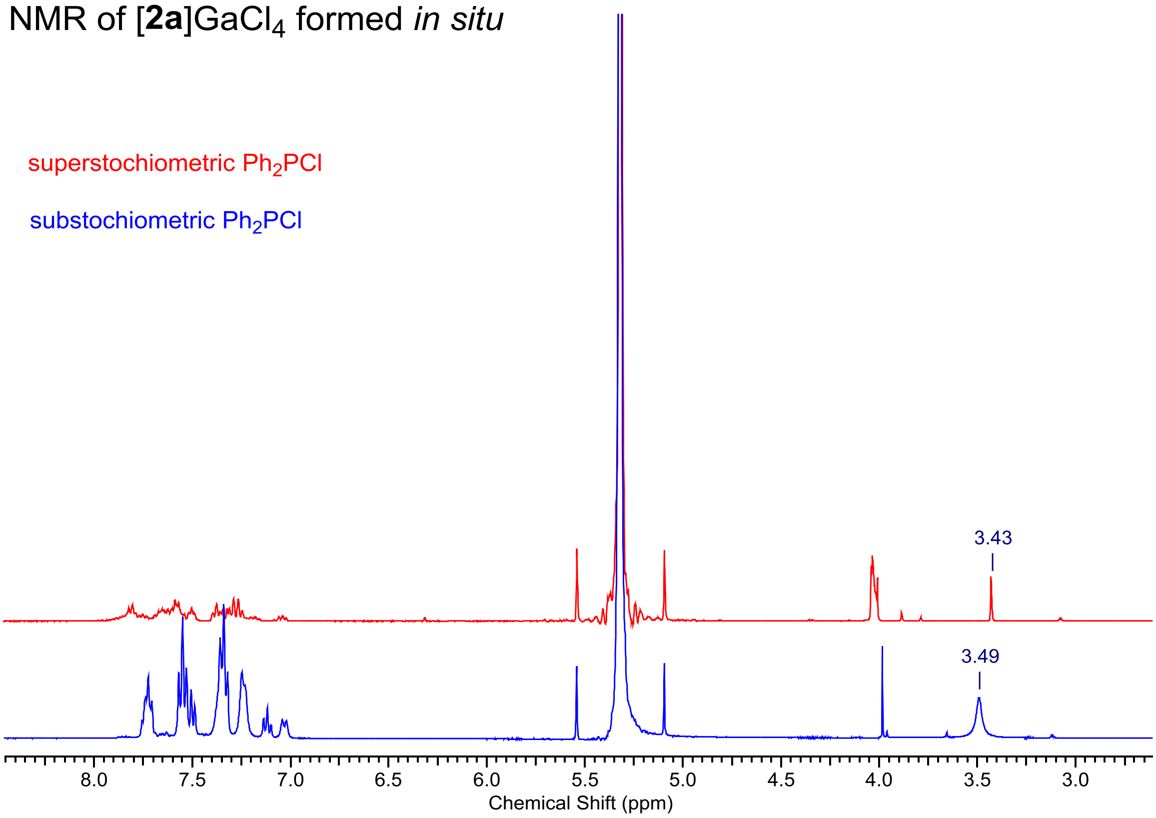
$^{31}P\{^1H\}$ NMR of [**2a**]$GaCl_4$ formed *in situ* with excess Ph_2PCl



$^{31}P\{^1H\}$ NMR of [**2a**]$GaCl_4$ formed *in situ* with substoichiometric Ph_2PCl

As might be expected, the ^1H NMR for the the superstoichiometric reaction is very complicated in the aromatic region, but comparison of the aliphatic regions of the spectra is informative. The OMe resonance for the superstoichiometric system is a sharp signal at δ3.43 ppm, whilst that of the substoichiometric reaction mixture is downfield at δ3.49 ppm. This is consistent with the substoichiometric spectrum, in which no free **1a** is observed, arising from a rapid dynamic exchange between free and bound **1a** and leading to the time averaged chemical shift for the methoxy protons between free and bound states, and the loss of P-P coupling.

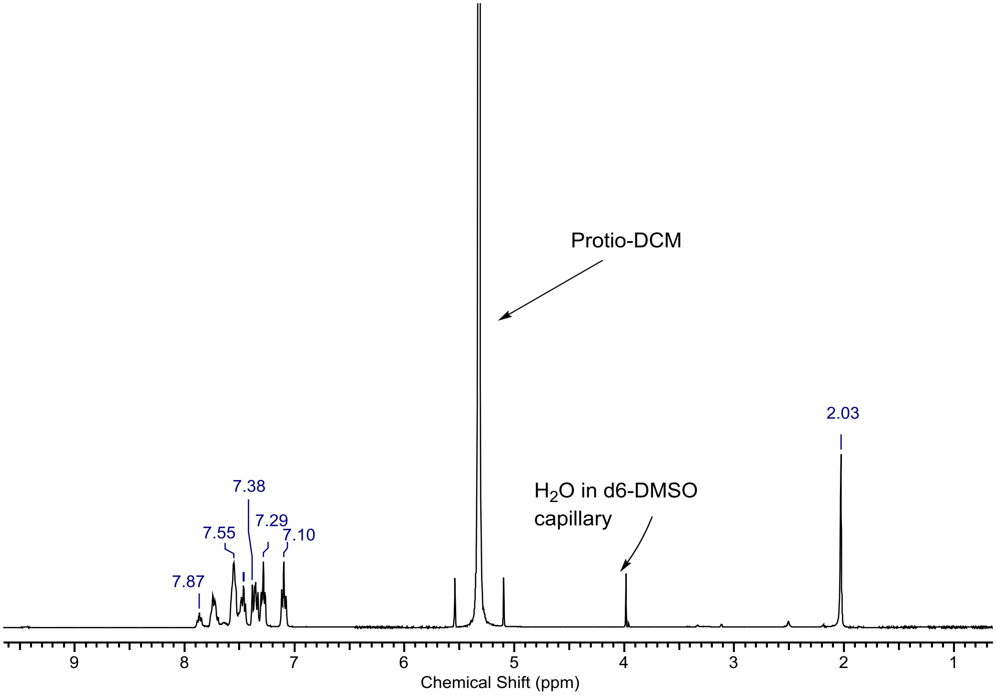
^{1}H NMR of [**2a**]$GaCl_4$ formed *in situ*

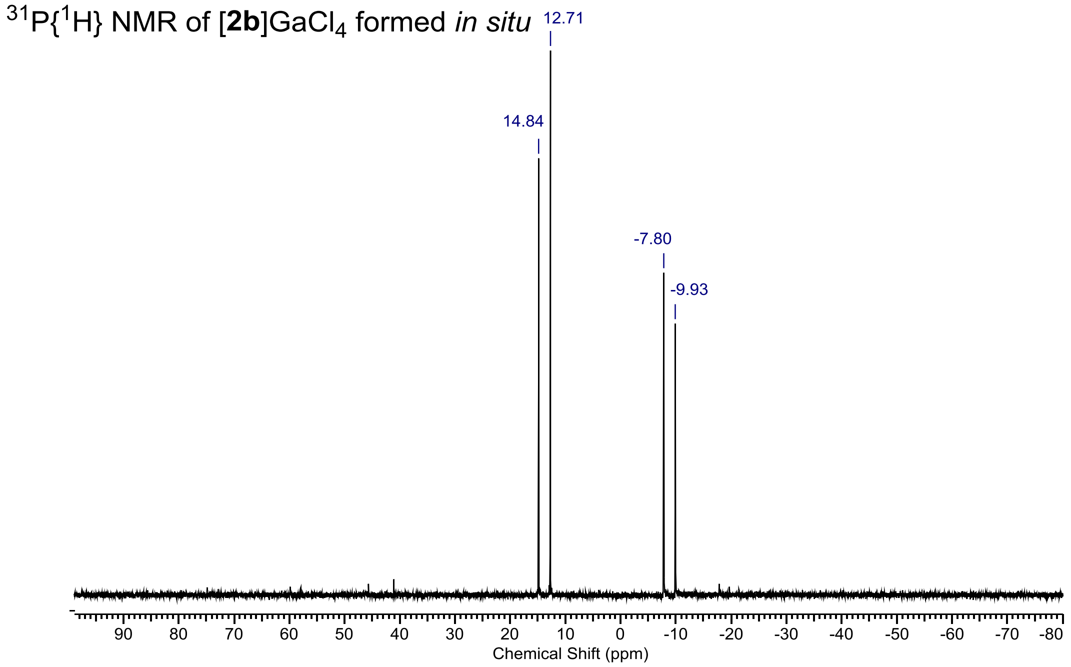


***in situ* formation of [2b]$GaCl_4$**

[2b]GaCl4 forms cleanly under the described conditions, with ^{1}H and ^{31}P NMR comparable to those of the salts of other counterions.

^{1}H NMR of [**2b**]$GaCl_4$ formed *in situ*



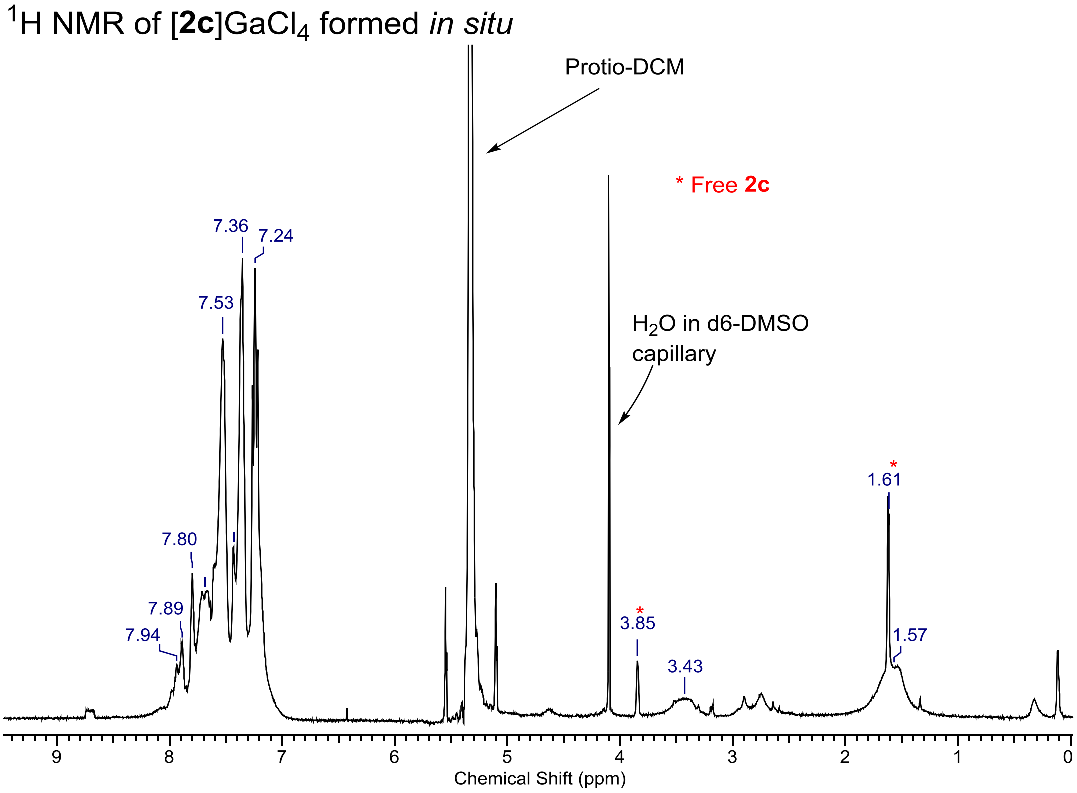


$^{31}P\{^1H\}$ NMR of [**2b**]$GaCl_4$ formed *in situ*

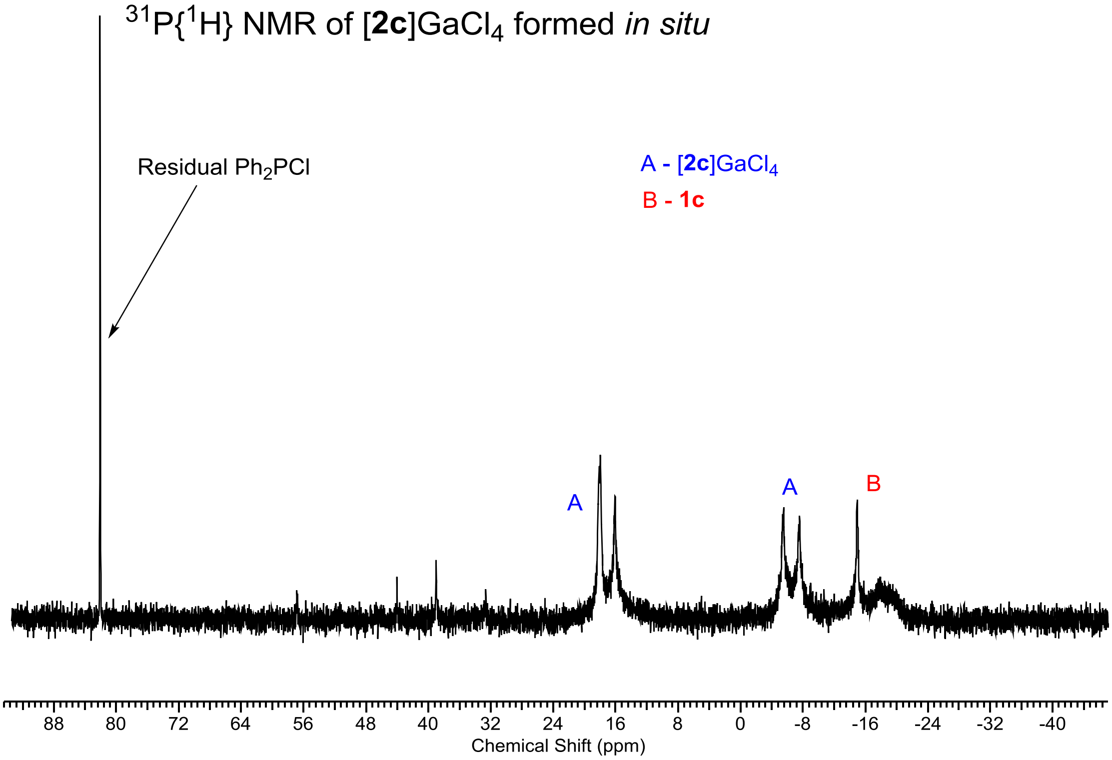
The phosphinophosphenium resonances are sharp doublets at δ13.8 ppm and δ-8.8 ppm, with $^1J_{P\text{-}P}$= 344 Hz.

***in situ* formation of [2c]$GaCl_4$**

As **1c** was isolated as a viscous oil, the experiment was scaled to the mass of **1c** successfully transferred into the NMR tube (57 mg, 0.21 mmol), with 0.21 mmol of the other reagents used. [**2c**]$GaCl_4$ does not form particularly cleanly, and as for [**2c**]OTf, the mixing results in very broad peaks for the benzyllic and methyl resonances in the ^1H NMR. The $GaCl_3$ was clearly the limiting reagent with small residual signals for Ph_2PCl and **1c** visible in the ^1H and ^{31}P NMR. These are comparatively sharp signals, indicating only slow exchange between free and bound **1c**.



^{1}H NMR of [**2c**]GaCl$_4$ formed *in situ*

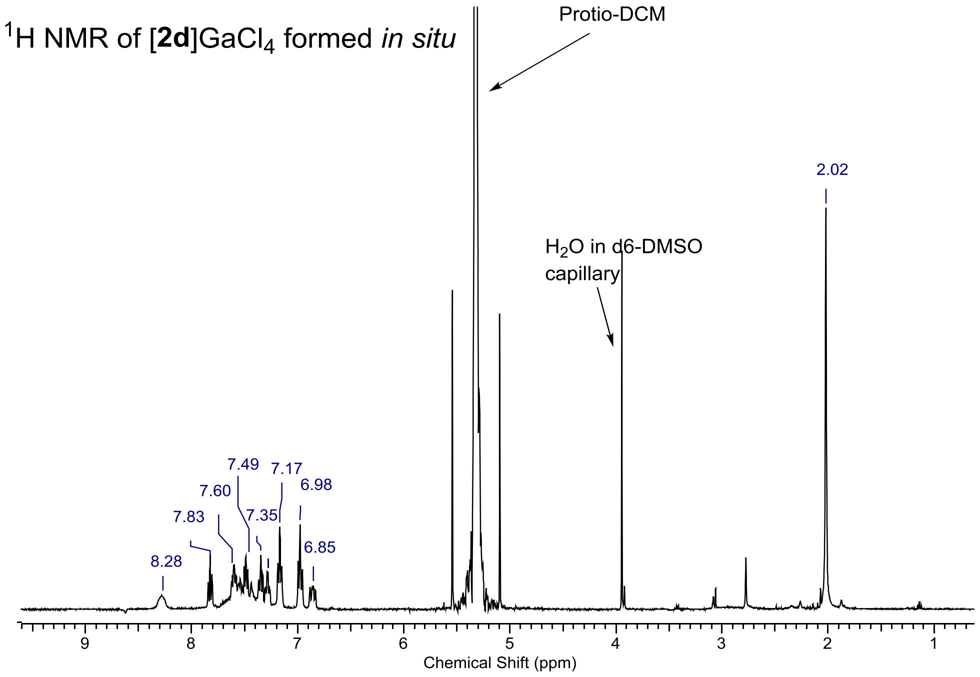


^{31}P{^{1}H} NMR of [**2c**]GaCl$_4$ formed *in situ*

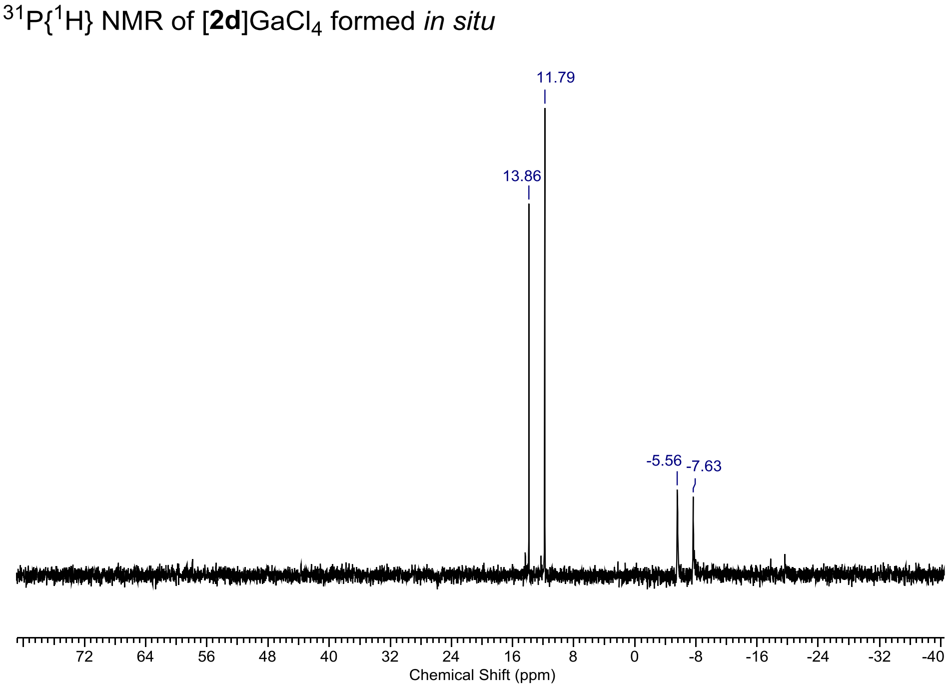
The ^{31}P resonances for [**2c**]GaCl$_4$ are found at δ17.0 ppm and δ-6.5 ppm respectively ($^1J_{P-P}$=332 Hz)

***in situ* formation of [2d]GaCl$_4$**

[**2d**]GaCl$_4$ forms under the described reaction conditions, with both the ^{1}H and ^{31}P NMR spectra in agreement with those of the BAr^F and triflate salts.



^{1}H NMR of [**2d**]$GaCl_4$ formed *in situ*



$^{31}P\{^1H\}$ NMR of [**2d**]$GaCl_4$ formed *in situ*

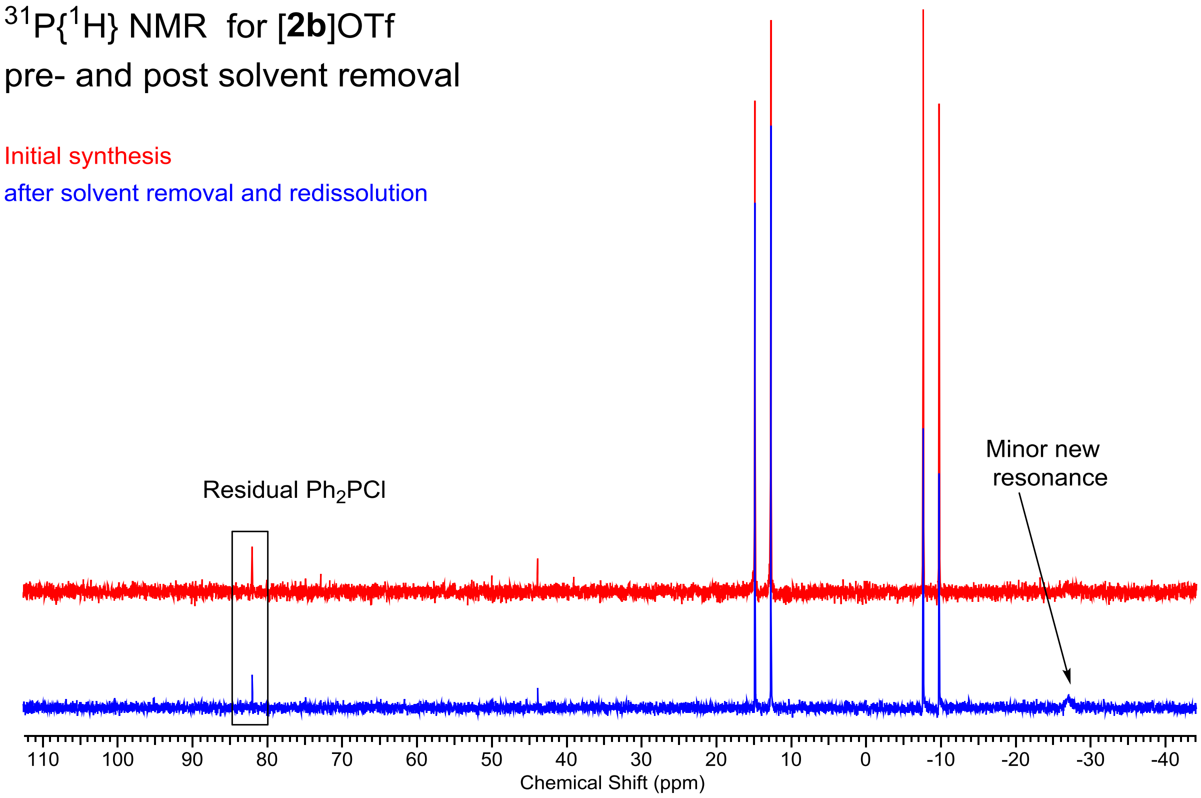
The phosphinophosphenium signals are seen at δ12.8 ppm and δ-6.6 ppm with a $^1J_{P\text{-}P}$ = 335 Hz.

Examination of the degradation products of [2b]OTf

In light of the continued inability to obtain solid products despite the crystalline nature of the compounds reported by Burford, we chose to examine the degradation of [**2b**]OTf in greater detail due to its easy formation.

Degradation of [2b]OTf on loss of solvent

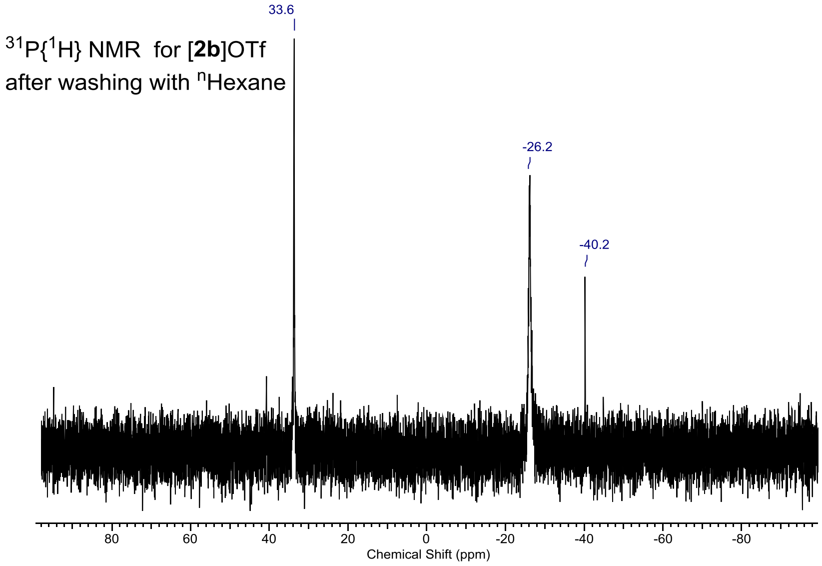
1b (10mg, 0.03mmol) was dissolved in DCM (0.8 cm^3) in a J. Young's NMR tube charged with a d6-DMSO capillary, to which was added first Ph_2PCl (5µl, 0.03mmol) and then Me_3SiOTf (5 µl, 0.03 mmol), after which the NMR spectra were recorded, showing clean formation of [**2b**]OTf. The solvent was removed *in vacuo* and then the sticky residue redissolved in DCM (0.8 cm^3) and the NMR spectra rerecorded, showing no significant change save a tiny new resonance at δ-27.0 ppm.



The reaction mixture was transferred to a J. Young's Schlenk and the solvent slowly removed under a flow of argon, but no crystalline materials were isolated, only a sticky residue.

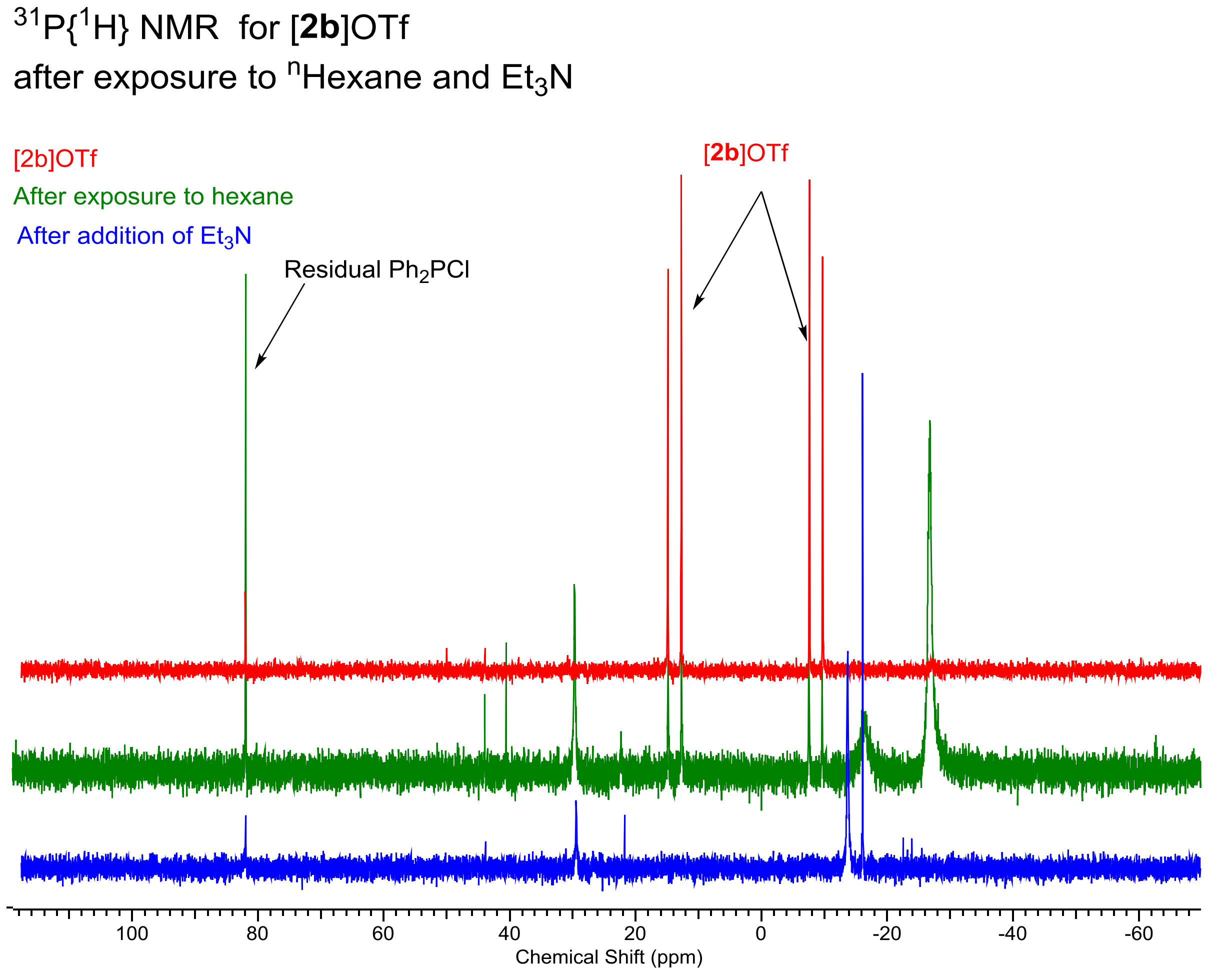
Degradation of [2b]OTf on exposure to hexane

The synthesis was repeated as above, and the [**2b**]OTf transferred to a Schlenk flask and the solvent removed *in vacuo* to give a sticky oil which was washed with ^{n}Hexane (2.5 cm^3) with stirring to. After drying in vacuo, the resulting colourless wax was redissolved in DCM (0.8 cm^3), transferred to a J. Young's NMR tube charged with a d6-DMSO capillary and the NMR spectra recorded.

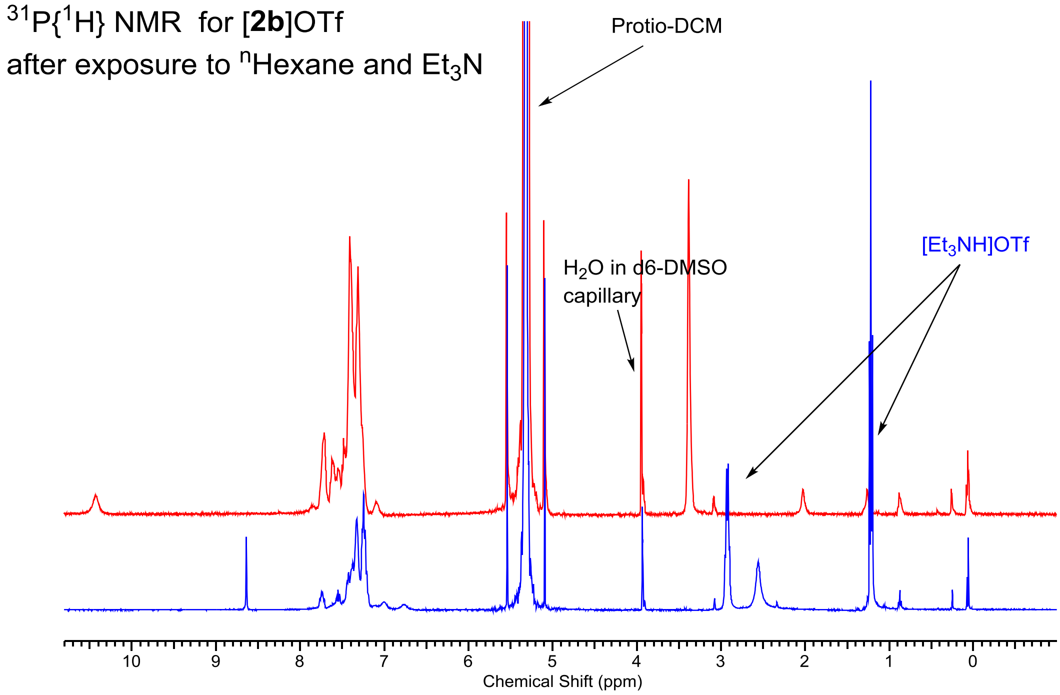


The ^{31}P NMR showed complete loss of [**2b**]OTf, and the formation of two new major products at δ33.6 ppm and δ-26.2 ppm, with a minor signal at δ-40.2 ppm, confirming total destruction of [**2b**]OTf on exposure to hexane and the absence of hydrolysis due to the lack of $Ph_2P(O)PPh_2$.[12]

The experiment was repeated once more in a single vessel. Once the [**2b**]OTf had formed as above, confirmed by NMR, the solvent was removed *in vacuo* and ^{n}Hexane (1 cm^3) added to the tube. No dissolution was observed, and the mixture was allowed to stand for 4 hours, after which the solvent was again removed *in vacuo*, DCM (0.8 cm^3) added and the NMR spectra recorded.



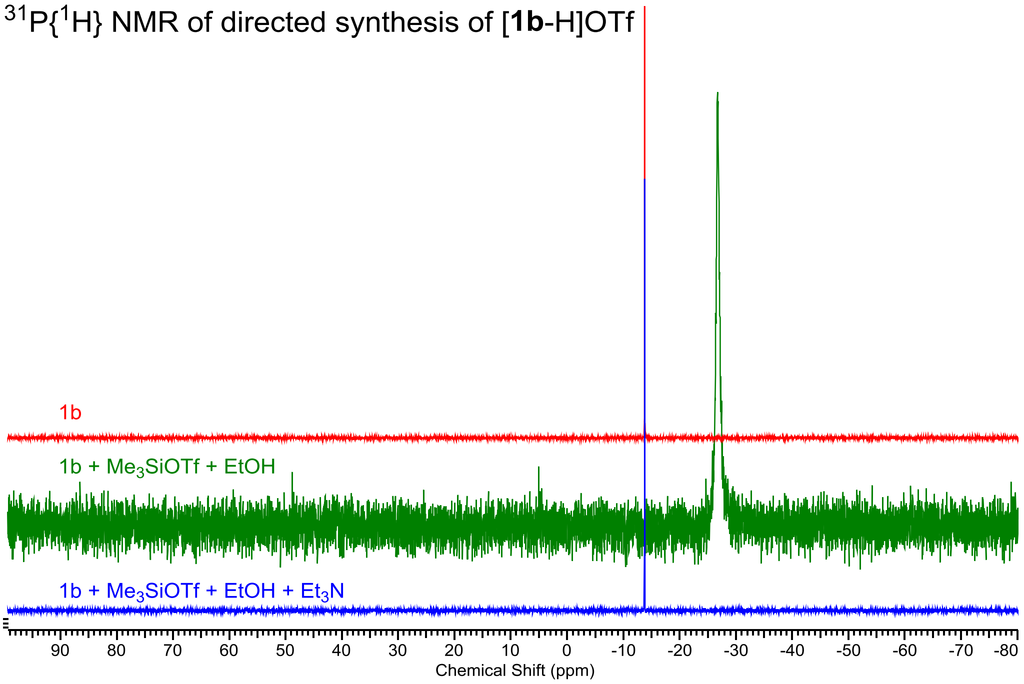
The ^{31}P NMR clearly shows the formation of three major new phosphorus containing species, with broad signals at (small) δ29.7 ppm, (small) δ-16.4 ppm and (strong) δ-26.8 ppm, as well as numerous minor components, with only trace [**2b**]OTf remaining. Upon addition of the Et_3N, these first two signals sharpen and shift slightly to δ29.4 ppm, δ-16.0 ppm, whilst the other peak significantly to δ-13.8 ppm, with relative integrals (by ^{31}P NMR) of 2:3:6. This latter is the chemical shift expected for free **1b**, confirmed by the change in the Me resonance in the ^1H NMR from δ3.39 ppm after exposure to ^{n}Hexane to δ2.55 ppm after Et_3N, and the independent synthesis of [**1b**-H]OTf below. The comparison of the integrals and confirmation of the formation of protonated phosphane indicates that the phosphacations are reacting with something to protonate the donor moiety. Hydrolysis can be ruled out as this transformation is complete rather than partial, and none of the residual Ph_2PCl is consumed and no $Ph_2P(O)Ph_2$[12] is formed, nor is any phosphorus –phosphorus coupling observed between the two new signals. We therefore conclude that **1b** is unable to stabilise the $[Ph_2P]^+$ cation sufficiently in non-polar environments and the likelihood is some form of phospha-Friedel-Krafts reactivity. We were unable to definitively characterise the remaining degradation products, however. The difference in product distribution seen in the degradation *via* washing (which would have removed any ^{n}hexane soluble products) *vs* that in the NMR tube is believed to be due to the more intimate mixing afforded by washing whilst stirring.



^{31}P{^{1}H} NMR for [**2b**]OTf after exposure to ^{n}Hexane and Et_3N

Direct Synthesis of [1b-H]OTf

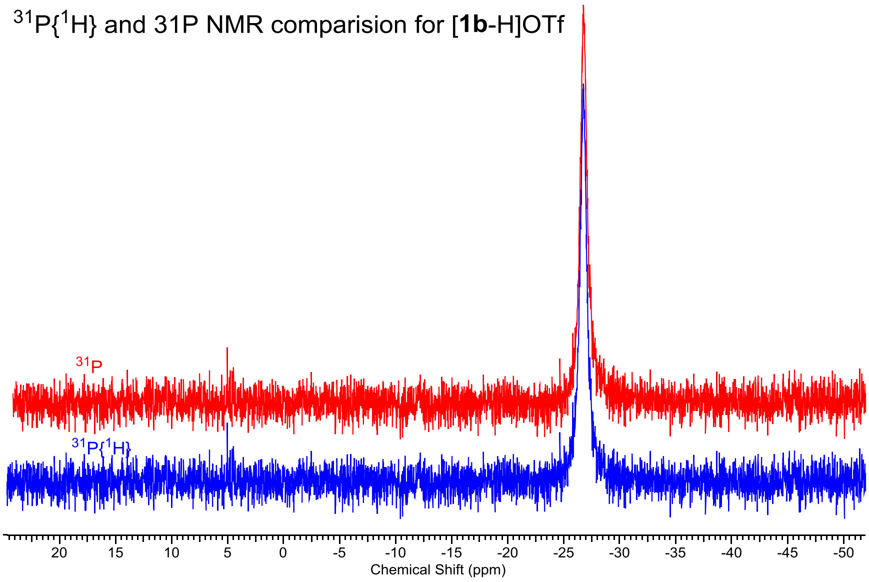
1b (10mg, 0.03mmol) was dissolved in DCM (0.8 cm^3) in a J. Young's NMR tube charged with a d6-DMSO capillary, to which was added first Me_3SiOTf (5 µl, 0.03 mmol) then EtOH (2 µl, 0.03 mmol) to generate HOTf *in situ* with NMR spectra recorded at each stage. The formation of the broad peak at δ-26.7 ppm can clearly be seen. Upon addition of Et_3N (5µl, 0.04 mmol), complete regeneration of free **1b** was observed.



^{31}P{^{1}H} NMR of directed synthesis of [**1b**-H]OTf

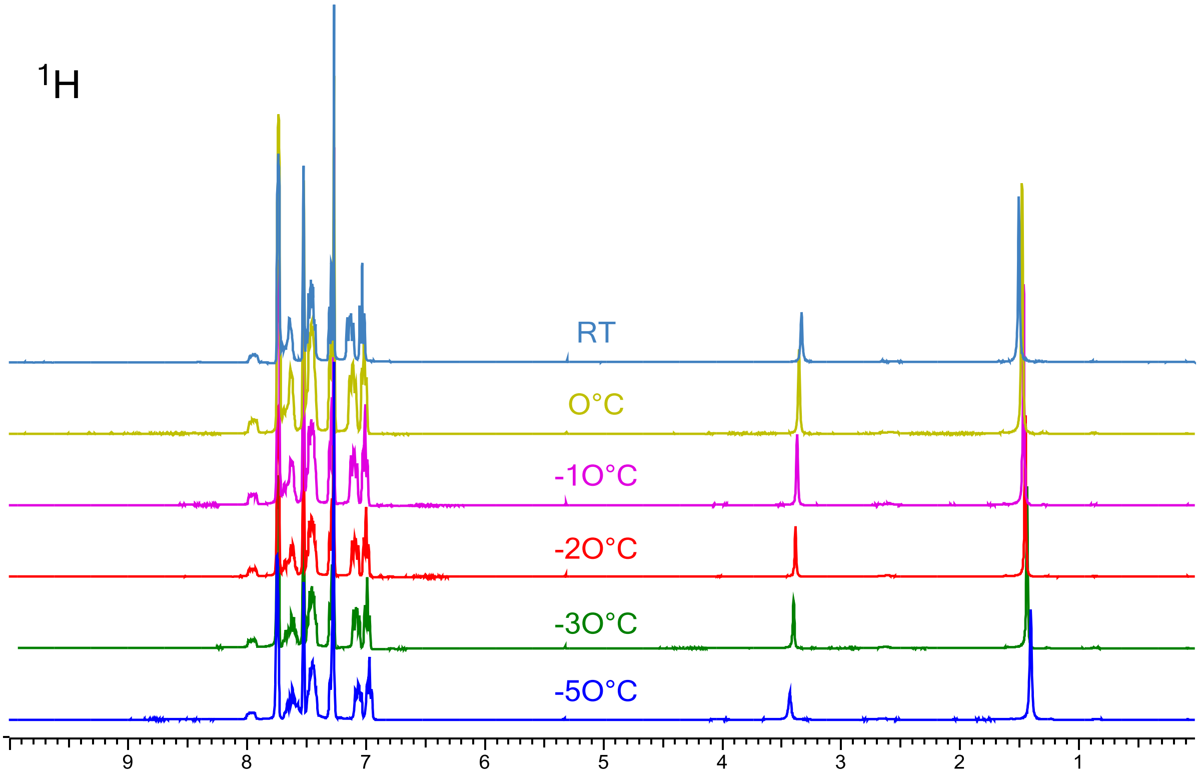
Comparison of the ^{31}P and $^{31}P\{^1H\}$ NMR for [**1b**-H]OTf confirms, as expected, protonation on the anilide moiety rather than at phosphorus, with no evidence for $^1J_{P\text{-}H}$ coupling.

$^{31}P\{^1H\}$ and 31P NMR comparision for [**1b**-H]OTf

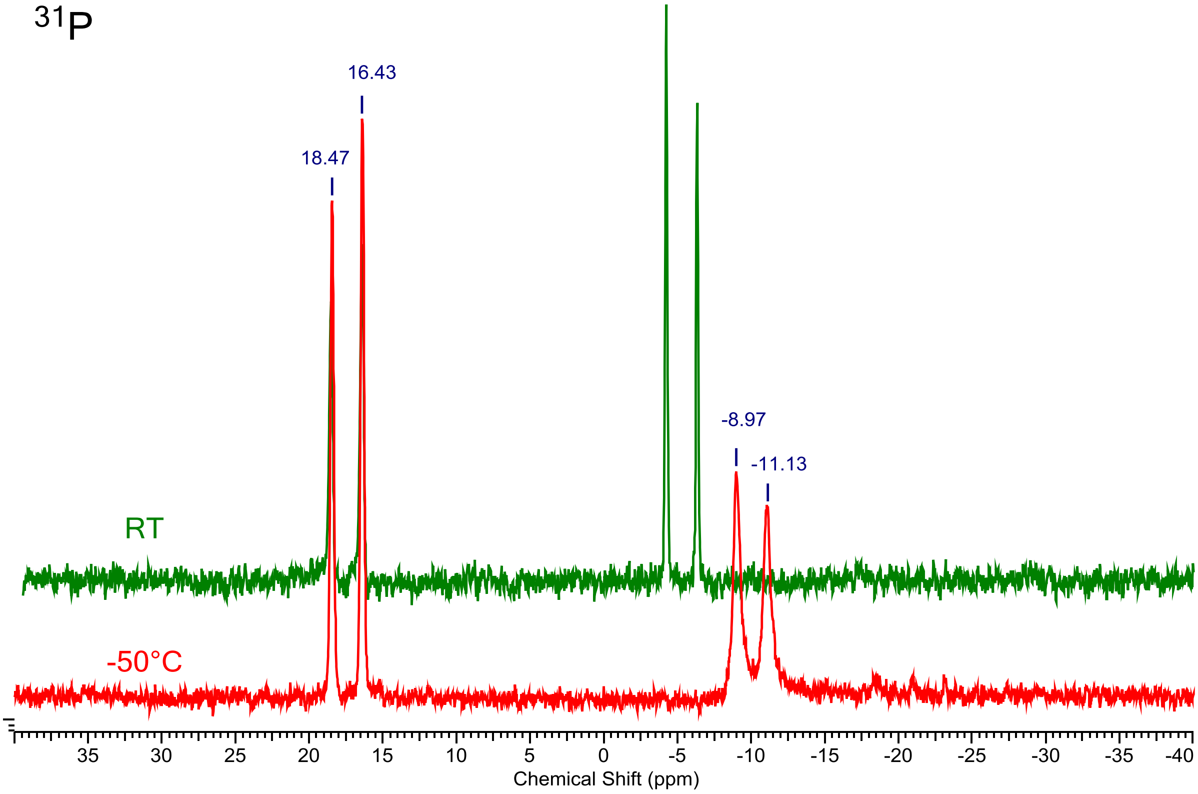


Variable Temperature studies on [2c]BArF

Despite the asymmetry of [**2c**]BAr^F in the crystal structure, both methyl groups are equivalent in the ^1H NMR at room temperature. Low temperature NMR studies were performed upon a sample of crystalline[**2c**]BAr^F in $CDCl_3$, but no splitting of the NMe_2 signal can be seen even down to -50°C, indicating that the species is highly fluxional in solution and that any barriers to interconversion of the phenyl rings from apical to equatorial must be low.



As the temperature is decreased, the benzylic peaks broaden and shift slightly downfield, whilst the NMe_2 resonances likewise broaden but shift downfield slightly. No new peaks become apparent and the aromatic region likewise shows no loss of symmetry.



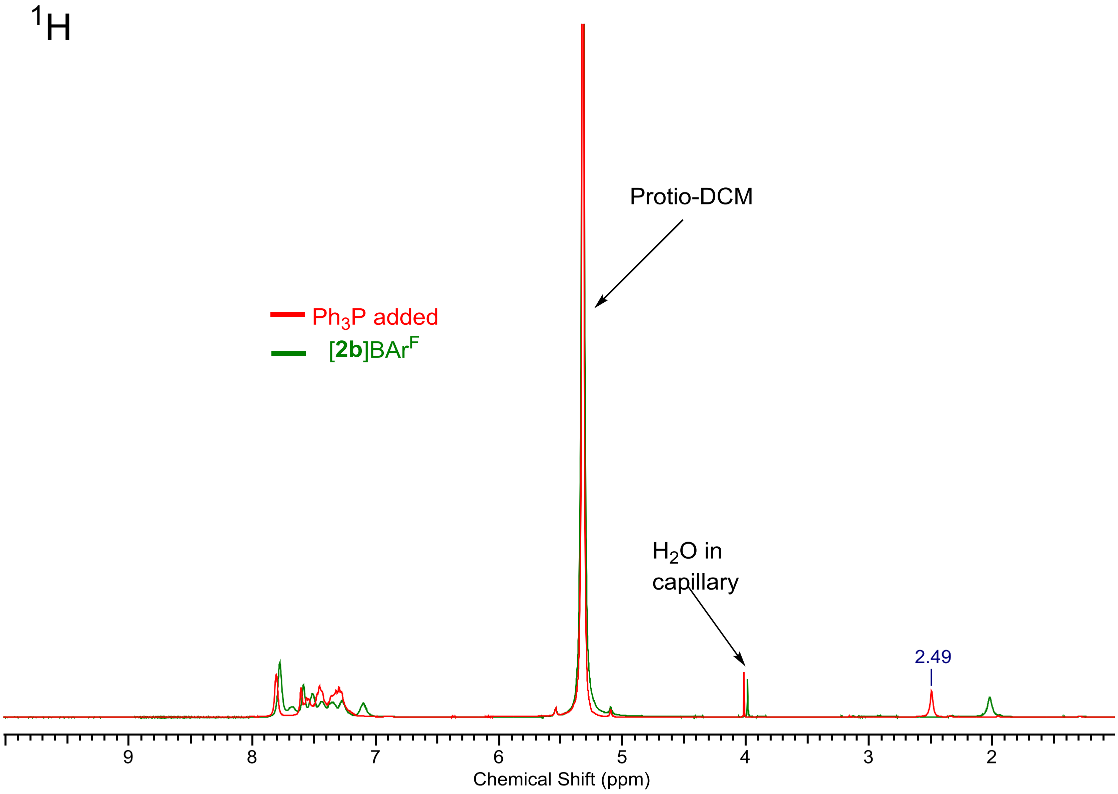
For the ^{31}P spectra over the same range (only the extremes are shown), the upfield resonance shifts slowly further upfield and broadens slightly, but no other changes are observed.

Competition studies with Ph_3P

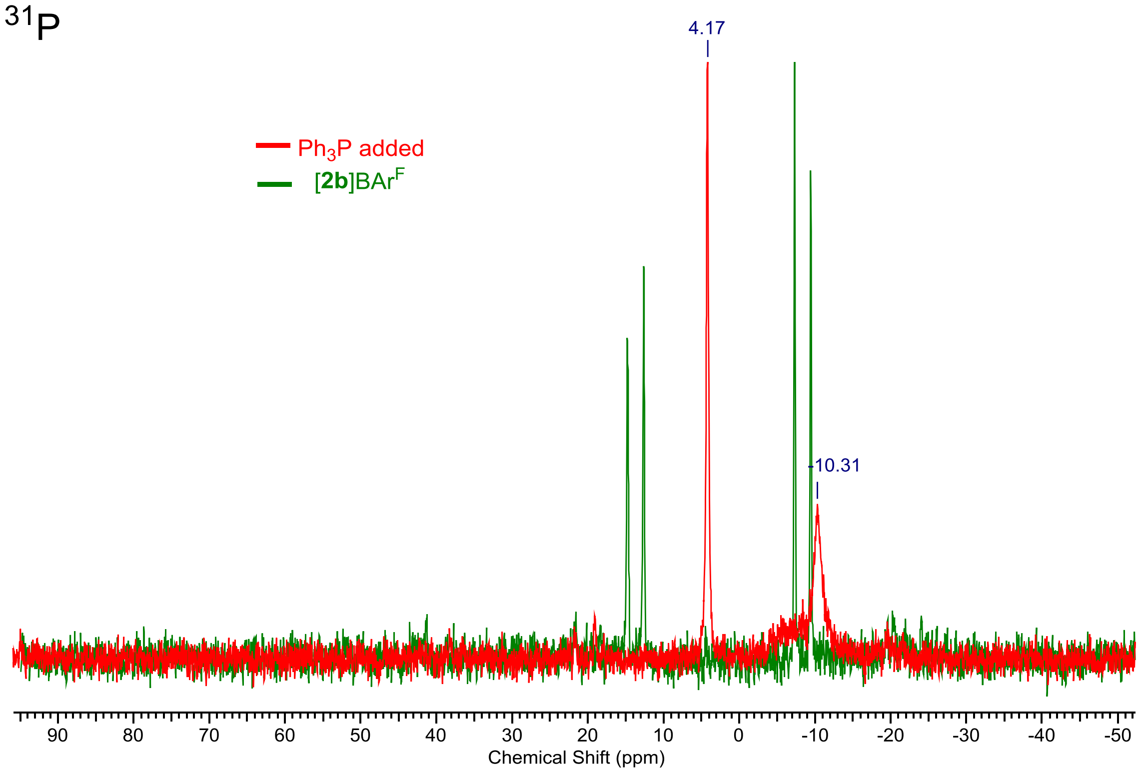
Initial competition studies were performed using *in situ* generated phosphinophosphenium species.

[2b]BAr^F + Ph_3P

1b (31mg, 0.1mmol) and NaBAr^F (89mg, 0.1mmol) were combined in a J. Young's NMR tube charged with a d6-DMSO capillary, and suspended in DCM (0.8cm^3). Ph_2PCl (17µl, 0.1mmol) was added, resulting in rapid dissolution and formation of a pale precipitate. The ^1H and ^{31}P NMR were recorded. Ph_3P (25mg, 0.1mmol) was added and the spectra reacquired.



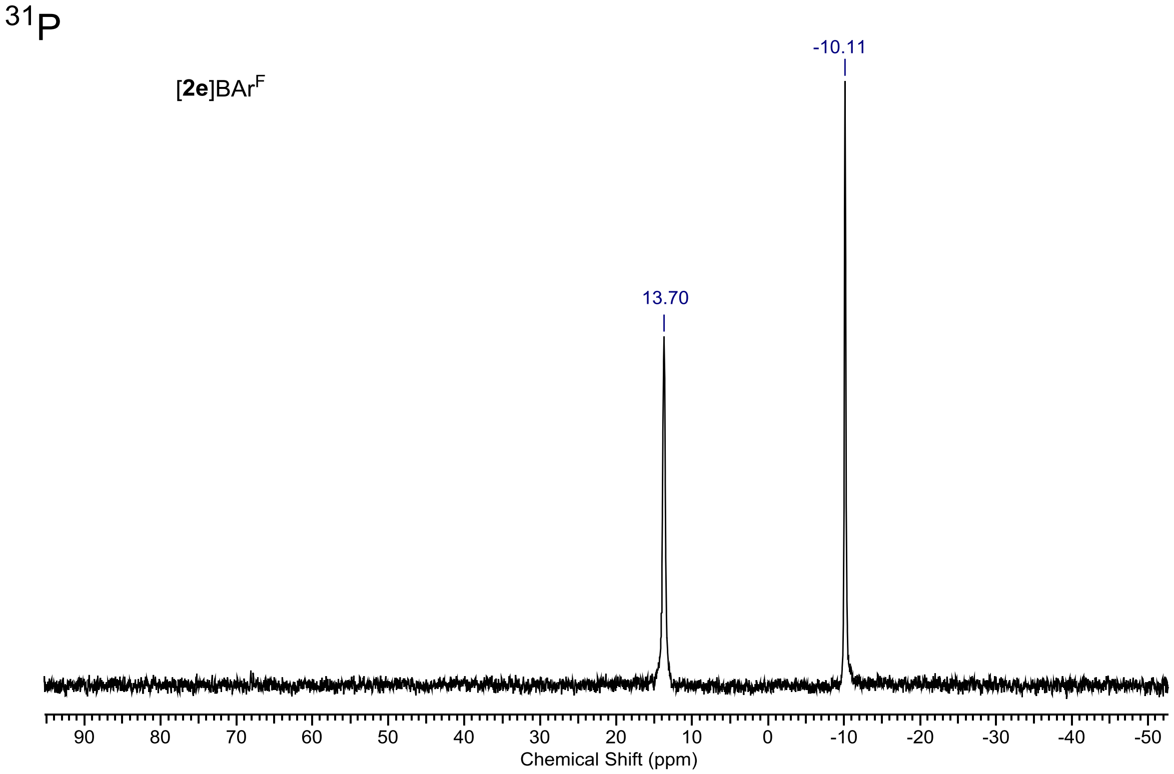
The ^1H NMR clearly shows that the NMe$_2$ resonances move downfield from 2.02ppm to 2.49ppm – closer to but not reaching the value for the free phosphane of 2.60ppm. The ^{31}P changes more dramatically – the resonances for [**2b**]BAr^F disappear completely and three new resonances are seen – two moderately sharp peaks at 4.2 ppm and -10.3 ppm, and a much broader peak at approximately -7 ppm. These correspond neither to any of the free phosphanes nor either of the potential phosphinophosphenium ions.

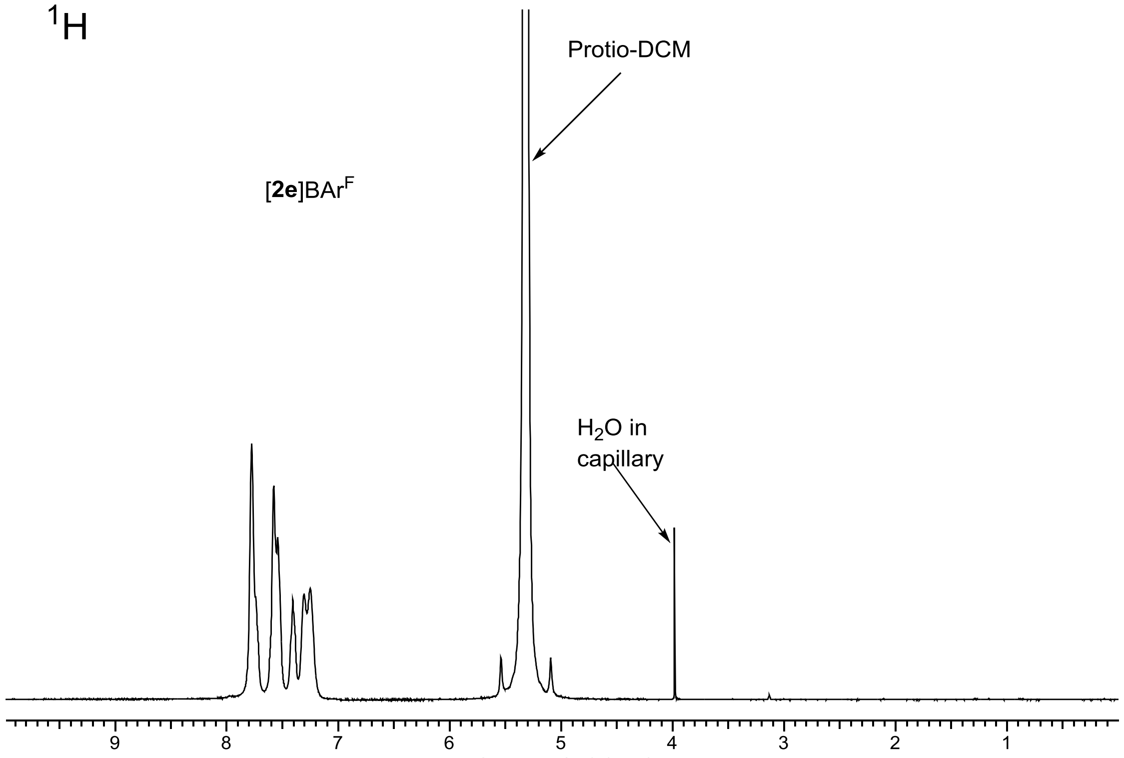


This small number of peaks, none clearly identifiable as any expected product, is indicative of extremely rapid equilibrium.

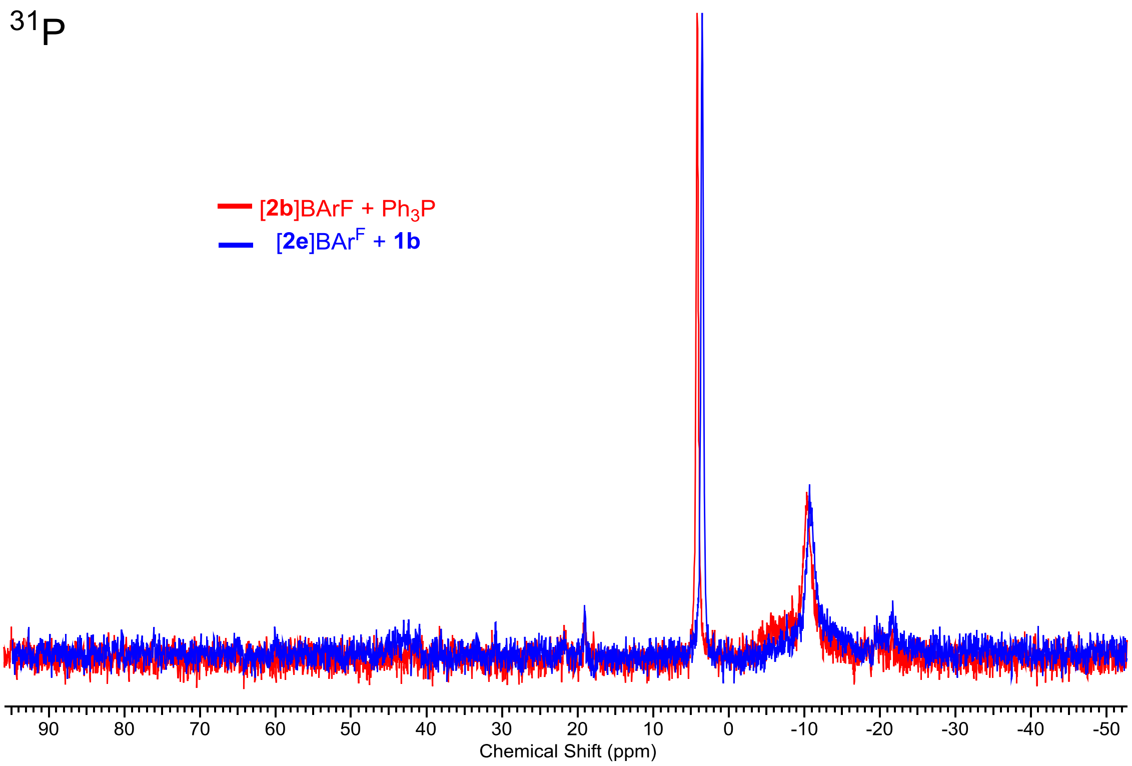
[2e]BAr^F + 1b

To confirm that this was the case, the equivalent reaction was performed this time approaching the equilibrium from the other direction. Ph$_3$P (25mg, 0.1mmol) and NaBAr^F (89mg, 0.1mmol) were combined in a J. Young's NMR tube fitted with a d6-DMSO capillary. DCM (0.8cm^3) was added, followed by Ph$_2$PCl (17µl, 0.1mmol) and the ^{1}H and ^{31}P NMR recorded, showing clearly the clean formation of [**2e**]BAr^F as evidenced by singlets in the ^{31}P NMR at 13.7 ppm and -10.1 ppm (literature values being 13 ppm and -12 ppm respectively for [**2e**]GaCl$_4$)[13], confirming that this is not one of the species visible in the above competition experiment.





1b (31mg, 0.1mmol) was then added, and the spectra rerecorded.

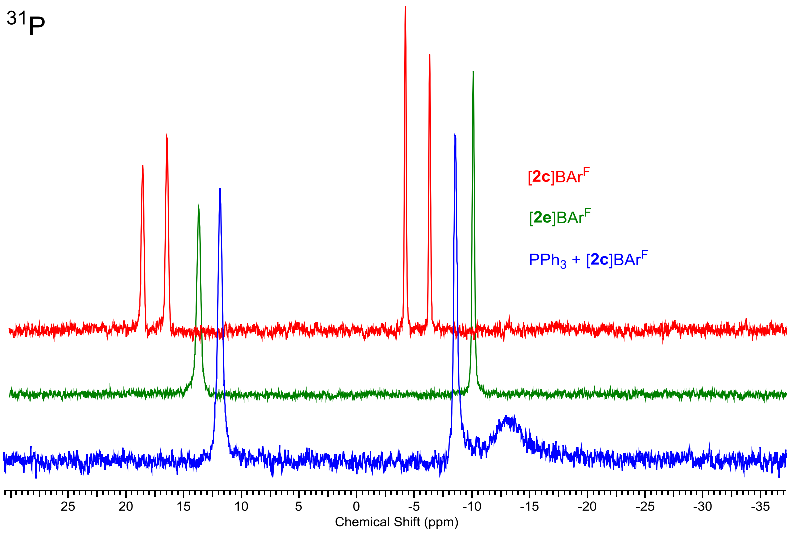


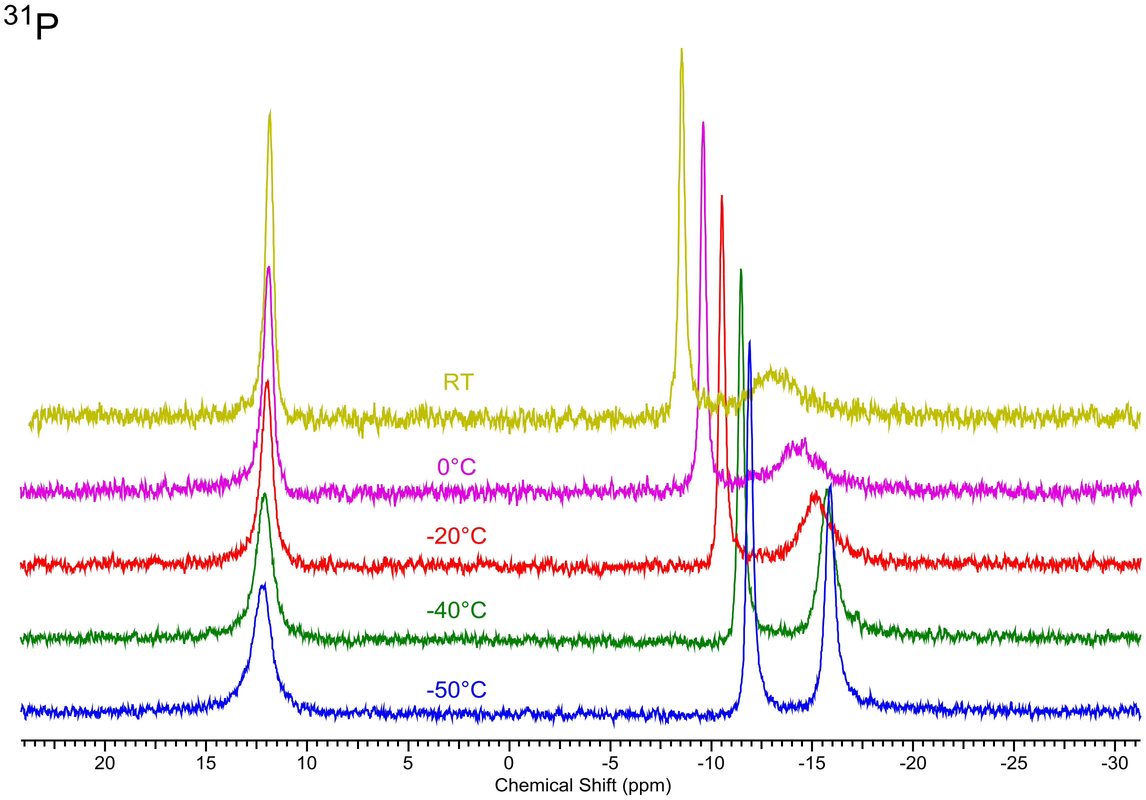
The ^{31}P NMR clearly shows that the same equilibrium mixture is attained, with slight peak position differences likely arising from minor concentration differences during formation.

In all these cases, the presence of capillary and NaCl precipitate gave comparatively broad linewidths, and the d6-DMSO capillary rendered variable temperature studies to low temperatures infeasible.

[2c]BAr^F + Ph$_3$P Variable Temperature Study

The isolation of pure, crystalline [**2c**]BAr^F made it possible to attempt a variable temperature study using this with Ph$_3$P to try to freeze out the equilibrium. One equivalent each of [**2c**]BAr^F and Ph$_3$P were combined in a J. Young's NMR tube in CDCl$_3$, giving a room temperature spectrum showing complete loss of coupling between the two phosphorus centres and signals not corresponding to either free phosphane nor either [**2c**] or [**2e**].



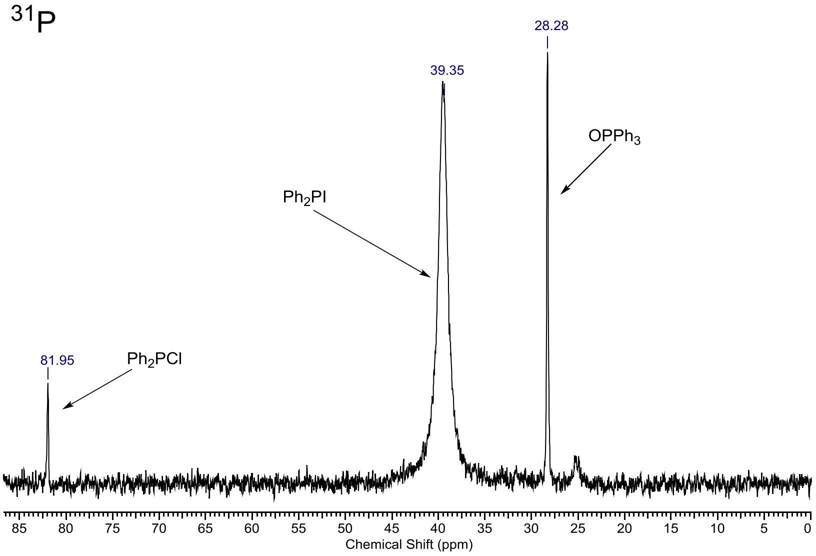


On cooling, the acceptor resonance sharpens (much as seen for [**2c**]BAr^F itself) and the donor resonance shifts upfield, but the otherwise broad peak sharpens and at -50°C is centred at -15.9 ppm, with the downfield pair at 12.1ppm and -11.9ppm respectively. These are therefore attributed to free [**2e**]BAr^F and **1c**. This is in agreement with the computed free energies which predict that [**2e**] is more stable than [**2c**].

Variable Temperature Studies with Ph_2PI

Synthesis of Ph_2PI: Ph_2PI was synthesised by modified literature preparation.[14] Ph_2PCl (1 cm^3, 5.6 mmol) was added to a suspension of KI (4.48 g, 27 mmol) in DCM (5 cm^3) and stirred rapidly at room temperature for 4 days, during which time the reaction mixture developed a fine, colourless precipitate and became yellow in colour. The reaction mixture was filtered directly into a Schlenk flask charged with a further quantity of KI (3.3 g, 20 mmol) and stirred for a further ten days. The reaction mixture was then filtered and the solvent removed *in vacuo* to give crude Ph_2PI as a red-orange oil (0.802 g, 2.5 mmol, 46% yield). **^{1}H NMR** (400MHz, DCM, 20.9°C): δ = 7.65 (bm, aromatic C-**H**, 4H), 7.36 (bm, aromatic C-**H**, 6H). **^{31}P NMR** (161.8MHz, DCM, 20.9°C) : δ = 39.4 (Literature value 40.3).

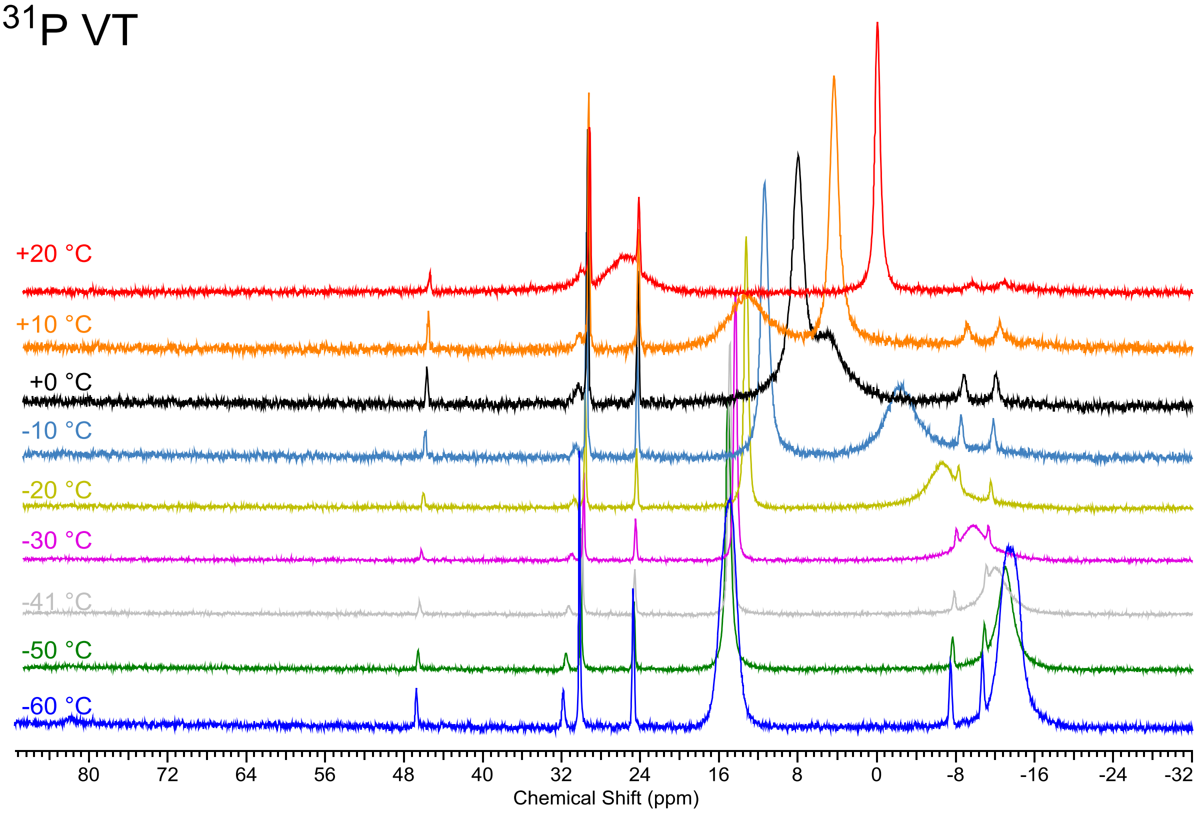
The isolated red oil was found to approximately 85% pure by ^{31}P NMR (see below), containing traces of Ph_2PCl starting material and some hydrolysis products, and deemed to be sufficient for further studies as these impurities do not interact with the species of interest.



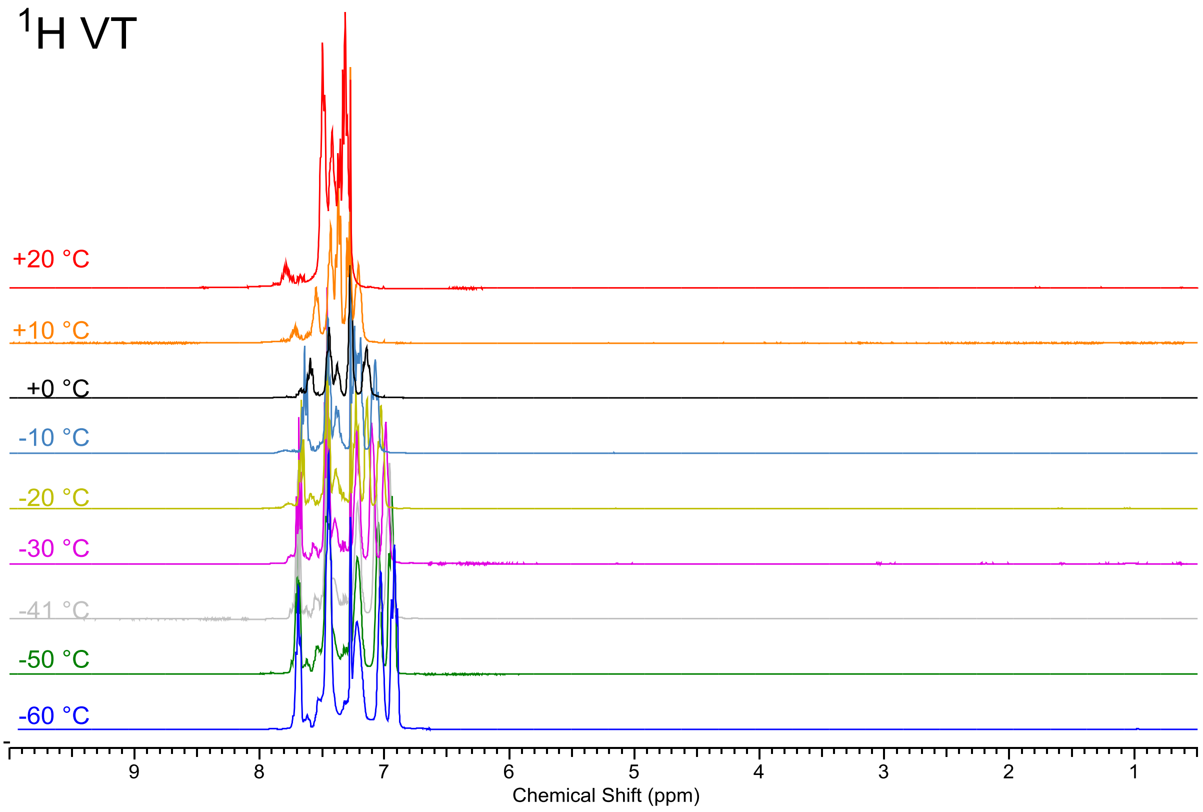
VT withPPh_3 and Ph_2PI

Ph_2PI (60 mg, 1.9 mmol) was dissolved in $CDCl_3$ (0.8cm^3) in a J. Young's NMR tube and Ph_3P (51 mg, 1.9 mmol) added, with no attendant colour change. The ^{31}P NMR spectrum showed clear evidence of a dynamic equilibrium present with changes in chemical shift of both species (*vide infra*), and further variable temperature NMR studies were performed.

^{31}P VT



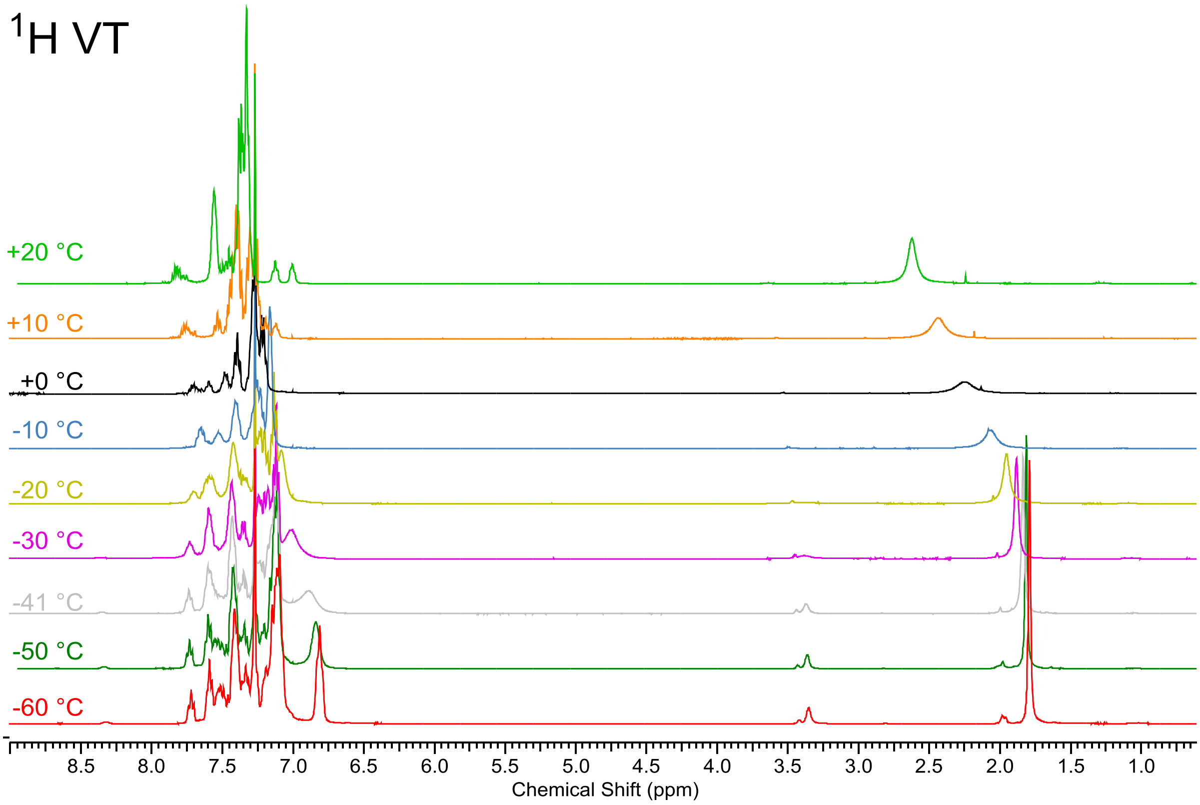
The ^{31}P NMR shows a dramatic difference between the NMR of the free species and the mixed Ph_2PI and Ph_3P – the signal for Ph_3P is shifted downfield from δ = -5 to δ-0.1 ppm on mixing, whilst the signal for Ph_2PI shifts upfield from δ39.4 ppm to δ25.3 ppm, with both broadening considerably, indicative of a dynamic equilibrium between free phosphanes and some other species. On cooling, the peaks broaden and then sharpen moving smoothly to δ15.0ppm for the "Ph_3P" signal and δ-13.6ppm for the "Ph_2PI" signal, clearly corresponding to the signals for [**2e**]. The non-participation of the impurities in the Ph_2PI can be seen by the temperature invariance of the associated signals. Interestingly, at no point is any intermediate identifiable corresponding to the un-ionised adduct predicted by DFT. However, as this system is in the fast exchange regime at all temperatures, it is not entirely surprising that no such intermediate can be spectroscopically observed or resolved.



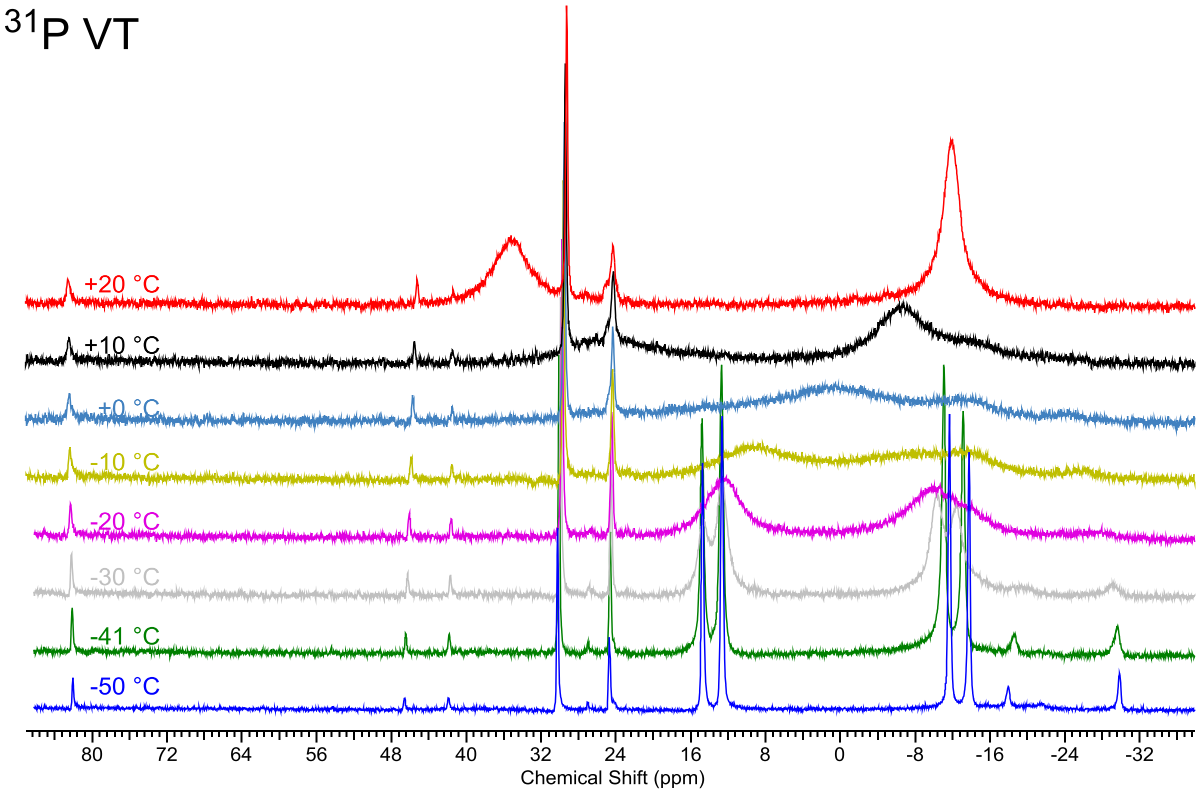
In contrast to the ^{31}P NMR spectra, there's very little to be seen in the ^{1}H VT NMR data – the peaks spread out slightly, but given that the transition is from simple phenyl rings in one species to simple phenyl rings in another, no real conclusions may be drawn.

VT of 1b and Ph_2PI

Ph_2PI (65 mg, 2.1 mmol) was dissolved in a J. Young's NMR tube in $CDCl_3$ (1 cm^3) and **1b** (64 mg, 2.1 mmol). The solution was then studied by variable temperature NMR between 20 °C and -60 °C.



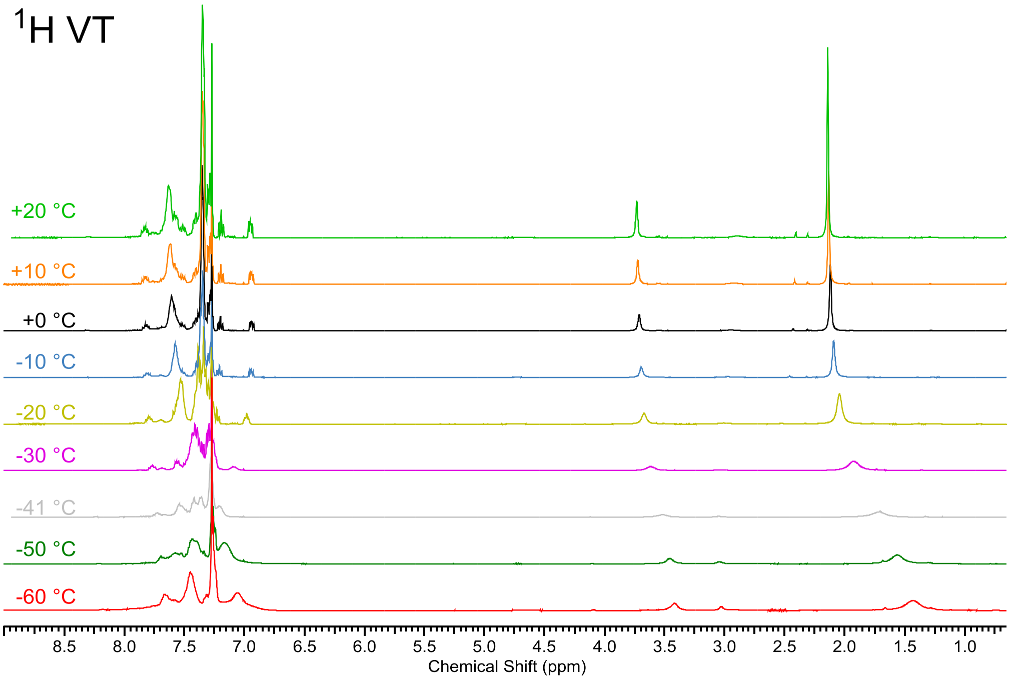
The existence of an equilibrium is suggested by the broadening of the NMe_2 resonance in the ^{1}H NMR, though no significant upfield shift is observed. On cooling, however, the NMe_2 resonance moves upfield and sharpens to until at -60 °C it rests at δ = 1.79 ppm (*cf.* 2.02ppm for [**2b**]BAr^F at 20 °C.



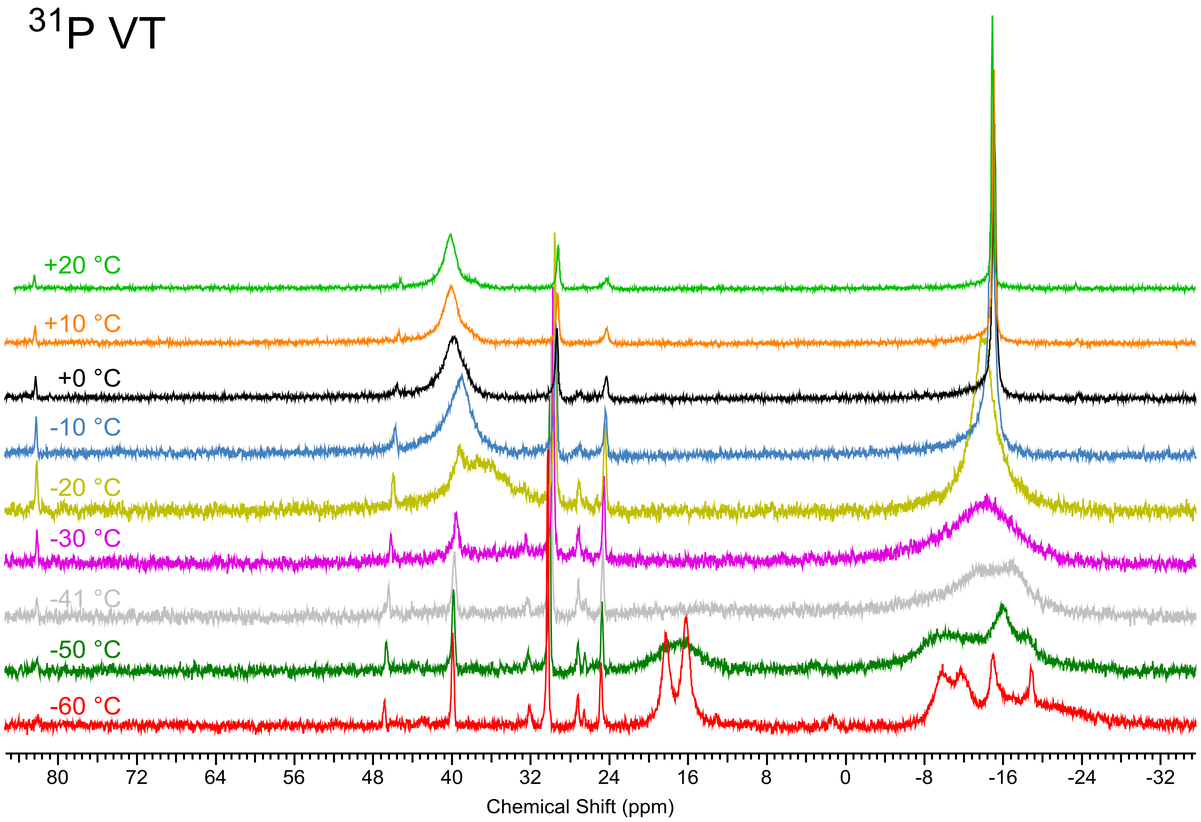
The non-interference of the impurities in the Ph_2PI can be seen as they remain unchanged across the temperature range of interest. In this case, indicating both a more thermodynamically stable product and a more rigid P-P bond, coalescence is achieved at only +0 °C, with the peaks for the ionic P-P adduct resolved poorly at -10°C, well at -20 °C and with the P-P coupling resolved at -30 °C. The pair of doublets δ=13.7ppm and δ-12.7 ppm, $^{1}J_{P-P}$ = 337 Hz is assigned to the formation of [**2b**]I

VT of 1c and Ph_2PI

Solutions of **1c** (91mg, 0.28 mmol) in $CDCl_3$ (1 cm^3) and Ph_2PI (124mg, 4 mmol) in $CDCl_3$ were prepared. Aliquots of the triarylphoshane solution (0.5cm_3) and diaryliodophoshane solution (0.4cm^3) were combined in a J. Young's NMR tube to give an approximately equimolar mixture, which was then studied by variable temperature NMR between 20 °C and -60 °C.



No significant change in ^{1}H NMR resonances are observed upon mixing at RT, and only slight line broadening is in evidence in the ^{31}P NMR spectrum, indicating that whilst an equilibrium has been established in fast exchange, the starting materials are the major component. Upon cooling, both benzylic CH_2 and NMe_2 resonances shift upfield in the ^{1}H NMR, approaching the peak positions expected for [**2c**]. Likewise, the peaks in the ^{31}P broaden on cooling and begin to approach the peak positions expected for [**2c**]. Unlike [**2b**], however, no P-P coupling can be resolved until -60 °C, and signals in both the ^{1}H and ^{31}P at that temperature are broad, indicating that significant exchange is ongoing. This does correlate qualitatively with the predicted stability of [**2b**] vs [**2c**] from the computational studies.



The non-participation of the residual Ph_2PCl and Ph_3PO impurities in the Ph_2PI can clearly be seen as they are effectively unchanged with temperature down to -60 °C.

Crystallography

Crystal Structure for [2c]BAr^F

Single crystals were mounted on nylon loops and X-ray diffraction data were recorded on an Agilent Super Nova Dual Diffractometer with Cu-Kα radiation (λ = 1.5418 Å) at 150 K. Unit cell determination, data reduction and absorption corrections were carried out using CrysAlisPro[15] . The structure was solved by direct methods and refined by full matrix least squares on the basis of F^2 using SHELX 2013[16] within the OLEX2 GUI[17]. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were included using a riding model. Significant disorder was evident about the CF_3 groups of the counterion, leading to minor issues with atomic displacement parameters with these moieties. However, these do not affect the structural interpretation of the cation.

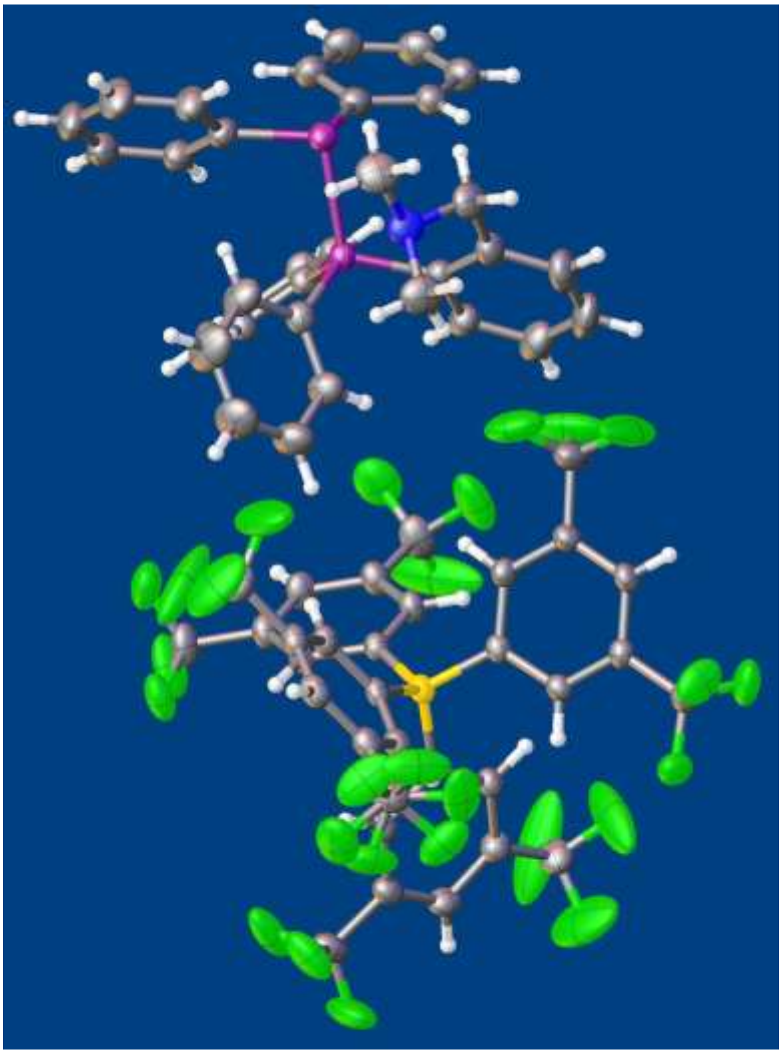


Table 1 Crystal data and structure refinement for [2c]BAr^F.

Identification code	xstr0487
Empirical formula	C65H44BF24NP2
Formula weight	1367.76
Temperature/K	150(1)
Crystal system	triclinic
Space group	P-1
a/Å	13.06366(17)
b/Å	13.20669(16)

c/Å	19.4224(2)
α/°	103.8699(11)
β/°	107.3045(11)
γ/°	91.5968(10)
Volume/Å3	3088.12(7)
Z	2
ρcalcg/cm3	1.471
μ/mm^{-1}	1.671
F(000)	1384.0
Crystal size/mm3	0.1 × 0.04 × 0.01
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.934 to 147.304
Index ranges	-16 ≤ h ≤ 16, -16 ≤ k ≤ 16, -24 ≤ l ≤ 23
Reflections collected	51501
Independent reflections	12249 [Rint = 0.0274, Rsigma = 0.0216]
Data/restraints/parameters	12249/0/867
Goodness-of-fit on F2	1.045
Final R indexes [I>=2σ (I)]	R1 = 0.0691, wR2 = 0.1847
Final R indexes [all data]	R1 = 0.0781, wR2 = 0.1930
Largest diff. peak/hole / e Å-3	1.16/-0.71

Table 2 Fractional Atomic Coordinates (×104) and Equivalent Isotropic Displacement Parameters (Å2×103) for [2c]BAr^F. Ueq is defined as 1/3 of of the trace of the orthogonalised UIJ tensor.

Atom	x	y	z	U(eq)
P1	6528.4(5)	1899.8(5)	2651.9(4)	27.98(16)
P2	5728.5(6)	785.9(6)	1525.7(4)	33.95(17)
N1	4915(2)	446(2)	2883.5(15)	43.3(6)
C1	5553(2)	2686(2)	2966.1(15)	32.7(6)
C2	5875(3)	3760(2)	3290.6(17)	38.6(6)
C3	5209(3)	4410(3)	3577(2)	52.0(8)
C4	4212(3)	3999(3)	3547(2)	61.7(10)
C5	3880(3)	2943(3)	3233(2)	56.3(9)
C6	4534(2)	2264(3)	2937.3(17)	40.9(7)
C7	4121(3)	1119(3)	2611(2)	46.7(7)
C8	5090(3)	533(3)	3678(2)	57.4(9)
C9	4590(3)	-654(3)	2463(2)	57.1(9)
C10	7552(2)	2799(2)	2592.0(15)	31.0(5)
C11	7266(2)	3549(2)	2189.7(16)	34.7(6)
C12	8060(3)	4200(2)	2123.8(18)	41.6(7)
C13	9138(3)	4103(2)	2445(2)	44.6(7)
C14	9426(2)	3363(2)	2836.6(19)	43.2(7)
C15	8640(2)	2709(2)	2919.6(17)	36.0(6)
C16	7228(2)	1289(2)	3372.9(16)	33.2(6)
C17	7565(3)	307(3)	3216(2)	51.7(8)
C18	8142(4)	-93(3)	3800(2)	72.0(13)
C19	8373(4)	476(3)	4528(2)	64.3(10)
C20	8052(3)	1460(3)	4686(2)	54.5(9)
C21	7479(3)	1871(2)	4107.8(18)	43.8(7)
C22	6885(2)	161(2)	1338.7(16)	37.7(6)
C23	6758(3)	-929(3)	1186(2)	49.3(8)
C24	7573(3)	-1509(3)	1045(3)	63.7(10)
C25	8516(3)	-1010(3)	1045(2)	61.9(10)

C26	8648(3)	73(3)	1186(2)	50.5(8)
C27	7841(2)	661(3)	1333.2(17)	40.2(6)
C28	5444(2)	1761(2)	981.9(16)	38.3(6)
C29	5977(3)	1917(3)	481.7(18)	45.2(7)
C30	5688(3)	2677(3)	95(2)	54.4(9)
C31	4875(3)	3282(3)	199(2)	53.8(8)
C32	4319(3)	3109(3)	669.7(19)	49.3(8)
C33	4591(2)	2348(3)	1053.3(17)	41.2(7)
F1	5510.7(16)	4252.6(18)	8866(1)	54.1(5)
F2	4224(2)	3034.1(18)	8262.8(13)	66.6(6)
F3	4129.5(19)	4532(2)	8040.7(13)	67.3(6)
F4	3477(2)	1988(5)	5467.7(17)	183(3)
F5	4767(3)	1259(2)	5260.0(13)	91.3(9)
F6	4588(4)	2726(3)	5089.5(15)	123.7(15)
F7	7576(4)	93(4)	9097(2)	89.6(18)
F8	9245(4)	497(5)	9594(2)	84.0(13)
F9	8192(4)	1666(3)	9642(2)	69.8(11)
F10	8771(4)	-1582.4(18)	6859.4(19)	112.5(13)
F11	9625(4)	-586(3)	6506(3)	156(2)
F12	8008(4)	-853(3)	6062.2(19)	155(2)
F13	7103(2)	4751(3)	5116.6(16)	90.6(10)
F14	8321(2)	4623(2)	4629.5(14)	77.1(7)
F15	8485(4)	5887(2)	5555(2)	171(3)
F16	11278(2)	2315(2)	5677.0(14)	71.5(7)
F17	11867.3(15)	2759.7(19)	6866.1(13)	59.5(6)
F18	11990.3(17)	3884(2)	6262.2(18)	79.0(8)
F19	7778(2)	7124(2)	8517(3)	154(2)
F20	8965(4)	7716(2)	9456(2)	141.3(18)
F21	9220(5)	7699(3)	8483(4)	201(3)
F91	12380.9(16)	4804(3)	9340.8(14)	86.6(9)
F92	11651.1(17)	4037(2)	9916.6(15)	72.9(7)
F93	11994(2)	5681(2)	10288.5(15)	95.9(10)
C34	6962(2)	3223.9(19)	7230.7(14)	26.5(5)
C35	6451(2)	3579.5(19)	7770.7(14)	26.9(5)
C36	5335(2)	3475(2)	7599.8(15)	28.6(5)
C37	4676(2)	3022(2)	6873.1(16)	32.5(6)
C38	5161(2)	2668(2)	6331.7(15)	34.4(6)
C39	6280(2)	2755(2)	6508.5(15)	30.4(5)
C40	4812(2)	3829(2)	8190.9(17)	36.2(6)
C41	4477(3)	2179(3)	5538.7(18)	51.6(8)
C42	8483.2(19)	2087(2)	7642.3(15)	27.5(5)
C43	8420(2)	1931(2)	8319.7(15)	30.4(5)
C44	8463(2)	950(2)	8463.5(16)	32.6(6)
C45	8592(2)	81(2)	7938.6(17)	34.8(6)
C46	8654(2)	214(2)	7267.1(17)	33.5(6)
C47	8595(2)	1200(2)	7122.5(15)	30.0(5)
C48	8362(3)	803(2)	9181.5(17)	41.5(7)
C49	8773(3)	-699(2)	6680(2)	46.0(7)
C50	8752(2)	3402.7(19)	6795.5(14)	27.4(5)
C51	8257(2)	3992(2)	6304.4(16)	31.8(5)
C52	8731(2)	4268(2)	5811.8(17)	37.8(6)
C53	9732(2)	3974(3)	5796.7(18)	40.7(7)
C54	10250(2)	3404(2)	6285.7(17)	35.5(6)

C55	9771(2)	3116(2)	6770.1(16)	30.6(5)
C56	8166(3)	4912(3)	5301(2)	53.2(9)
C57	11337(3)	3092(3)	6271(2)	46.6(8)
C58	8925(2)	4215(2)	8159.3(14)	27.0(5)
C59	9927(2)	4148(2)	8658.2(15)	30.2(5)
C60	10553(2)	5026(2)	9182.9(15)	33.1(6)
C61	10191(2)	6010(2)	9232.1(16)	36.3(6)
C62	9196(2)	6096(2)	8746.7(16)	34.5(6)
C63	8582(2)	5218(2)	8220.5(15)	28.4(5)
C64	11640(2)	4909(3)	9680.8(17)	42.5(7)
C65	8797(3)	7153(2)	8778(2)	45.2(7)
B1	8276(2)	3222(2)	7453.5(16)	26.5(5)
F9A	7511(12)	1208(15)	9278(7)	87(4)
F8A	9177(10)	1232(12)	9720(5)	72(3)
F7A	8253(16)	-169(8)	9160(8)	81(5)

Table 3 Bond Lengths for [2c]BAr^F.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P1	P2	2.2477(9)	F13	C56	1.324(4)
P1	C1	1.818(3)	F14	C56	1.346(5)
P1	C10	1.812(3)	F15	C56	1.273(5)
P1	C16	1.808(3)	F16	C57	1.329(4)
P2	C22	1.830(3)	F17	C57	1.338(4)
P2	C28	1.832(3)	F18	C57	1.339(4)
N1	C7	1.447(5)	F19	C65	1.271(4)
N1	C8	1.467(4)	F20	C65	1.299(5)
N1	C9	1.465(4)	F21	C65	1.232(4)
C1	C2	1.403(4)	F91	C64	1.318(4)
C1	C6	1.410(4)	F92	C64	1.336(4)
C2	C3	1.379(5)	F93	C64	1.311(4)
C3	C4	1.376(6)	C34	C35	1.401(4)
C4	C5	1.381(6)	C34	C39	1.398(4)
C5	C6	1.397(5)	C34	B1	1.642(4)
C6	C7	1.507(5)	C35	C36	1.391(4)
C10	C11	1.396(4)	C36	C37	1.391(4)
C10	C15	1.395(4)	C36	C40	1.493(4)
C11	C12	1.383(4)	C37	C38	1.379(4)
C12	C13	1.384(5)	C38	C39	1.393(4)
C13	C14	1.372(5)	C38	C41	1.503(4)
C14	C15	1.393(4)	C42	C43	1.405(4)
C16	C17	1.375(4)	C42	C47	1.393(4)
C16	C21	1.385(4)	C42	B1	1.637(4)
C17	C18	1.391(5)	C43	C44	1.388(4)
C18	C19	1.371(6)	C44	C45	1.392(4)
C19	C20	1.370(5)	C44	C48	1.496(4)
C20	C21	1.390(5)	C45	C46	1.382(4)
C22	C23	1.393(4)	C46	C47	1.396(4)
C22	C27	1.399(4)	C46	C49	1.495(4)
C23	C24	1.383(5)	C48	F9A	1.291(11)
C24	C25	1.382(6)	C48	F8A	1.252(10)
C25	C26	1.386(6)	C48	F7A	1.277(10)
C26	C27	1.385(5)	C50	C51	1.396(4)

C28	C29	1.400(4)	C50	C55	1.407(4)
C28	C33	1.397(4)	C50	B1	1.639(4)
C29	C30	1.389(5)	C51	C52	1.392(4)
C30	C31	1.380(6)	C52	C53	1.382(4)
C31	C32	1.378(5)	C52	C56	1.501(4)
C32	C33	1.383(5)	C53	C54	1.383(4)
F1	C40	1.331(4)	C54	C55	1.389(4)
F2	C40	1.342(4)	C54	C57	1.496(4)
F3	C40	1.328(4)	C58	C59	1.397(4)
F4	C41	1.283(4)	C58	C63	1.401(4)
F5	C41	1.321(5)	C58	B1	1.644(4)
F6	C41	1.294(5)	C59	C60	1.392(4)
F7	C48	1.316(5)	C60	C61	1.387(4)
F8	C48	1.330(5)	C60	C64	1.498(4)
F9	C48	1.338(5)	C61	C62	1.385(4)
F10	C49	1.295(4)	C62	C63	1.387(4)
F11	C49	1.271(4)	C62	C65	1.498(4)
F12	C49	1.279(5)			

Table 5 Bond Angles for [2c]BAr^F.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C1	P1	P2	110.52(9)	C44	C43	C42	122.0(3)
C10	P1	P2	109.89(9)	C43	C44	C45	120.6(3)
C10	P1	C1	107.12(13)	C43	C44	C48	120.8(3)
C16	P1	P2	114.99(10)	C45	C44	C48	118.6(2)
C16	P1	C1	108.97(13)	C46	C45	C44	118.5(2)
C16	P1	C10	104.95(13)	C45	C46	C47	120.6(3)
C22	P2	P1	100.88(10)	C45	C46	C49	120.4(3)
C22	P2	C28	106.73(14)	C47	C46	C49	118.9(3)
C28	P2	P1	97.81(10)	C42	C47	C46	122.2(3)
C7	N1	C8	110.8(3)	F7	C48	F8	105.0(4)
C7	N1	C9	111.6(3)	F7	C48	F9	104.9(4)
C9	N1	C8	109.1(3)	F7	C48	C44	114.1(3)
C2	C1	P1	117.0(2)	F8	C48	F9	103.8(4)
C2	C1	C6	119.2(3)	F8	C48	C44	112.9(3)
C6	C1	P1	123.6(2)	F9	C48	C44	114.9(3)
C3	C2	C1	121.2(3)	F9A	C48	C44	108.0(5)
C4	C3	C2	119.6(3)	F8A	C48	C44	111.1(5)
C3	C4	C5	120.3(3)	F8A	C48	F9A	110.1(11)
C4	C5	C6	121.6(3)	F8A	C48	F7A	108.1(10)
C1	C6	C7	123.3(3)	F7A	C48	C44	111.2(6)
C5	C6	C1	118.1(3)	F7A	C48	F9A	108.3(11)
C5	C6	C7	118.5(3)	F10	C49	C46	113.7(3)
N1	C7	C6	112.0(3)	F11	C49	F10	107.0(4)
C11	C10	P1	120.7(2)	F11	C49	F12	104.3(5)
C15	C10	P1	119.8(2)	F11	C49	C46	113.2(3)
C15	C10	C11	119.5(2)	F12	C49	F10	104.9(4)
C12	C11	C10	119.9(3)	F12	C49	C46	112.8(3)
C11	C12	C13	120.4(3)	C51	C50	C55	115.8(2)
C14	C13	C12	120.1(3)	C51	C50	B1	122.2(2)
C13	C14	C15	120.5(3)	C55	C50	B1	121.4(2)
C14	C15	C10	119.6(3)	C52	C51	C50	122.5(3)

C17	C16	P1	122.6(2)
C17	C16	C21	119.7(3)
C21	C16	P1	117.6(2)
C16	C17	C18	119.4(3)
C19	C18	C17	120.9(4)
C20	C19	C18	119.8(3)
C19	C20	C21	119.8(3)
C16	C21	C20	120.3(3)
C23	C22	P2	113.9(2)
C23	C22	C27	119.1(3)
C27	C22	P2	127.0(2)
C24	C23	C22	120.5(3)
C25	C24	C23	120.0(4)
C24	C25	C26	120.1(3)
C27	C26	C25	120.3(3)
C26	C27	C22	120.0(3)
C29	C28	P2	125.0(3)
C33	C28	P2	116.3(2)
C33	C28	C29	118.6(3)
C30	C29	C28	120.0(3)
C31	C30	C29	120.4(3)
C32	C31	C30	120.0(3)
C31	C32	C33	120.2(3)
C32	C33	C28	120.6(3)
C35	C34	B1	121.8(2)
C39	C34	C35	115.9(2)
C39	C34	B1	121.8(2)
C36	C35	C34	122.1(2)
C35	C36	C37	120.7(2)
C35	C36	C40	121.1(2)
C37	C36	C40	118.3(2)
C38	C37	C36	118.2(2)
C37	C38	C39	120.9(3)
C37	C38	C41	119.8(3)
C39	C38	C41	119.2(3)
C38	C39	C34	122.1(2)
F1	C40	F2	106.0(3)
F1	C40	C36	113.6(2)
F2	C40	C36	111.9(2)
F3	C40	F1	106.8(3)
F3	C40	F2	105.3(3)
F3	C40	C36	112.5(2)
F4	C41	F5	104.4(4)
F4	C41	F6	110.6(4)
F4	C41	C38	113.3(3)
F5	C41	C38	112.3(3)
F6	C41	F5	103.3(3)
F6	C41	C38	112.2(3)
C43	C42	B1	120.3(2)
C47	C42	C43	116.2(2)
C47	C42	B1	123.1(2)
C51	C52	C56	120.2(3)
C53	C52	C51	120.6(3)
C53	C52	C56	119.2(3)
C52	C53	C54	118.2(3)
C53	C54	C55	121.2(3)
C53	C54	C57	118.1(3)
C55	C54	C57	120.7(3)
C54	C55	C50	121.7(2)
F13	C56	F14	101.7(3)
F13	C56	C52	112.6(3)
F14	C56	C52	112.0(3)
F15	C56	F13	110.6(4)
F15	C56	F14	106.1(4)
F15	C56	C52	113.2(3)
F16	C57	F17	106.0(3)
F16	C57	F18	106.8(3)
F16	C57	C54	112.2(3)
F17	C57	F18	105.5(3)
F17	C57	C54	113.2(3)
F18	C57	C54	112.6(3)
C59	C58	C63	116.1(2)
C59	C58	B1	122.2(2)
C63	C58	B1	121.0(2)
C60	C59	C58	122.1(3)
C59	C60	C64	119.5(3)
C61	C60	C59	120.5(3)
C61	C60	C64	119.9(3)
C62	C61	C60	118.4(3)
C61	C62	C63	120.7(3)
C61	C62	C65	119.5(3)
C63	C62	C65	119.8(3)
C62	C63	C58	122.1(2)
F91	C64	F92	103.0(3)
F91	C64	C60	113.1(2)
F92	C64	C60	112.8(2)
F93	C64	F91	108.5(3)
F93	C64	F92	105.4(3)
F93	C64	C60	113.3(3)
F19	C65	F20	100.5(4)
F19	C65	C62	114.1(3)
F20	C65	C62	112.8(3)
F21	C65	F19	108.9(5)
F21	C65	F20	105.1(4)
F21	C65	C62	114.2(3)
C34	B1	C58	112.6(2)
C42	B1	C34	103.60(19)
C42	B1	C50	113.7(2)
C42	B1	C58	112.6(2)
C50	B1	C34	112.9(2)
C50	B1	C58	101.74(19)

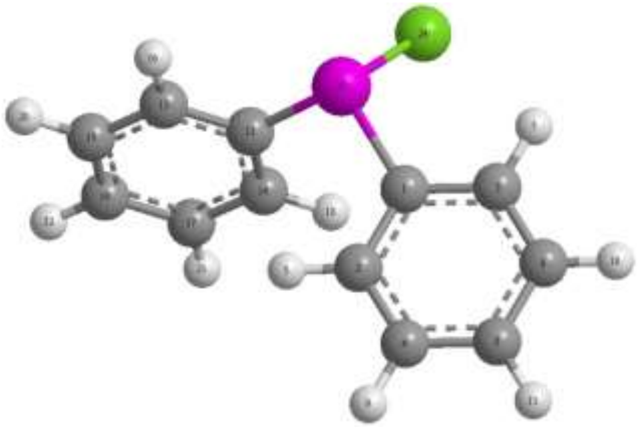
Table 8 Atomic Occupancy for xstr0487.

Atom	Occupancy	Atom	Occupancy	Atom	Occupancy
F7	0.75	F8	0.75	F9	0.75
F9A	0.25	F8A	0.25	F7A	0.25

Computational SI

Calculations were performed using the Gaussian09[18]suite of programmes. Structures were preoptimised at the HF/3-21G level followed by optimisation at the M06-2X/6-311+G(d,p) level with PCM(Dichloromethane) solvation[19]. NBO calculations and NAO Wiberg Bond Index determination were performed using NBO 3.1[20] Mayer Bond indices[21] and Mayer's Fuzzy Bond Indices[22] were calculated using Multiwfn.[23] The Mayer Bond Indices are included for reference only and should not be interpreted as chemically meaningful – the use of diffuse functions to model the π-rich species makes the conventional Mayer bond index formulation inapplicable.[24] The Fuzzy bond indices were used to describe the nature of bonding in the compounds as they show stronger correlation between changes in bond index and bond length than the NAO-adjusted Wiberg Bond Indices. In all cases, structures were confirmed as minima by frequency analysis and the absence of imaginary frequencies. Full Cartesian coordinates for the optimised geometries are provided below.

Ph_2PCl



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 Number     Number       Type             X           Y           Z
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      2          6           0        2.391024   -1.994059    0.620242
      3          6           0        0.485674   -2.613900   -0.723084
      4          6           0        2.740860   -3.335795    0.738587
      5          1           0        3.002654   -1.239959    1.103427
      6          6           0        0.833793   -3.953815   -0.594664
      7          1           0       -0.394798   -2.342892   -1.295030
      8          6           0        1.962068   -4.318001    0.135593
      9          1           0        3.619636   -3.611231    1.309763
     10          1           0        0.222787   -4.713847   -1.067046
     11          1           0        2.231432   -5.362780    0.234426
     12          6           0        1.368573    0.875258    1.209606
     13          6           0        2.196975    1.997386    1.205757
     14          6           0        0.929027    0.340976    2.425897
     15          6           0        2.591691    2.580186    2.409483
     16          1           0        2.534728    2.418019    0.264330
     17          6           0        1.314912    0.927772    3.621865
     18          1           0        0.285477   -0.532883    2.429322
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     19          6           0        2.150266    2.046619    3.613572
     20          1           0        3.237476    3.450040    2.402132
     21          1           0        0.969660    0.515458    4.562636
     22          1           0        2.452877    2.500784    4.549863
     23         15           0        0.918401    0.158792   -0.414626
     24         17           0       -1.194176    0.135101   -0.213615
 ---------------------------------------------------------------------
```

Total Energy (Hartree): -1264.780774

Sum of electronic and thermal Free Energies(Hartree)= -1264.636867

Selected Bond Lengths:

P(23)-Cl(24)	2.12225

Selected NBO Charges:

P(23)	0.891
Cl(24)	-0.344

Selected Wiberg Bond Indices:

P(23)-Cl(24)	0.8502

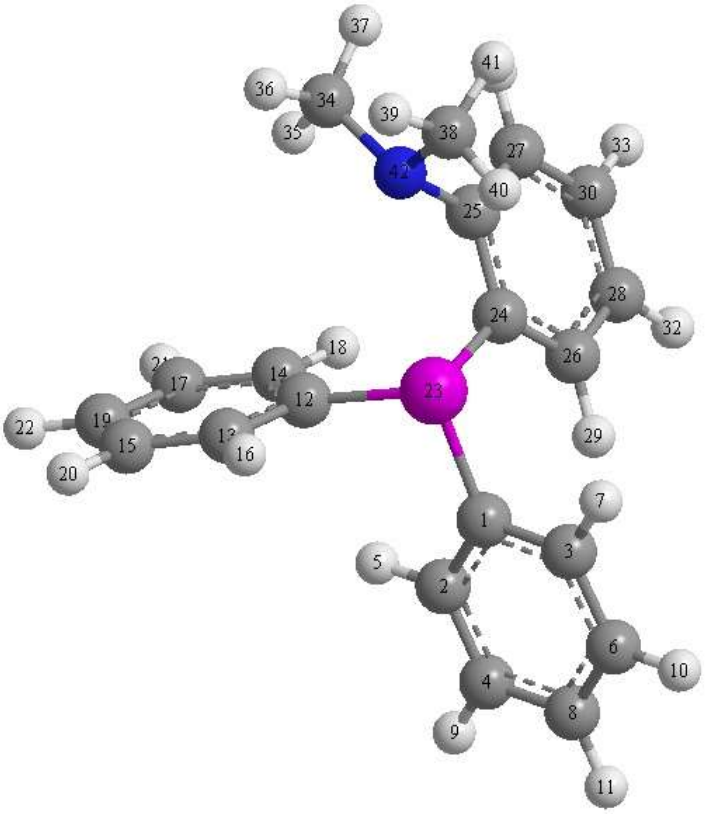
Selected Mayer Bond Indices:

P(23)-Cl(24)	1.73917237

Selected Fuzzy Bond Indices:

P(23)-Cl(24)	1.34854420

1b



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      2          6           0        1.553277   -2.232337    1.120666
      3          6           0        1.257849   -2.848076   -1.187179
      4          6           0        1.914497   -3.542825    1.420865
      5          1           0        1.532140   -1.488826    1.909941
      6          6           0        1.605982   -4.161756   -0.885925
      7          1           0        1.013166   -2.578724   -2.210285
      8          6           0        1.937397   -4.510638    0.420106
      9          1           0        2.175537   -3.808673    2.438920
     10          1           0        1.628131   -4.908109   -1.671544
     11          1           0        2.216965   -5.530817    0.656274
     12          6           0        1.335817    0.828495    0.720333
     13          6           0        2.645303    1.305202    0.614017
     14          6           0        0.600137    1.127645    1.869606
     15          6           0        3.213957    2.057121    1.638055
     16          1           0        3.224786    1.088142   -0.278174
     17          6           0        1.165180    1.887170    2.890618
     18          1           0       -0.417623    0.766320    1.972455
     19          6           0        2.472870    2.352182    2.778543
     20          1           0        4.230953    2.418963    1.540885
     21          1           0        0.583307    2.114056    3.776820
     22          1           0        2.910747    2.943130    3.574486
     23         15           0        0.698535   -0.172498   -0.694577
     24          6           0       -1.104533   -0.241177   -0.293987
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     25          6           0       -1.827853    0.953046   -0.461058
     26          6           0       -1.767351   -1.380018    0.162511
     27          6           0       -3.181686    0.994648   -0.131867
     28          6           0       -3.125766   -1.335781    0.473907
     29          1           0       -1.221356   -2.306786    0.297953
     30          6           0       -3.829223   -0.145811    0.337765
     31          1           0       -3.734258    1.920367   -0.244906
     32          1           0       -3.624269   -2.227143    0.836134
     33          1           0       -4.882259   -0.102012    0.590753
     34          6           0       -1.488432    3.360669   -0.340558
     35          1           0       -1.467253    3.255333    0.745416
     36          1           0       -0.751291    4.112571   -0.630342
     37          1           0       -2.480803    3.726228   -0.645212
     38          6           0       -1.169653    2.173569   -2.418885
     39          1           0       -0.495773    2.964782   -2.754143
     40          1           0       -0.836339    1.229079   -2.851144
     41          1           0       -2.184058    2.394726   -2.785397
     42          7           0       -1.125022    2.093963   -0.959682
 ---------------------------------------------------------------------
```

Total Energy (Hartree): -1170.112564

Sum of electronic and thermal Free Energies(Hartree)= -1169.815721

HOMO Energy (Hartree): -0.26401

Selected Bond Lengths(Angstroms):

P(42)-N(23)	2.92104

Selected Bond Angles (degrees):

P(42)-N(23)-C(1)	156.0

Selected NBO Charges:

P(42)	0.858
N(23)	-0.587
C(1)	-0.348

Selected Wiberg Bond Indices:

P(42)-N(23)	0.0188

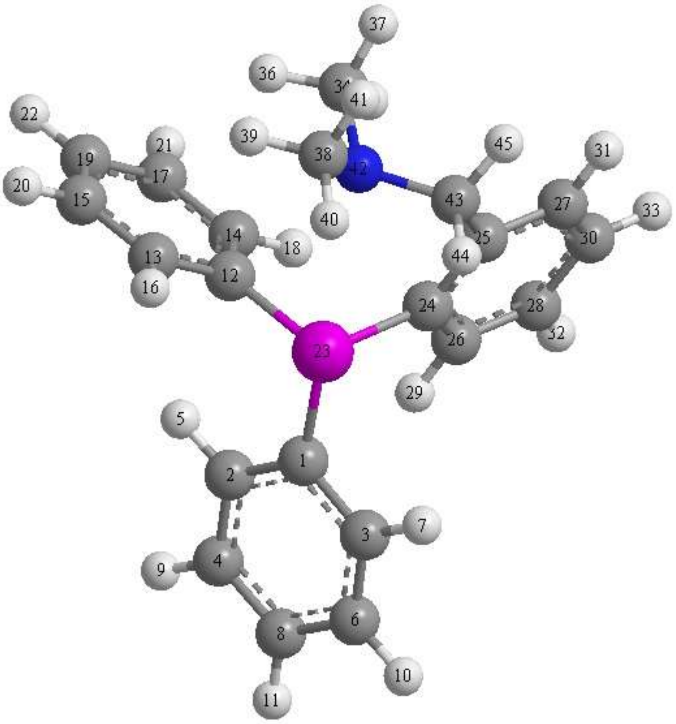
Selected Mayer Bond Indices:

P(42)-N(23)	0.05684630

Selected Fuzzy Bond Indices:

P(42)-N(23)	0.14452528

1c



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      2          6           0        1.820987   -2.286448    1.770376
      3          6           0        0.800068   -2.909751   -0.314842
      4          6           0        2.084365   -3.630311    2.036891
      5          1           0        2.127152   -1.534082    2.488044
      6          6           0        1.048377   -4.249554   -0.044005
      7          1           0        0.304991   -2.635655   -1.242329
      8          6           0        1.694529   -4.614424    1.136517
      9          1           0        2.593128   -3.904309    2.954098
     10          1           0        0.745205   -5.009041   -0.755544
     11          1           0        1.895613   -5.658310    1.347331
     12          6           0        1.416882    0.762911    1.582897
     13          6           0        2.614052    1.472954    1.467834
     14          6           0        0.721850    0.801768    2.792900
     15          6           0        3.109722    2.207766    2.541389
     16          1           0        3.154850    1.460785    0.526700
     17          6           0        1.214196    1.538156    3.867335
     18          1           0       -0.213358    0.261628    2.897128
     19          6           0        2.408426    2.243117    3.743841
     20          1           0        4.039511    2.755303    2.437532
     21          1           0        0.662842    1.562720    4.800412
     22          1           0        2.789361    2.818737    4.579442
     23         15           0        0.825091   -0.158223    0.096952
     24          6           0       -1.019960   -0.116336    0.329445
     25          6           0       -1.760383    0.911279   -0.285846
     26          6           0       -1.702581   -1.088921    1.065078
     27          6           0       -3.145777    0.941193   -0.140610
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     28          6           0       -3.088289   -1.051037    1.200764
     29          1           0       -1.149306   -1.890717    1.541551
     30          6           0       -3.814277   -0.033518    0.594746
     31          1           0       -3.706230    1.742946   -0.610797
     32          1           0       -3.593663   -1.814867    1.780297
     33          1           0       -4.892595    0.006516    0.695951
     34          6           0       -0.442475    3.362678    0.789452
     35          1           0       -1.091312    2.750428    1.419369
     36          1           0        0.418318    3.669395    1.390123
     37          1           0       -1.000952    4.262173    0.478875
     38          6           0        0.918506    3.350177   -1.190515
     39          1           0        1.749209    3.725044   -0.587771
     40          1           0        1.323642    2.705772   -1.974356
     41          1           0        0.420037    4.211530   -1.666538
     42          7           0        0.021708    2.585542   -0.345921
     43          6           0       -1.064998    1.980478   -1.098039
     44          1           0       -0.627355    1.519970   -1.990971
     45          1           0       -1.802202    2.726749   -1.440200
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```

Total Energy (Hartree): -1209.418727

Sum of electronic and thermal Free Energies(Hartree)= -1209.092482

HOMO Energy (Hartree): -0.26313

Selected Bond Lengths (Angstroms):

P(23)-N(42)   2.89306

Selected Bond Angles (Degrees):

N(42)-P(23)-C(1)   171.5

Selected NBO Charges:

P(23)   0.871

N(42)   -0.586

C(1)   -0.348

Selected Wiberg Bond Indices:

P(23)-N(42)   0.0285

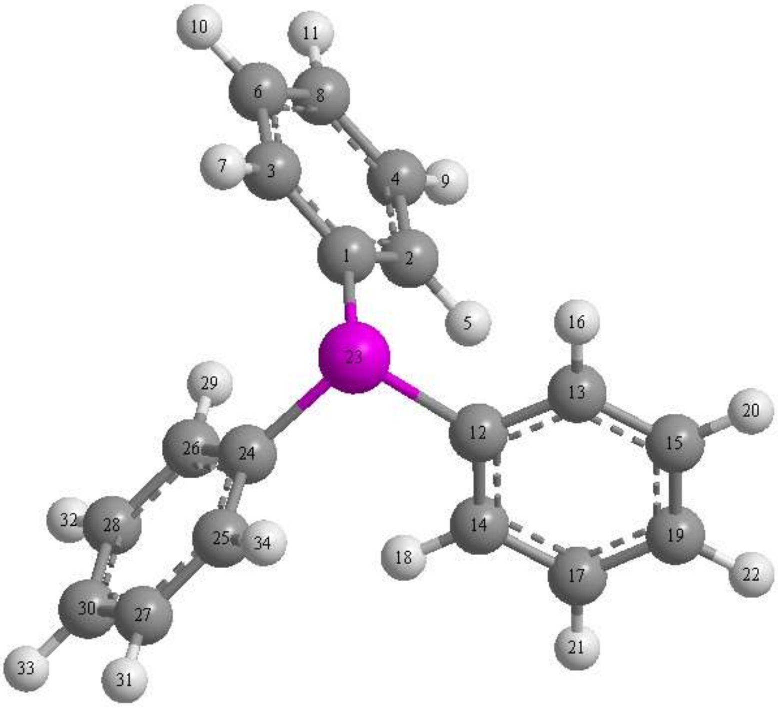
Selected Mayer Bond Indices:

P(23)-N(42)   0.06426618

Selected Fuzzy Bond Indices:

P(23)-N(42)   0.19122325

1e



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      3          6           0        1.128427   -2.837295   -1.178300
      4          6           0        2.067806   -3.528544    1.343117
      5          1           0        1.811656   -1.458499    1.848808
      6          6           0        1.469616   -4.157343   -0.903474
      7          1           0        0.770793   -2.569430   -2.167860
      8          6           0        1.941747   -4.505098    0.359635
      9          1           0        2.437750   -3.793745    2.326797
     10          1           0        1.373560   -4.911320   -1.676102
     11          1           0        2.214244   -5.531811    0.574579
     12          6           0        1.336431    0.832344    0.774729
     13          6           0        2.646346    1.313890    0.679388
     14          6           0        0.596992    1.106066    1.928018
     15          6           0        3.213906    2.038018    1.722543
     16          1           0        3.226045    1.118854   -0.217687
     17          6           0        1.161910    1.840468    2.967969
     18          1           0       -0.421735    0.745086    2.019003
     19          6           0        2.470495    2.304237    2.869331
     20          1           0        4.231168    2.401582    1.636369
     21          1           0        0.578622    2.048773    3.857550
     22          1           0        2.908000    2.874736    3.680235
     23         15           0        0.705569   -0.147712   -0.655427
     24          6           0       -1.097798   -0.217084   -0.272063
     25          6           0       -1.867379    0.887883   -0.654056
     26          6           0       -1.725078   -1.290822    0.363556
     27          6           0       -3.231583    0.928175   -0.388469
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     28          6           0       -3.094738   -1.255606    0.617540
     29          1           0       -1.147410   -2.157868    0.664295
     30          6           0       -3.849107   -0.147152    0.246632
     31          1           0       -3.813616    1.793420   -0.684047
     32          1           0       -3.570900   -2.095789    1.109822
     33          1           0       -4.913737   -0.121942    0.447052
     34          1           0       -1.393299    1.723967   -1.159535
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Total Energy (Hartree): -1036.17058

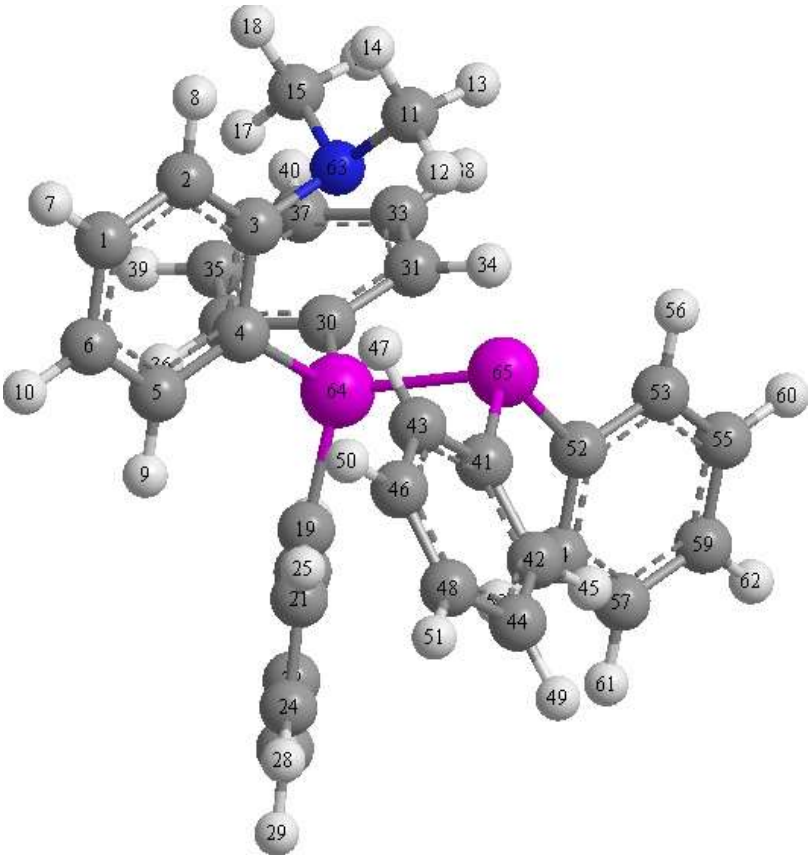
Sum of electronic and thermal Free Energies(Hartree)= -1035.942163

HOMO Energy (Hartree): -0.27429

Selected NBO Charges:

P(23)	0.84
C(1)	-0.324
C(12)	-0.324
C(24)	-0.324

2b



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      3          6           0        1.497307    0.450634    0.541531
      4          6           0        0.760875    1.525129    0.019857
      5          6           0       -0.324737    1.297834   -0.828827
      6          6           0       -0.651982   -0.003193   -1.191446
      7          1           0       -0.153265   -2.083684   -0.997338
      8          1           0        1.727453   -1.682224    0.556237
      9          1           0       -0.917976    2.121432   -1.203890
     10          1           0       -1.491191   -0.180677   -1.852175
     11          6           0        3.842954    0.166527    1.069971
     12          1           0        4.080368    0.443656    0.042127
     13          1           0        4.615898    0.578230    1.721701
     14          1           0        3.862315   -0.928410    1.156958
     15          6           0        2.208898    0.357548    2.833480
     16          1           0        2.979067    0.738867    3.506839
     17          1           0        1.252052    0.799005    3.115507
     18          1           0        2.145437   -0.733499    2.949163
     19          6           0        0.236552    4.406847   -0.337480
     20          6           0       -0.312659    5.459121    0.401657
     21          6           0        0.100415    4.389078   -1.733332
     22          6           0       -0.998120    6.478960   -0.249226
     23          1           0       -0.193971    5.500803    1.477192
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     24          6           0       -0.583444    5.414823   -2.373373
     25          1           0        0.530579    3.589498   -2.325446
     26          6           0       -1.129210    6.461052   -1.633780
     27          1           0       -1.420719    7.291618    0.328581
     28          1           0       -0.683246    5.396883   -3.451747
     29          1           0       -1.656210    7.261988   -2.138476
     30          6           0        1.115916    3.393744    2.266467
     31          6           0        2.203859    3.674704    3.089443
     32          6           0       -0.154732    3.188057    2.812530
     33          6           0        2.017793    3.759617    4.465097
     34          1           0        3.195465    3.805119    2.674064
     35          6           0       -0.330834    3.271844    4.187890
     36          1           0       -0.999287    2.954428    2.171591
     37          6           0        0.754867    3.557699    5.012651
     38          1           0        2.862504    3.975959    5.107461
     39          1           0       -1.313064    3.110196    4.614601
     40          1           0        0.615109    3.618777    6.085208
     41          6           0        3.172001    3.409899   -1.955441
     42          6           0        3.323582    4.501377   -2.813951
     43          6           0        2.850995    2.156362   -2.495105
     44          6           0        3.104770    4.351217   -4.180576
     45          1           0        3.618115    5.469002   -2.429664
     46          6           0        2.613720    2.016299   -3.857046
     47          1           0        2.777539    1.282398   -1.856032
     48          6           0        2.730926    3.117392   -4.701943
     49          1           0        3.224244    5.205002   -4.836757
     50          1           0        2.348990    1.045128   -4.257592
     51          1           0        2.549612    3.008190   -5.764427
     52          6           0        3.642414    5.274412    0.264448
     53          6           0        4.689829    5.561141    1.148845
     54          6           0        2.842725    6.324907   -0.204975
     55          6           0        4.929521    6.866299    1.565366
     56          1           0        5.323242    4.758535    1.513230
     57          6           0        3.080984    7.626775    0.218655
     58          1           0        2.042184    6.141076   -0.910566
     59          6           0        4.120433    7.899042    1.104971
     60          1           0        5.745406    7.072592    2.247262
     61          1           0        2.453982    8.430464   -0.148729
     62          1           0        4.301132    8.916377    1.431231
     63          7           0        2.555447    0.741955    1.460781
     64         15           0        1.306363    3.193595    0.478946
     65         15           0        3.464671    3.487854   -0.140260
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Total Energy (Hartree): -1974.527096

Sum of electronic and thermal Free Energies(Hartree)= -1974.054936

Selected Bond Lengths:

N(63)-P(64)	2.92143
P(64)-P(65)	2.26457

Selected Bond Angles:

N(63)-P(64)-C(19)	165.0

Selected NBO Charges:

N(63)	-0.606

P(64)	1.313
P(65)	0.725
C(19)	-0.402

Selected Wiberg Bond Indices:

N(63)-P(64)	0.0231
P(64)-P(65)	0.8498

Selected Mayer Bond Indices:

N(63)-P(64)	-0.03048788
P(64)-P(65)	0.71221565

Selected Fuzzy Bond Indices:

N(63)-P(64)	0.13113318
P(64)-P(65)	1.02173767

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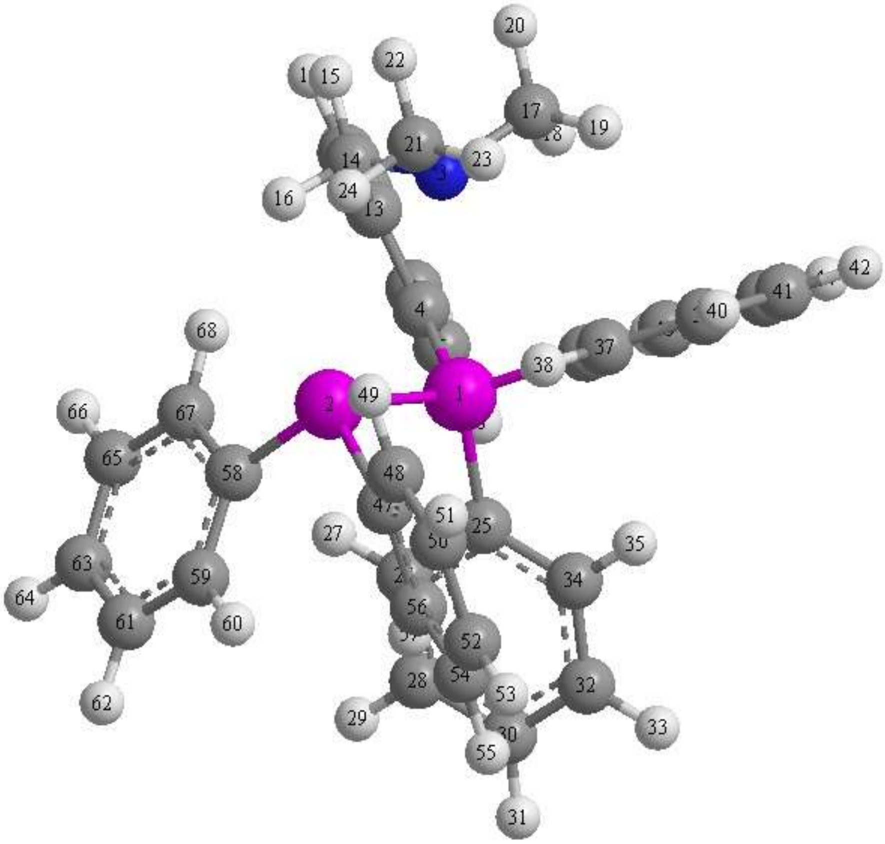

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 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
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      1         15           0        6.907375    1.195314    4.772972
      2         15           0        6.585071    0.262934    2.724018
      3          7           0        4.707572   -0.787445    5.230673
      4          6           0        5.416211    2.106585    5.314118
      5          6           0        5.619372    3.377088    5.864995
      6          1           0        6.619476    3.776042    5.971750
      7          6           0        4.545128    4.150885    6.289857
      8          1           0        4.725080    5.129888    6.716053
      9          6           0        3.254719    3.659436    6.162146
     10          1           0        2.407456    4.254113    6.481892
     11          6           0        3.049219    2.385806    5.640791
     12          1           0        2.041616    1.991730    5.570919
     13          6           0        4.107348    1.587336    5.215687
     14          6           0        3.797044    0.204558    4.685311
     15          1           0        2.745204   -0.032638    4.911282
     16          1           0        3.893618    0.187877    3.593918
     17          6           0        4.507768   -0.962622    6.665955
     18          1           0        4.623345   -0.009208    7.184885
     19          1           0        5.258448   -1.655343    7.053565
     20          1           0        3.506126   -1.362728    6.887375
     21          6           0        4.574955   -2.066655    4.545059
     22          1           0        3.577794   -2.509859    4.693501
     23          1           0        5.321624   -2.762250    4.935713
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    24          1           0        4.744358   -1.934222    3.475451
    25          6           0        8.266148    2.400936    4.660915
    26          6           0        8.121746    3.561746    3.887869
    27          1           0        7.163835    3.823119    3.452471
    28          6           0        9.212663    4.394955    3.679556
    29          1           0        9.094035    5.289209    3.079876
    30          6           0       10.450535    4.081715    4.236621
    31          1           0       11.299512    4.733170    4.067249
    32          6           0       10.594718    2.937681    5.013334
    33          1           0       11.553927    2.692788    5.452620
    34          6           0        9.508650    2.094585    5.224885
    35          1           0        9.642140    1.194046    5.811312
    36          6           0        7.426998    0.009153    6.044027
    37          6           0        7.820993   -1.289958    5.728789
    38          1           0        7.803477   -1.643802    4.706170
    39          6           0        8.227687   -2.147658    6.744806
    40          1           0        8.530358   -3.158853    6.501381
    41          6           0        8.239927   -1.711086    8.067164
    42          1           0        8.553815   -2.384005    8.855947
    43          6           0        7.846597   -0.413181    8.377681
    44          1           0        7.851486   -0.071438    9.405398
    45          6           0        7.441176    0.452637    7.367259
    46          1           0        7.129887    1.462299    7.616500
    47          6           0        8.281205   -0.364840    2.394339
    48          6           0        8.342244   -1.737806    2.123853
    49          1           0        7.428761   -2.324170    2.106251
    50          6           0        9.563903   -2.358705    1.885945
    51          1           0        9.596101   -3.421064    1.677380
    52          6           0       10.737390   -1.612760    1.918758
    53          1           0       11.691365   -2.094406    1.739702
    54          6           0       10.686271   -0.244718    2.175371
    55          1           0       11.597955    0.340656    2.192670
    56          6           0        9.467211    0.380544    2.408795
    57          1           0        9.450219    1.447364    2.592162
    58          6           0        6.442427    1.842090    1.792293
    59          6           0        7.390150    2.304291    0.875551
    60          1           0        8.286203    1.733540    0.671040
    61          6           0        7.184992    3.507293    0.205137
    62          1           0        7.928677    3.857220   -0.500911
    63          6           0        6.039630    4.259450    0.442226
    64          1           0        5.891648    5.202011   -0.070918
    65          6           0        5.071079    3.784800    1.323303
    66          1           0        4.161844    4.348576    1.493483
    67          6           0        5.262684    2.575472    1.979632
    68          1           0        4.487903    2.213283    2.645822
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Total Energy (Hartree): -2013.832393

Sum of electronic and thermal Free Energies(Hartree)= -2013.329251

Selected Bond Lengths:

N(3)-P(1)	2.99666
P(1)-P(2)	2.27408

Selected Bond Angles:

N(3)-P(1)-C(25)	174.7

Selected NBO Charges:

N(3)	-0.596
P(1)	1.325
P(2)	0.719
C(25)	-0.429

Selected Wiberg Bond Indices:

N(3)-P(1)	0.0294
P(1)-P(2)	0.8502

Selected Mayer Bond Indices:

N(3)-P(1)	-0.01177609
P(1)-P(2)	0.66231300

Selected Fuzzy Bond Indices:

N(3)-P(1)	0.14401149
P(1)-P(2)	1.01674015

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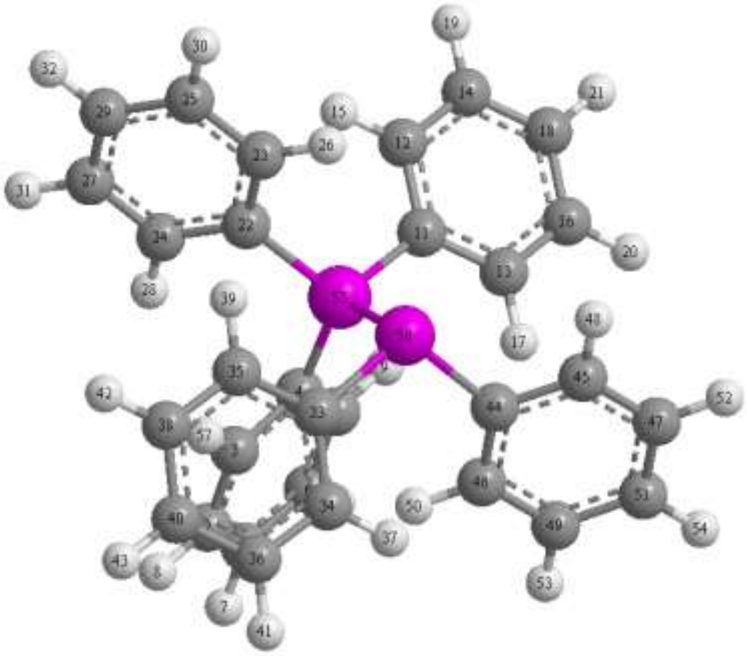

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 Number     Number       Type             X           Y           Z
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      1          6           0        0.241409   -1.210718    0.953906
      2          6           0        1.324825   -0.662090    1.636230
      3          6           0        1.672767    0.667498    1.440132
      4          6           0        0.927444    1.452734    0.549148
      5          6           0       -0.170991    0.908128   -0.120568
      6          6           0       -0.509181   -0.425054    0.085733
      7          1           0       -0.021947   -2.250330    1.107037
      8          1           0        1.901922   -1.268367    2.323541
      9          1           0       -0.765072    1.512546   -0.794423
     10          1           0       -1.361468   -0.846527   -0.432557
     11          6           0        0.329284    3.955188   -0.945064
     12          6           0       -0.395274    5.077072   -0.532249
     13          6           0        0.184585    3.466625   -2.251111
     14          6           0       -1.253352    5.709705   -1.425097
     15          1           0       -0.299718    5.457681    0.477071
     16          6           0       -0.675115    4.108048   -3.132694
     17          1           0        0.721781    2.585899   -2.582047
     18          6           0       -1.390156    5.230308   -2.723058
     19          1           0       -1.814939    6.577520   -1.102080
     20          1           0       -0.786411    3.726102   -4.139988
     21          1           0       -2.058555    5.727444   -3.415665
     22          6           0        1.510307    4.088840    1.753460
     23          6           0        2.112931    5.352601    1.741004
     24          6           0        0.967565    3.574446    2.931379
     25          6           0        2.178699    6.092376    2.913354
     26          1           0        2.530041    5.755989    0.824077
     27          6           0        1.044465    4.322808    4.102511
     28          1           0        0.489389    2.602536    2.941921
     29          6           0        1.650727    5.573757    4.094499
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     30          1           0        2.645224    7.069478    2.906166
     31          1           0        0.628946    3.924086    5.019663
     32          1           0        1.710064    6.149904    5.010002
     33          6           0        4.419152    2.218666    0.549890
     34          6           0        4.922137    0.953818    0.236236
     35          6           0        4.629751    2.742129    1.833671
     36          6           0        5.576892    0.203225    1.208939
     37          1           0        4.817993    0.549452   -0.762011
     38          6           0        5.266085    1.980075    2.805439
     39          1           0        4.291687    3.742622    2.081111
     40          6           0        5.731337    0.703680    2.497427
     41          1           0        5.962858   -0.776852    0.955581
     42          1           0        5.407983    2.388597    3.798755
     43          1           0        6.230224    0.110685    3.254456
     44          6           0        3.254158    2.291490   -2.153629
     45          6           0        3.434920    2.967859   -3.364229
     46          6           0        2.766838    0.977262   -2.165882
     47          6           0        3.125732    2.346053   -4.570699
     48          1           0        3.801600    3.988425   -3.362705
     49          6           0        2.454922    0.362318   -3.371754
     50          1           0        2.612365    0.437013   -1.239254
     51          6           0        2.628755    1.047789   -4.573708
     52          1           0        3.266288    2.879098   -5.502974
     53          1           0        2.070546   -0.650512   -3.373407
     54          1           0        2.378786    0.565361   -5.511096
     55         15           0        1.464348    3.145534    0.213250
     56         15           0        3.544317    3.301203   -0.650163
     57          1           0        2.512421    1.084847    1.983916
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Total Energy (Hartree): -1840.582741

Sum of electronic and thermal Free Energies(Hartree)= -1840.180995

Selected Bond Lengths (Angstroms):

P(55)-P(56)	2.25743

Selected NBO Charges:

P(55)	1.284
P(56)	0.71
C(4)	-0.415
C(11)	-0.406
C(22)	-0.410

Selected Wiberg Bond Indices:

P(55)-P(56)	0.8546

Selected Mayer Bond Indices:

P(55)-P(56)	1.05219178

Selected Fuzzy Bond Indices:

P(55)-P(56)	1.04591081

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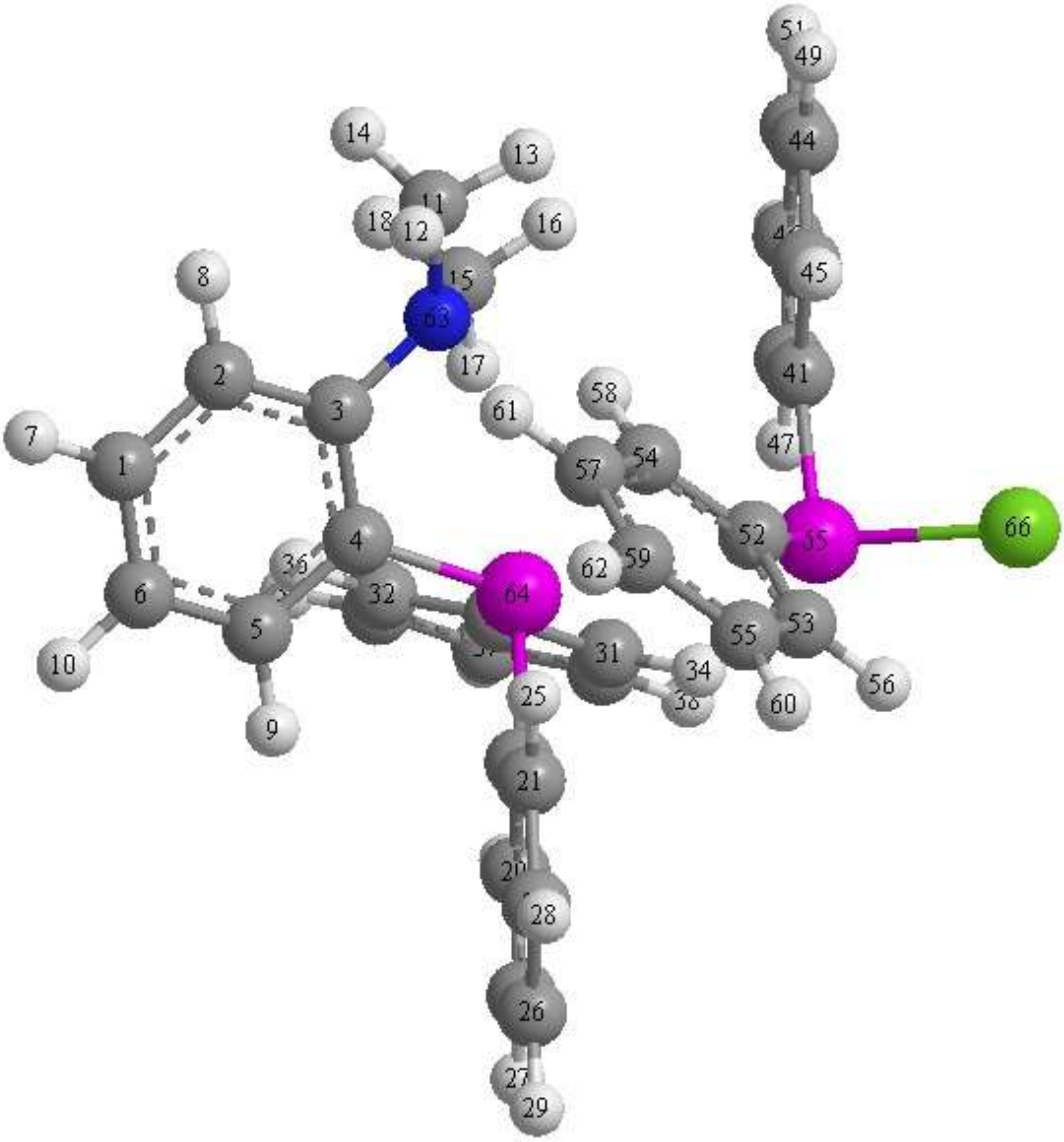

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 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
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      1          6           0       -1.061809   -1.023502    0.751831
      2          6           0        0.313601   -1.091896    0.936595
      3          6           0        1.105420    0.065164    0.916389
      4          6           0        0.482647    1.309236    0.670795
      5          6           0       -0.904836    1.356026    0.507280
      6          6           0       -1.681964    0.204742    0.551762
      7          1           0       -1.648957   -1.934564    0.773828
      8          1           0        0.775686   -2.055953    1.107991
      9          1           0       -1.382309    2.311496    0.316830
     10          1           0       -2.754830    0.266043    0.415360
     11          6           0        3.141813   -1.276932    0.832959
     12          1           0        2.792768   -1.668268   -0.124040
     13          1           0        4.220324   -1.112126    0.768047
     14          1           0        2.959428   -2.031373    1.612733
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     15          6           0        2.976529    0.544620    2.385637
     16          1           0        4.064592    0.613676    2.354753
     17          1           0        2.579748    1.543359    2.562606
     18          1           0        2.682117   -0.101404    3.227354
     19          6           0        0.457379    3.760348   -0.775308
     20          6           0       -0.218165    4.943952   -0.471974
     21          6           0        0.388991    3.259376   -2.082265
     22          6           0       -0.949200    5.611564   -1.453634
     23          1           0       -0.186153    5.349045    0.532680
     24          6           0       -0.346136    3.922388   -3.057273
     25          1           0        0.905161    2.339181   -2.338435
     26          6           0       -1.015698    5.104285   -2.746449
     27          1           0       -1.471717    6.527192   -1.201618
     28          1           0       -0.391567    3.517702   -4.062093
     29          1           0       -1.584536    5.624583   -3.508126
     30          6           0        1.267202    3.783273    1.970915
     31          6           0        1.976093    4.985834    2.087589
     32          6           0        0.466036    3.365598    3.035171
     33          6           0        1.871816    5.762323    3.235752
     34          1           0        2.603338    5.320913    1.265857
     35          6           0        0.373496    4.137620    4.192088
     36          1           0       -0.086620    2.434868    2.966159
     37          6           0        1.071309    5.336410    4.293846
     38          1           0        2.418924    6.695153    3.307318
     39          1           0       -0.249310    3.800986    5.012872
     40          1           0        0.995938    5.935717    5.193586
     41          6           0        5.185965    2.614414    0.257438
     42          6           0        5.895294    1.446929   -0.037356
     43          6           0        5.244079    3.144148    1.548954
     44          6           0        6.647319    0.819028    0.949267
     45          1           0        5.873424    1.038120   -1.041579
     46          6           0        6.010533    2.524071    2.531855
     47          1           0        4.694586    4.049472    1.787090
     48          6           0        6.711459    1.360424    2.232548
     49          1           0        7.195387   -0.085864    0.713509
     50          1           0        6.055399    2.946849    3.528545
     51          1           0        7.307247    0.874271    2.996236
     52          6           0        3.729861    2.398769   -2.247421
     53          6           0        3.554090    2.834880   -3.564484
     54          6           0        3.299002    1.117979   -1.889904
     55          6           0        2.970248    2.000524   -4.511422
     56          1           0        3.870925    3.830834   -3.854287
     57          6           0        2.713265    0.285795   -2.840877
     58          1           0        3.384644    0.782182   -0.862265
     59          6           0        2.546553    0.723370   -4.151440
     60          1           0        2.841419    2.351606   -5.528483
     61          1           0        2.377245   -0.703549   -2.550930
     62          1           0        2.087449    0.074542   -4.888131
     63          7           0        2.506349    0.001720    1.112309
     64         15           0        1.510301    2.823708    0.418538
     65         15           0        4.284483    3.621647   -0.987303
     66         17           0        6.031638    4.333993   -2.048538
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Total Energy (Hartree): -2434.911345

Sum of electronic and thermal Free Energies(Hartree)= -2434.44472

Selected Bond Lengths (Angstroms):

N(63)-P(64)	3.07198
P(64)-P(65)	3.21079
P(65)-Cl(66)	2.16476

Selected Bond Angles (Degrees):

N(63)-P(64)-C(19)	142.8
P(64)-P(65)-Cl(66)	173.6

Selected NBO Charges:

N(63)	-0.572
P(64)	0.911
P(65)	0.916
Cl(66)	-0.380

Selected Wiberg Bond Indices:

N(63)-P(64)	0.0091
P(64)-P(65)	0.097
P(65)-Cl(66)	0.7783

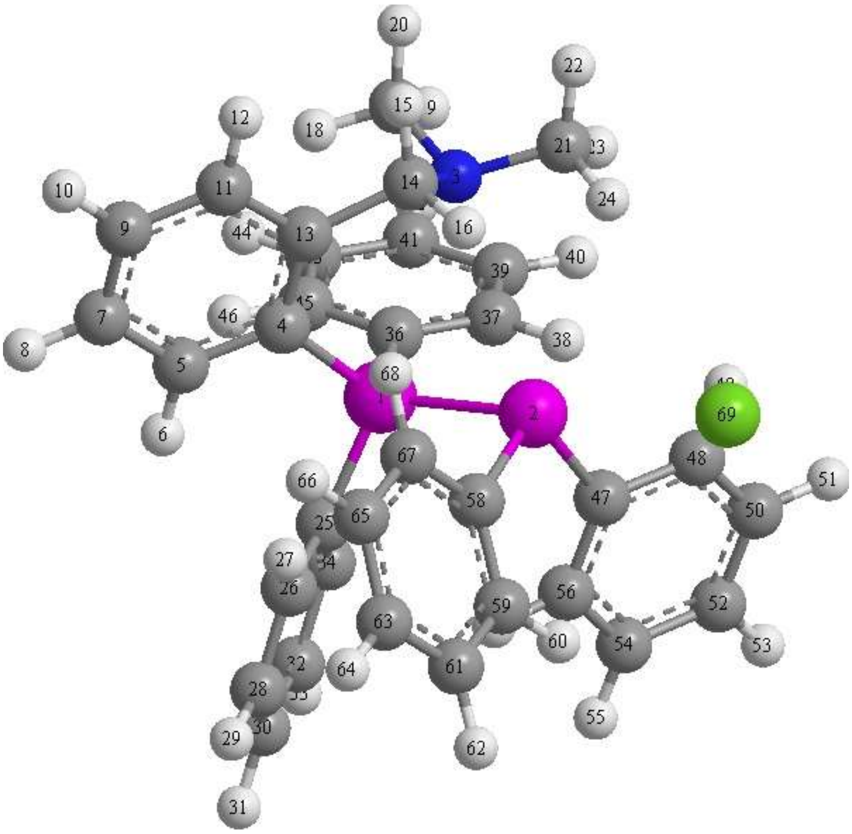
Selected Mayer Bond Indices:

N(63)-P(64)	-0.23425516
P(64)-P(65)	1.55244327
P(65)-Cl(66)	3.08199544

Selected Fuzzy Bond Indices:

N(63)-P(64)	0.09072844
P(64)-P(65)	0.27177287
P(65)-Cl(66)	1.27578268

3c



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 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
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      2         15           0        6.538317    0.225187    2.655586
      3          7           0        4.710041   -0.803039    5.209187
      4          6           0        5.432545    2.099113    5.299480
      5          6           0        5.634763    3.365095    5.860093
      6          1           0        6.634624    3.767467    5.956276
      7          6           0        4.563979    4.131826    6.306942
      8          1           0        4.746394    5.108115    6.738775
      9          6           0        3.273715    3.636758    6.193426
     10          1           0        2.428221    4.224810    6.529915
     11          6           0        3.067778    2.367375    5.662477
     12          1           0        2.060795    1.969980    5.600955
     13          6           0        4.123513    1.577354    5.213813
     14          6           0        3.805905    0.199328    4.673148
     15          1           0        2.752894   -0.034010    4.900005
     16          1           0        3.900550    0.189614    3.581718
     17          6           0        4.514537   -0.988838    6.641801
     18          1           0        4.635048   -0.039418    7.167309
     19          1           0        5.265048   -1.686207    7.021954
     20          1           0        3.512352   -1.388393    6.865519
     21          6           0        4.573098   -2.073502    4.509126
     22          1           0        3.575793   -2.517769    4.657350
     23          1           0        5.321116   -2.774263    4.888742
     24          1           0        4.738095   -1.928799    3.440164
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      25          6           0        8.272141    2.416035    4.636841
      26          6           0        8.125591    3.576419    3.864155
      27          1           0        7.170298    3.825346    3.415708
      28          6           0        9.209477    4.422042    3.667287
      29          1           0        9.086751    5.315069    3.066281
      30          6           0       10.446163    4.120736    4.233282
      31          1           0       11.290487    4.780187    4.071434
      32          6           0       10.594186    2.975521    5.007497
      33          1           0       11.552655    2.737359    5.452524
      34          6           0        9.513604    2.122268    5.208922
      35          1           0        9.651568    1.221096    5.793491
      36          6           0        7.438873    0.021770    6.011531
      37          6           0        7.829346   -1.280813    5.705781
      38          1           0        7.809715   -1.638979    4.684679
      39          6           0        8.233183   -2.135391    6.726161
      40          1           0        8.532600   -3.148824    6.487313
      41          6           0        8.245806   -1.693192    8.046516
      42          1           0        8.557280   -2.362997    8.839060
      43          6           0        7.854689   -0.392614    8.349535
      44          1           0        7.859194   -0.045741    9.375723
      45          6           0        7.452700    0.468611    7.333630
      46          1           0        7.143578    1.480333    7.576854
      47          6           0        8.253452   -0.390006    2.366774
      48          6           0        8.339653   -1.769204    2.140522
      49          1           0        7.428681   -2.354885    2.079394
      50          6           0        9.575702   -2.384293    1.980533
      51          1           0        9.626263   -3.451932    1.803913
      52          6           0       10.741948   -1.626409    2.041139
      53          1           0       11.707045   -2.103846    1.917390
      54          6           0       10.666523   -0.252751    2.250023
      55          1           0       11.570546    0.343952    2.286906
      56          6           0        9.430120    0.365676    2.409397
      57          1           0        9.397240    1.437284    2.559716
      58          6           0        6.427470    1.834722    1.769288
      59          6           0        7.376005    2.296506    0.854601
      60          1           0        8.245677    1.698292    0.615721
      61          6           0        7.199131    3.524069    0.223016
      62          1           0        7.942990    3.872623   -0.483820
      63          6           0        6.076595    4.300822    0.493705
      64          1           0        5.948604    5.260892    0.007774
      65          6           0        5.103809    3.825418    1.368674
      66          1           0        4.209285    4.405698    1.561431
      67          6           0        5.271477    2.592796    1.989517
      68          1           0        4.492387    2.229056    2.649792
      69         17           0        5.682885   -1.021734   -0.035485
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Total Energy (Hartree): -2474.214707

Sum of electronic and thermal Free Energies(Hartree)= -2473.715649

Selected Bond Lengths (Angstroms):

N(3)-P(1)	3.01817
P(1)-P(2)	2.31104
P(2)-Cl(69)	3.08682

Selected Bond Angles (Degrees):

N(3)-P(1)-C(25)	173.2
P(1)-P(2)-Cl(69)	173.4

Selected NBO Charges:

N(3)	-0.594
P(1)	1.284
P(2)	0.813
Cl(69)	-0.913

Selected Wiberg Bond Indices:

N(3)-P(1)	0.0271
P(1)-P(2)	0.7877
P(2)-Cl(69)	0.0953

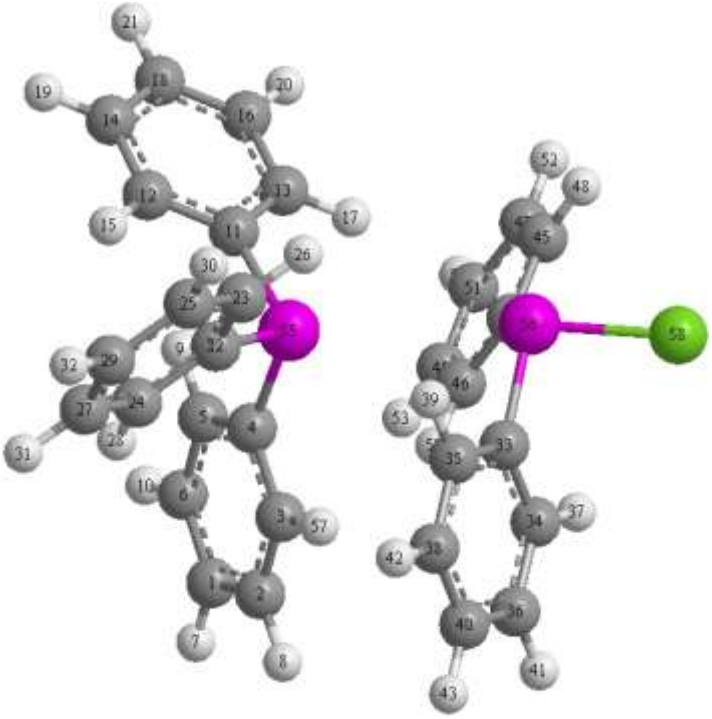
Selected Mayer Bond Indices:

N(3)-P(1)	0.05060327
P(1)-P(2)	0.02659623
P(2)-Cl(69)	0.53538382

Selected Fuzzy Bond Indices:

N(3)-P(1)	0.13619943
P(1)-P(2)	0.97610787
P(2)-Cl(69)	0.38310981

3e



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 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
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      1          6           0        0.257841   -1.007732    0.966435
      2          6           0        1.417688   -0.505610    1.555198
      3          6           0        1.798812    0.811165    1.330220
      4          6           0        1.021137    1.652339    0.523011
      5          6           0       -0.139727    1.143312   -0.060331
      6          6           0       -0.517156   -0.180887    0.160792
      7          1           0       -0.037099   -2.036734    1.135302
      8          1           0        2.030655   -1.141739    2.184026
      9          1           0       -0.754131    1.773901   -0.693278
     10          1           0       -1.421550   -0.563523   -0.298258
     11          6           0        0.338267    4.078771   -0.828165
     12          6           0       -0.717764    4.836578   -0.318626
     13          6           0        0.406534    3.843501   -2.206231
     14          6           0       -1.693654    5.343968   -1.173616
     15          1           0       -0.781794    5.033697    0.745882
     16          6           0       -0.576757    4.338286   -3.056496
     17          1           0        1.229884    3.264603   -2.614514
     18          6           0       -1.628049    5.092481   -2.540943
     19          1           0       -2.507380    5.934614   -0.768874
     20          1           0       -0.515701    4.142399   -4.121006
     21          1           0       -2.389919    5.486376   -3.203379
     22          6           0        1.420909    4.164648    1.828965
     23          6           0        2.102678    5.366317    2.049045
     24          6           0        0.587973    3.663564    2.832553
     25          6           0        1.939141    6.064902    3.241105
     26          1           0        2.762906    5.758575    1.280685
     27          6           0        0.432959    4.357198    4.029422
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     28          1           0        0.056248    2.731094    2.678836
     29          6           0        1.104332    5.559474    4.234318
     30          1           0        2.467803    6.997898    3.397392
     31          1           0       -0.217180    3.959939    4.800267
     32          1           0        0.980567    6.098301    5.166339
     33          6           0        5.039482    2.099867    0.212382
     34          6           0        5.345585    0.737944    0.147120
     35          6           0        4.939493    2.722377    1.459424
     36          6           0        5.520085    0.004843    1.315148
     37          1           0        5.456022    0.253252   -0.817226
     38          6           0        5.125846    1.990539    2.629148
     39          1           0        4.706078    3.780993    1.516514
     40          6           0        5.408340    0.629823    2.556378
     41          1           0        5.750023   -1.052569    1.258432
     42          1           0        5.043431    2.481384    3.591764
     43          1           0        5.548744    0.056799    3.465460
     44          6           0        3.808918    2.192854   -2.427859
     45          6           0        3.713173    2.697668   -3.731121
     46          6           0        3.029835    1.091878   -2.068697
     47          6           0        2.865507    2.104907   -4.658618
     48          1           0        4.301815    3.562623   -4.021599
     49          6           0        2.170252    0.506461   -2.996170
     50          1           0        3.067879    0.694356   -1.062659
     51          6           0        2.086063    1.009493   -4.289820
     52          1           0        2.803321    2.504519   -5.663878
     53          1           0        1.562255   -0.340115   -2.697895
     54          1           0        1.414452    0.554693   -5.008475
     55         15           0        1.675858    3.345081    0.201117
     56         15           0        4.829324    3.181601   -1.256199
     57          1           0        2.712577    1.186880    1.780824
     58         17           0        6.734526    2.791096   -2.175413
 ---------------------------------------------------------------------
```

Total Energy (Hartree): -2300.968202

Sum of electronic and thermal Free Energies(Hartree)= -2300.572556

Selected Bond Lengths (Angstroms):

P(55)-P(56)	3.47776
P(56)-Cl(58)	2.1511

Selected Bond Angles (Degrees):

P(55)-P(56)-Cl(58)	172.178

Selected NBO Charges:

P(55)	0.877
P(56)	0.912
Cl(65)	-0.369

Selected Wiberg Bond Indices:

P(55)-P(56)	0.0483
P(56)-Cl(58)	0.8018

Selected Mayer Bond Indices:

P(55)-P(56)	1.32628702
P(56)-Cl(58)	2.57757290

Selected Fuzzy Bond Indices:

P(55)-P(56)	0.18465366
P(56)-Cl(58)	1.30305002

Analysis of Computational Data:

The relative stabilities of the adducts was determined by simple comparison of the energies according to the following pseudo-reaction:

$$Donor\ +\ Acceptor\ =\ Adduct$$

Therefore: $\Delta E = E(Adduct) - E(Donor) - E(Acceptor)$

Zero point corrected Free energies were derived from the frequency calculations and analysed analogously. In comparing the relative stabilities of the cationic species, a similar logic was used.

$$Donor\ +\ Acceptor\ =\ Adduct + Anion$$

Therefore: $\Delta E = E(Adduct) + E(Anion) - E(Donor) - E(Acceptor)$. Since for comparision the Anions must be identical, direct comparision may be made for $\Delta E = E(Adduct) + E(Donor) - E(Acceptor)$. As in all cases the energy of the anion will cancel when comparisons are made.

References:

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[1] E.B. Pedersen, *J. Chem. Soc., Perkin Trans. 2*, 1977, 473-476

[2] J. Scholz, V. Hager, X. Wang, F. T. U. Kohler, M. Sternberg , M. Haumann, N. Szesni, K. Meyer, and P. Wasserscheid, *ChemCatChem*, 2014, **6**, 162 – 169

[3] D. K. Duttaa, B. Deba, G. Hua, and J. D. Woollins, *J. Mol. Cat. A: Chem.*, 2012, 353–**354**, 7–12

[4] W. Chuang, I. Lin, H. Chen, Y. Chang, and S. C. N. Hsu, *Inorg. Chem.*, 2010, **49**, 5377–5384

[5] A. Pagnoux-Ozherelyev, D. Bolien, S. Gaillard, F. Peudru, J-F. Lohier, R. J. Whitby , and J-L. Renaud, *Journal of Organometallic Chemistry*, 2014, **774**, 35-42

[6] E. Shirakawa, Y. Yamamoto, Y. Nakao, S. Oda, T. Tsuchimoto, and T. Hiyama, *Angew. Chem. Int. Ed.*, 2004, **43**, 3448 –3451

[7] D. C. Mudalige, E. S.F. Ma, S. J. Rettig, B. O. Patrick, and B. R. James, *Can. J. Chem.*, 2014, 92, 716–723

[8] L. J. Hounjet, R. McDonald, M. J. Ferguson, and M. Cowie, *Inorg. Chem.*, 2011, **50**, 5361–5378

[9] L. J. Hounjet, M. Bierenstiel, M. J. Ferguson, R. McDonald, and M. Cowie, *Dalton Trans.*, 2009, 4213–4226

[10] Z. Wanga, W. Jiangb, J. Liua, W. Jianga, Y. Wanga, B. Åkermarkc, L. Suna, *Journal of Organometallic Chemistry*, 2008, **693**, 17, 2828–2834

[11] G. S. Ananthnaga, N. Edukondalua, J. T. Magueb, M. S. Balakrishnaa, *Polyhedron*, 2013, **62**, 203–207

[12] See ESI: S. Molitor, J. Becker, and V. H. Gessner; J. Am. *Chem. Soc.*, **2014**, *136* (44), pp 15517–15520

[13] N. Burford, P. J. Ragogna, R. McDonald and M. J. Ferguson, *J. Am. Chem. Soc.,* 2003, **125**, 14404-14410.

[14] V. P. Morgalyuk, P. V. Petrovskii, K. A. Lysenko, and E. E. Nifant'ev, *Russ. J. Gen. Chem.*, 2010, Vol. 80, No. 1, pp. 100–105

[15] CrysAlisPRO, Agilent Technologies UK Ltd, Yarnton, England

[16] G. M. Sheldrick, Acta Cryst. (2008), A64, 112-122

[17] Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H., OLEX2: A complete structure solution, refinement and analysis program (2009). J. Appl. Cryst., 42, 339-341

[18] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009

[19] http://comp.chem.umn.edu/info/DFT.htm

[20] NBO Version 3.1, E. D. Glendening, A. E. Reed, J. E. Carpenter, and F. Weinhold.

[21] a) A. J. Bridgeman, G. Cavigliasso, L. R. Ireland, and J. Rothery, *J. Chem. Soc.*, *Dalton Trans*., 2001, 2095 – 2108. b) O. V. Sizova, L. V. Skripnikov, and A.Y. Sokolov, *Journal of Molecular Structure: THEOCHEM*, 2008, **870**, 1–9

[22] I. Mayer, P. Salvador, *Chemical Physics Letters*,2004, **383**, 368–375

[23] T. Lu and F. Chen, "Multiwfn: A Multifunctional Wavefunction Analyzer", *J. Comp. Chem.*,2012, **33**, 580-592

[24] E. Matito, J. Poater, M. Sola, M. Duran, and P. Salvador, *J. Phys. Chem. A*, 2005, **109**, 9904-9910