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Phospha-Peterson reactions with esters and thioesters: isolation of phosphalkenes bearing C-heteroatom substituents

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Several phospha-Peterson routes to phosphalkenes from silylphosphines and various ester or thioester reagents are investigated. Treatment of $\text{MesP}(\text{SiMe}_3)_2$ with $\text{PhCO}(\text{OPh})$ in the presence of KOH (10 mol%) affords the Becker-type phosphalkene, $\text{MesP}=\text{C}(\text{OSiMe}_3)\text{Ph}$ rather than $\text{MesP}=\text{C}(\text{OPh})\text{Ph}$. Using stoichiometric $\text{Li}[\text{MesPSiMe}_3]$ rather than catalytic KOH permitted isolation of the presumptive phosphoenolate intermediate following ester cleavage, $\text{MesP}=\text{C}(\text{OLi})\text{Ph}$. The analogous $\text{MesP}=\text{C}(\text{ONa})\text{Ph}$ was obtained by treating a mixture of MesPH_2 and NaOt-Bu with $\text{PhC}(\text{O})\text{Cl}$. Both are dimers in the solid-state. Treatment of the rare alkali metal phosphoenolates with Me_3SiCl afforded known $\text{MesP}=\text{C}(\text{OSiMe}_3)\text{Ph}$. When using ϵ -thiocaprolactone, $\text{O}=\text{CS}(\text{CH}_2)_5$, as the substrate in the Lewis acid-mediated phospha-Peterson reaction with $\text{ArP}(\text{SiMe}_3)_2$, three new C-chalcogen-substituted phosphalkenes, $\text{RP}=\text{CS}(\text{CH}_2)_5$ ($\text{R} = \text{Mes}, m\text{-Xyl}, \text{Tripp}$) were obtained.

Introduction

The carbon-carbon double bond of olefins ($\text{R}_2\text{C}=\text{CR}_2$) is amongst the most important building blocks in fundamental and applied chemistry. Originally believed to be inaccessible, the isolobal phosphorus-carbon double bond of phosphalkenes ($\text{RP}=\text{CR}_2$) has emerged as an important synthon for phosphorus chemistry. For instance, a wide range of applications for $\text{P}=\text{C}$ bonds have been reported, such as: cyclization reactions to produce P-heterocycles,^{1–3} polymerizations to produce novel functional materials,^{4–6} π -acceptor ligands for transition metal catalysts,^{7–10} and substrates for asymmetric hydrogenation reactions to form enantiopure secondary phosphines.⁷ The ability to synthesize phosphalkenes with a variety of substituents permits fine tuning of steric and electronic properties, thereby broadening their potential applications. Due to the limited kinetic and thermodynamic stability of the $\text{P}=\text{C}$ bond, in general, isolable phosphalkenes require bulky and/or electronically-delocalizing substituents to impart kinetic and/or thermodynamic stabilization to the $(3p-2p)\pi$ -bond.

Although numerous methods for synthesizing phosphalkenes are known, most are only amenable to large alkyl or aryl substituents at the $\text{P}=\text{C}$ bond, leading to a limited pool of possible phosphalkenes. In 1976, the first Becker-type phosphalkenes, $\text{RP}=\text{C}(\text{OSiMe}_3)\text{R}'$ ($\text{R} = \text{Ph}, \text{Cy}, t\text{-Bu}$; $\text{R}' = t\text{-Bu}$),¹¹

were reported with a heteroatom substituent at carbon. Despite the many successful syntheses and applications of Becker-type phosphalkenes (**A** in Fig. 1),^{12–26} there have been fewer reports of non-Becker-type phosphalkenes bearing $-\text{O}$ - or $-\text{S}$ -alkyl or aryl substituents at carbon (**B**,²⁷ **C**,^{28–31} **D**,³² **E**,^{33–35} **F**,^{33–36} **G**,³² and **H**^{37,38} in Fig. 1). Notably, the two isolable phosphalkenes **B** were in equilibrium with the corres-

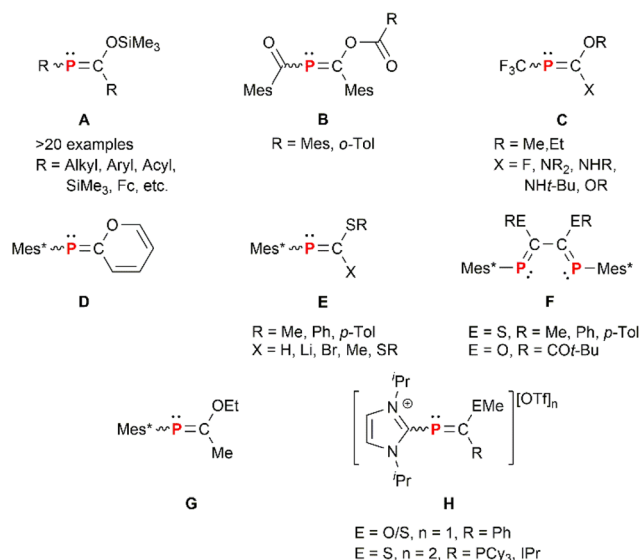


Fig. 1 Examples of chalcogen-substituted phosphalkenes.

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ponding tris(acyl)phosphine. The synthesis of **C** requires harsh conditions due to the challenge of synthesizing intermediate, $F_3CP=CF_2$.³¹ This highly reactive intermediate is subsequently treated with alcohol (+ROH) followed by base [-(HB)F] to afford isolable **C**. In contrast, employing the bulky Mes* [Mes* = 2,4,6-tri(*tert*-butyl)phenyl] substituent provides kinetic stabilization to phosphalkenes (**D–G**), but often renders the P=C bond relatively inert to further chemistry. Furthermore, the Mes* substituent is known to undergo undesirable intramolecular insertion reactions into the C–H bond of the *ortho*-*t*-Bu group.^{39,40} Bulky NHC substituents are a promising new substituent type for novel cationic phosphalkenes bearing O/S-substituents (**H**).³⁷ This methodology requires thiocarbonyls (S=CRR') and, thus far, is incompatible with readily available carbonyls which are popular for the synthesis of phosphalkenes bearing less sterically bulky P-substituents.^{39,41–45} The vast majority of carbonyl substrates used to prepare phosphalkenes have been ketones or aldehydes that do not permit incorporation of –OR substituents (R = alkyl or aryl).

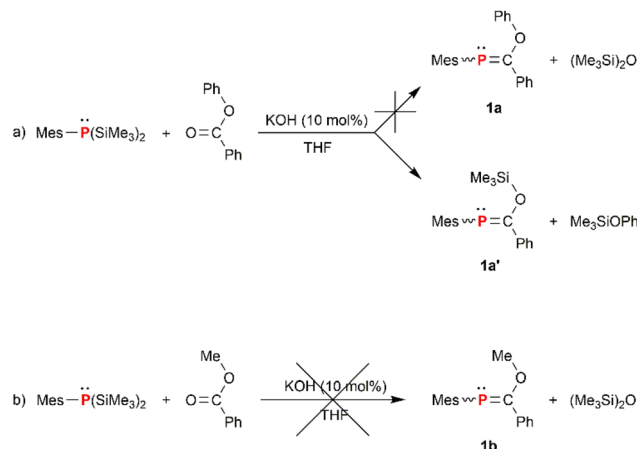
The work presented herein seeks to explore the efficacy of ester and thioester substrates towards the formation of O- and S-substituted phosphalkenes. In particular, we show that esters can be used to form alkali metal phospho-enolate salts. We have also isolated alkylthioether-substituted phosphalkenes bearing a 2,4,6-trimethylphenyl (Mes), 2,6-dimethylphenyl (*m*-Xyl), or 2,4,6-triisopropylphenyl (Tripp) substituent at phosphorus.

Results and discussion

Base-mediated phospho-Peterson reaction with esters

To investigate the possibility of preparing P-analogues of vinyl ethers, we first attempted the base-catalyzed phospho-Peterson reaction as a route to $MesP=C(OPh)Ph$ (**1a**).⁴² Thus, a solution of $MesP(SiMe_3)_2$ in THF was treated with a solution of $PhCO(OPh)$ (1 equiv.) in THF. To the resultant stirred solution was added a suspension of anhydrous KOH (10 mol%) in THF (Scheme 1). The reaction mixture was stirred for 1 h and an aliquot was transferred to an NMR tube. Analysis by ³¹P NMR spectroscopy revealed two new downfield signals at 142.5 and 141.4 ppm (ratio: 7 : 93) which are in the region expected for phosphalkenes.

After work-up, the crude product was isolated as a yellow oil. Expectedly, the ¹H NMR spectrum of a CDCl₃ solution of the crude product showed signals assigned to Mes and Ph moieties. In addition, an unexpected signal was observed at –0.18 ppm with an integrated ratio of 9H relative to the signals at 2.42 and 2.29 ppm assigned to the *o*- and *p*-Me moieties of Mes (6H and 3H, respectively). Signals were observed at 7.24 (dd, *J* = 8.2, 7.5 Hz, 2H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 2H), and 0.27 (s, 9H) ppm which match nearly identically to those previously reported for Me_3SiOPh [δ = 7.24 (dd, *J* = 8.8, 6.6 Hz, 2H); 6.96 (t, *J* = 7.3 Hz, 1H); 6.84 (d, *J* = 6.6 Hz, 2H); 0.26 (s, 9H)].⁴⁶ Taken together, these data permit assignment of the major signal in the ³¹P NMR spectra to known

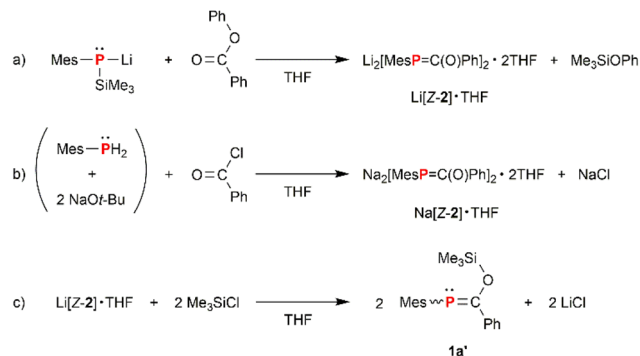


Scheme 1 Reaction scheme using the base-catalyzed phospho-Peterson reaction. (a) Attempted synthesis of **1a** which instead produced **1a'**. (b) Attempted synthesis of **1b**.

Becker phosphoalkene, $Z-MesP=C(OSiMe_3)Ph$ (**Z-1a'**; δ = 141.4).¹² The minor signal was assigned to $E-MesP=C(OSiMe_3)Ph$ (**E-1a'**; δ = 142.5) (*vide infra*). Interestingly, **E-1a'** has not been reported previously since the classical Becker reaction, $[MesP(SiMe_3)_2 + PhC(O)Cl]$ in THF, affords **Z-1a'** selectively.¹²

Given that $PhCO(OMe)$ possesses the poorer methoxide leaving group, we hypothesized that its base-mediated phospho-Peterson reaction may afford $MesP=C(OMe)Ph$ (**1b**) rather than **1a'**. Under the same experimental conditions as described above, the synthesis of $MesP=C(OMe)Ph$ was attempted. After 1 h, the reaction mixture had changed from colourless to yellow. An aliquot was removed from the reaction solution and its ³¹P NMR spectrum showed only the resonance for the unreacted $MesP(SiMe_3)_2$ (δ = –162.6). No change was observed upon monitoring reaction progress for 24 h indicating that there was no reaction.

To further explore the possible preparation of **1a**, the classical phospho-Peterson reaction was explored.¹⁴ To an *in situ*-prepared solution of $Li[MesP(SiMe_3)_2]$ (δ = –189.2)⁴⁷ in THF/ Et_2O was added $PhCO(OPh)$ (1 equiv.) in THF [Scheme 2(a)].



Scheme 2 Synthesis of phospho-enolates (a) $Li[Z-2] \cdot THF$ and (b) $Na[Z-2] \cdot THF$, and (c) the reaction of $Li[Z-2] \cdot THF$ with Me_3SiCl forming **1a'**.

The reaction mixture was stirred overnight, and an aliquot was transferred to an NMR tube. The ^{31}P NMR spectrum displayed a new broad singlet at 60.2 ppm and several smaller signals [Fig. 2(a)]. After work up, the crude product was dissolved in minimal THF, and pentane was slowly diffused into the solution. Yellow crystals were obtained and one was analyzed by X-ray crystallography to identify the molecular structure of $\text{Li}[Z-2]\cdot\text{THF}$ [Fig. 3(a)].

Noting that the related $\text{Na}[\text{PhP}=\text{C}(\text{O})\text{Mes}]$ has been reported and characterized by ^{31}P NMR spectroscopy,^{48,49} we employed a similar strategy to access $\text{Na}[2]$. Specifically, a mixture of MesPH_2 and $\text{NaO}t\text{-Bu}$ (2 equiv.) in THF was treated with a solution of $\text{PhC}(\text{O})\text{Cl}$ (1 equiv.) in THF [Scheme 2(b)]. Analysis of an aliquot removed from the reaction mixture by ^{31}P NMR spectroscopy displayed a new broad singlet at 58.3 ppm [Fig. 2(b)]. The crude product was recrystallized as described for $\text{Li}[Z-2]\cdot\text{THF}$ and analyzed by single crystal X-ray crystallography, producing the molecular structure of $\text{Na}[Z-2]\cdot\text{THF}$ [Fig. 3(b)].

^{31}P NMR analysis of a solution of the crystals in THF-d_8 permitted unequivocal assignment of the major signals, given above for the reaction mixtures, to $\text{Li}[Z-2]\cdot\text{THF}$ and $\text{Na}[Z-2]\cdot\text{THF}$ ($\delta = 58.0$ and 57.4 , respectively). Each signal was much

sharper than in the reaction mixture, suggesting minimal interconversion of the pure product, even over a broad temperature range (-85 to 60°C). In our experience with Becker phosphalkenes, the *E*-isomer will be downfield of the *Z*-isomer.¹² Therefore, the smaller resonances observed in the reaction mixtures at 79.0 and 70.1 ppm, were assigned to $\text{Li}[E-2]\cdot\text{THF}$ and $\text{Na}[E-2]\cdot\text{THF}$, respectively. Each product was further characterized by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy which showed that the coordinated THF remains in solution.

Both $\text{Li}[Z-2]\cdot\text{THF}$ and $\text{Na}[Z-2]\cdot\text{THF}$ crystallized as discrete dimers with bridging alkali metal atoms bound by the formally anionic oxygen atoms. Of the eight crystallographically characterized alkali metal “phospha-enolates”, four adopt a similar dimeric structure.^{50–53} The $\text{P1}–\text{C1}$ bond lengths within $\text{Li}[Z-2]\cdot\text{THF}$ and $\text{Na}[Z-2]\cdot\text{THF}$ [1.737(1) and 1.741(1) Å, respectively] are similar to reported phospho-enolate $\text{P}=\text{C}$ bond lengths (1.712(2)–1.796(3) Å)^{50–53} and slightly longer to that of neutral *Z*-1a [1.708(1) Å].¹² These distances are slightly longer than the typical range for $\text{P}=\text{C}$ bonds in phosphalkenes (1.61–1.71 Å) and are consistent with considerable double bond character.⁵⁴ In addition, $\text{Li}[Z-2]\cdot\text{THF}$ and $\text{Na}[Z-2]\cdot\text{THF}$ have shorter $\text{C1}–\text{O1}$ bonds [1.300(2) and 1.288(2) Å respectively] than *Z*-1a' [1.371(1) Å] indicating delocalization of the negative charge throughout the $\text{P}=\text{C}–\text{O}$ moiety.

Interestingly, the Mes-substituent is η^2 -coordinated to Li^+ via the *ipso*- and *ortho*-carbon atoms and the angle between the best plane of the Mes moiety and the $\text{P}=\text{C}$ plane is $66.33(4)^\circ$. In contrast, the Mes-substituent is η^3 -coordinated to Na^+ and, consequently, shows a much higher tilt angle [$89.48(4)^\circ$]. These side-on bindings of the Mes-moiety are accompanied by more acute Mes– $\text{P}=\text{C}$ angles in $\text{Li}[Z-2]\cdot\text{THF}$ and $\text{Na}[Z-2]\cdot\text{THF}$ [$101.60(6)$ and $99.04(6)^\circ$, respectively] when compared to *Z*-1a [$104.20(6)^\circ$]. The angle between the 5-atom plane containing the $\text{P}=\text{C}$ bond and the plane of the phenyl substituent is very similar in $\text{Li}[Z-2]\cdot\text{THF}$ and $\text{Na}[Z-2]\cdot\text{THF}$ [$26.95(4)$ and $25.90(4)^\circ$, respectively]. These angles closely match that in *Z*-1a [$27.8(2)^\circ$] and suggest significant π -conjugation between the $\text{P}=\text{C}$ and Ph moieties.

We propose that $[2]^-$ represents an intermediate in the base-catalyzed phospho-Peterson reaction with esters. To support this assertion, an excess of Me_3SiCl was added to a solution of $\text{Li}[Z-2]$ in THF. This solution was lightly shaken until the clear yellow solution became faintly cloudy and colourless (*ca.* 30 s). The ^{31}P NMR spectrum showed only two new signals at 142.0 and 143.1 ppm (99 : 1) assigned to *Z*-1a' and *E*-1a', respectively, just as with the base-catalyzed reaction (*vide supra*). Furthermore, the *Z* conformation about the $\text{P}=\text{C}$ bond, observed in the molecular structure of $\text{Li}[Z-2]\cdot\text{THF}$, was retained upon silylation.

Lewis acid-mediated phospho-Peterson reactions with esters and thioesters

The Lewis acid-mediated phospho-Peterson reaction has proven successful with substrates where base-catalyzed approaches failed.⁴¹ Thus, a series of reactions were performed wherein solutions of $\text{MesP}(\text{SiMe}_3)_2$ and $\text{PhCO}(\text{OR})$ (1 equiv., R

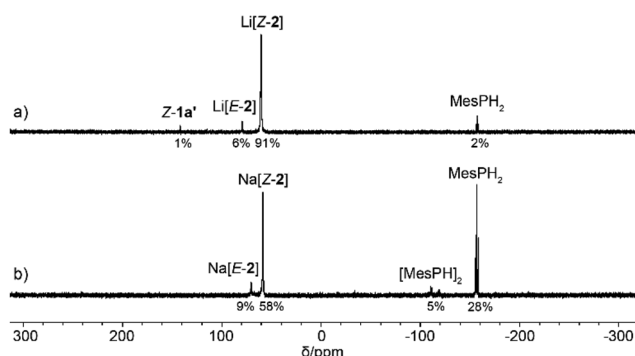


Fig. 2 ^{31}P NMR spectrum (162 MHz, THF) of the reaction mixture for the synthesis of (a) $\text{Li}[Z-2]\cdot\text{THF}$ and (b) $\text{Na}[Z-2]\cdot\text{THF}$.

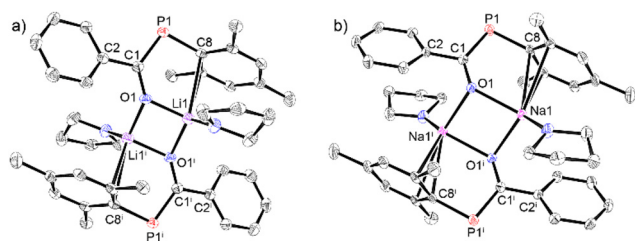
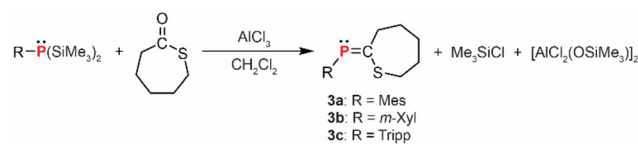


Fig. 3 Molecular structures of (a) $\text{Li}[Z-2]\cdot\text{THF}$ and (b) $\text{Na}[Z-2]\cdot\text{THF}$. Thermal ellipsoids are drawn at 50% probability level. Hydrogens are omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): (a) $\text{P1}–\text{C1}$ 1.737(1), $\text{P1}–\text{C8}$ 1.842(1), $\text{C1}–\text{O1}$ 1.300(1), $\text{O1}–(\text{Li1})$ 1.896(2), $\text{Li1}–\text{C8}$ 2.710(2), $\text{C1}–\text{P1}–\text{C8}$ 100.50(5), $\text{P1}–\text{C1}–\text{O1}$ 127.40(8). (b) $\text{P1}–\text{C1}$ 1.741(1), $\text{P1}–\text{C8}$ 1.851(1), $\text{C1}–\text{O1}$ 1.288(2), $\text{O1}–\text{Na1}$ 2.2482(9), $\text{Na1}–\text{C8}$ 2.816(1), $\text{C1}–\text{P1}–\text{C8}$ 99.04(6), $\text{P1}–\text{C1}–\text{O1}$ 126.90(9).

= Ph, Me, Cy, *t*-Bu) in CH_2Cl_2 were added dropwise to AlCl_3 (1 equiv.) in CH_2Cl_2 . Over 1–3 h, the stirred reaction solution slowly changed from colourless to red. In all cases, the ^{31}P NMR spectra showed two signals at 145.4 (*ca.* 5–10%) and 141.4 ppm (*ca.* 90–95%), respectively assigned to *Z*-**1a'** and *E*-**1a'** (Scheme 3).

In an effort to inhibit ester cleavage and RO^- elimination, cyclic ϵ -caprolactone was tested as a substrate. Thus, a solution of $\text{MesP}(\text{SiMe}_3)_2$ and ϵ -caprolactone (1 equiv.) in CH_2Cl_2 was added to AlCl_3 (1 equiv.) in CH_2Cl_2 (Scheme 4). ^{31}P NMR analysis of an aliquot removed from the reaction mixture showed that the signal assigned to $\text{MesP}(\text{SiMe}_3)_2$ ($\delta = -161.4$) was no longer present. The only resonances detected were characteristic of the *D*-/*L*- and *meso*-isomers of the previously reported $(\text{MesPH})_2$.⁵⁵ It was initially postulated that this outcome is a consequence of the enolizable protons on the ester substrate. However, we also observed small amounts of $(\text{MesPH})_2$ in analogous reactions involving esters without enolizable protons [*e.g.* $\text{PhCO}(\text{O}t\text{-Bu})$]. Furthermore, $(\text{MesPH})_2$ has been reported to be a decomposition product of $\text{MesP}=\text{CH}(t\text{-Bu})$ which was synthesized using this same procedure.⁴¹ Thus far, the mechanism to form $(\text{MesPH})_2$ has not been ascertained and is beyond the scope of the present study.

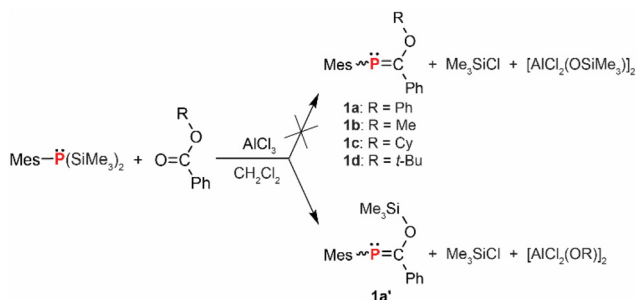
We next turned our attention to ϵ -thiocaprolactone as a potential substrate for phospho-Peterson reactions. Thus, a solution of $\text{MesP}(\text{SiMe}_3)_2$ and ϵ -thiocaprolactone (1 equiv.) in CH_2Cl_2 was added to a stirred suspension of AlCl_3 (1 equiv.) in CH_2Cl_2 (Scheme 5). The initially pale yellow and cloudy reaction mixture slowly changed to red and transparent after being stirred for 1 h at 25 °C. Analysis of an aliquot removed from the reaction mixture by ^{31}P NMR spectroscopy revealed that the signal assigned to $\text{MesP}(\text{SiMe}_3)_2$ ($\delta = -161.4$) was no longer



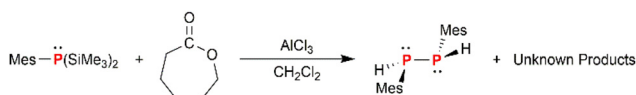
Scheme 5 Reaction scheme for the synthesis of **3a–c** using the Lewis acid-mediated phospho-Peterson reaction.

present and a new triplet resonance was observed at 180.0 ppm ($J_{\text{PH}} = 21$ Hz), as expected for desired **3a**. Analogous reactions employing $\text{ArP}(\text{SiMe}_3)_2$ [$\text{Ar} = m\text{-Xyl}$, Tripp] resulted in the successful formation of **3b** and **3c** [$\delta = 179.2$ (**3b**), 179.8 (**3c**)]. For **3a–c**, saturated solutions in hexanes were cooled to -35 °C to afford colourless crystals suitable for X-ray crystallography.

The molecular structures of thio-substituted phosphoalkenes **3a–c** are shown in Fig. 4. All three molecules are exclusively in the *Z*-conformation about the $\text{P}=\text{C}$ bond. This result agrees with the detection of only one triplet signal in the ^{31}P NMR spectrum of each product. This also aligns with previously reported observations showing that bulky *P*-substituents favour the *Z*-isomer in Becker phosphoalkenes.¹² The $\text{P}=\text{C}$ bond lengths are virtually identical [range: 1.691(2)–1.694(2) Å] and are similar to known *S*-substituted phosphoalkenes [range: 1.655(4)–1.74(2) Å].^{16,33–35,38} These are at the long end of the range for $\text{P}=\text{C}$ bond lengths (1.61–1.71 Å).⁵⁴ The $\text{C}=\text{S}$ bond lengths are virtually identical [range: 1.736(1)–1.740(1) Å] are typical of vinyl thioethers (*ca.* 1.75 Å)⁵⁶ and are indicative of π -conjugation within the $\text{P}=\text{C}=\text{S}$ moiety. The aryl *P*-substituent plane is nearly orthogonal to the 5-atom plane containing the $\text{P}=\text{C}$ bond in each of **3a–c** [$80.87(3)^\circ$, $88.86(3)^\circ$, and $80.63(5)^\circ$, respectively] consistent



Scheme 3 Reaction scheme using the Lewis acid-mediated phospho-Peterson reaction, attempting to synthesize **1a–d** which instead produced **1a'** in each case.



Scheme 4 Attempted reaction using the Lewis acid-mediated phospho-Peterson reaction with ϵ -caprolactone producing the previously reported $(\text{MesPH})_2$.

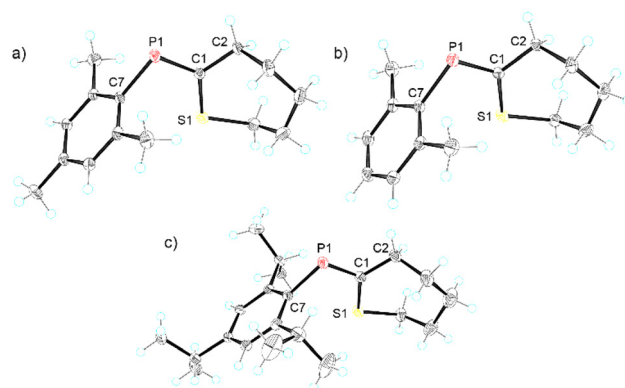


Fig. 4 Molecular structures of **3a–c**. One of the two unique molecules of **3c** in the asymmetric unit are shown. Thermal ellipsoids are drawn at 50% probability level. Selected bond lengths (Å) and angles ($^\circ$): (a) $\text{P}(1)-\text{C}(1)$ 1.691(2), $\text{P}(1)-\text{C}(7)$ 1.835(1), $\text{C}(1)-\text{S}(1)$ 1.736(1); $\text{P}(1)-\text{C}(1)-\text{C}(2)$ 117.47(8), $\text{P}(1)-\text{C}(1)-\text{S}(1)$ 122.40(7), $\text{C}(1)-\text{P}(1)-\text{C}(7)$ 103.02(5). (b) $\text{P}(1)-\text{C}(1)$ 1.694(1), $\text{P}(1)-\text{C}(7)$ 1.842(1), $\text{C}(1)-\text{S}(1)$ 1.740(1); $\text{P}(1)-\text{C}(1)-\text{C}(2)$ 117.9(1), $\text{P}(1)-\text{C}(1)-\text{S}(1)$ 122.31(8), $\text{C}(1)-\text{P}(1)-\text{C}(7)$ 102.64(6). (c) $\text{P}(1)-\text{C}(1)$ 1.694(2), $\text{P}(1)-\text{C}(7)$ 1.845(2), $\text{C}(1)-\text{S}(1)$ 1.739(2); $\text{P}(1)-\text{C}(1)-\text{C}(2)$ 117.6(1), $\text{P}(1)-\text{C}(1)-\text{S}(1)$ 121.5(1), $\text{C}(1)-\text{P}(1)-\text{C}(7)$ 104.27(9).

with minimal π -conjugation between the $P=C$ moiety and the bulky aryl substituent.

Analytically pure phosphalkenes **3a–c** were obtained by successive recrystallization from hexanes. The formulation and purity of each compound was confirmed by 1H , ^{31}P and ^{13}C $\{^1H\}$ NMR spectroscopy, mass spectrometry, and elemental analysis.

Conclusions

In summary, the work presented herein demonstrated that esters appear to be unsuitable substrates for formation of non-Becker type O-substituted phosphalkenes using base and acid mediated phospho-Peterson reactions due to ester-bond cleavage. However, using a stoichiometric amount of base has led to the formation of alkali-metal phospho-enolates $Li[Z-2]$ and $Na[Z-2]$. The synthesis of phosphalkenes **3a–c** demonstrates that the Lewis acid-mediated phospho-Peterson reaction can successfully be used to synthesize phosphalkenes bearing S-substituents with thioesters. Future work will investigate applications of these new phosphalkenes and phospho-enolates as novel building blocks for functional molecules, complexes and polymers.

Experimental section

General considerations

All experiments were performed under an inert atmosphere using standard Schlenk and glovebox techniques unless otherwise specified. Methyl benzoate, sodium *tert*-butoxide, anhydrous aluminum trichloride, potassium hydroxide, methyl lithium solution, benzoyl chloride, trimethylsilyl chloride, ϵ -caprolactone and all solvents were purchased from commercial sources. Potassium hydroxide was made anhydrous by recrystallization from ethanol and subsequently heated *in vacuo* according to a literature procedure.⁵⁷ THF was dried over sodium in the presence of benzophenone and freshly distilled prior to use. Pentane was dried over CaH_2 and distilled prior to use. Dichloromethane, toluene and hexanes were purified by a solvent purification system containing an activated alumina column and collected over activated 4 Å molecular sieves. Phenyl benzoate,⁵⁸ cyclohexyl benzoate,⁵⁹ *tert*-butyl benzoate,⁵⁹ ϵ -thiocaprolactone,⁶⁰ $MesP(H_2)$,¹⁹ $MesP(SiMe_3)_2$,¹⁹ *m*-XylP($SiMe_3$)₂,⁶¹ and TrippP($SiMe_3$)₂⁶² were prepared according to literature procedures. 1H , $^{13}C\{^1H\}$, ^{31}P , COSY, and 1H - ^{13}C HSQC NMR spectra were measured at room temperature on a Bruker Avance III HD 400 spectrometer. Chemical shifts were reported in parts per million relative to residual proton and carbon signals of the solvent. Chemical shifts of ^{31}P NMR spectra were reported in parts per million downfield from 85% H_3PO_4 as an external standard ($\delta = 0$). FD mass spectra were collected with a Jeol AccuTOF-GCv 4G, a GC-TOF MS instrument equipped with a field desorption/ionization (FD/FI) ion source. Electrospray ionization (ESI) mass spectra

were collected on a Bruker HCT Ultra PTM Discovery system, directly infused at a flow rate of $500 \mu L h^{-1}$. Spectra were obtained in negative-ion mode. Elemental analyses were performed by UBC Mass Spectrometry/Elemental Analysis Facility using a Thermo Flash 2000 Elemental Analyzer.

X-ray diffraction studies

X-ray data were collected at 100 K on a Bruker APEX-II DUO CCD diffractometer using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) or on a Bruker D8-Venture using Cu-K α radiation ($\lambda = 1.54178 \text{ \AA}$). Data was integrated using the Bruker SAINT software package⁶³ and corrected for absorption effects using SADABS,⁶⁴ unless otherwise noted. The structures were each solved with the XT (Sheldrick, 2015) solution program using Intrinsic Phasing methods⁶⁵ and refined with XL (Sheldrick, 2015)⁶⁶ using full matrix least squares minimisation on F^2 via the Olex2 interface.⁶⁷ Non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

Reaction of $MesP(SiMe_3)_2$ and $PhCO(OPh)$ mediated by KOH (10 mol%) to afford $MesP=C(OSiMe_3)Ph$ (*E/Z*-1a')

To a stirred solution of $MesP(SiMe_3)_2$ (0.500 g, 1.69 mmol) and $PhCO(OPh)$ (1.69 mmol, 0.334 g) in THF (5 mL) was added a suspension of anhydrous KOH (0.010 g, 0.178 mmol) in THF (5 mL) under an inert atmosphere. The reaction mixture was stirred for 1 h and ^{31}P NMR spectroscopy of an aliquot taken from the mixture revealed the signal assigned to $MesP(SiMe_3)_2$ was no longer present. The reaction mixture was then added to hexanes (10 mL) producing a precipitate. The mixture was filtered, and volatiles were removed *in vacuo* from the soluble fraction to afford a yellow oil (0.673 g). The data below suggested that the oil consisted of a mixture of *Z*-1a, *E*-1a and $PhOSiMe_3$.^{12,46} It was not purified further.

Z-1a' (93%): ^{31}P NMR ($CDCl_3$, 162 MHz): δ 141.6. 1H NMR ($CDCl_3$, 400 MHz): δ 7.82 (m, 2H), 7.33 (m, 3H), 6.89 (s, 2H), 2.42 (s, 6H), 2.29 (s, 3H), -0.18 (s, 9H).

E-1a' (7%): ^{31}P NMR ($CDCl_3$, 162 MHz): δ 145.6.

$PhOSiMe_3$: 1H NMR ($CDCl_3$, 400 MHz): 7.24 (dd, $J = 8.2$, 7.5 Hz, 2H), 6.97 (t, $J = 7.4$ Hz, 1H), 6.85 (d, $J = 7.6$ Hz, 2H), 0.27 (s, 9H) ppm.

Attempted reaction of $MesP(SiMe_3)_2$ and $PhCO(OMe)$ mediated by KOH (10 mol%)

To a stirred solution of $MesP(SiMe_3)_2$ (0.500 g, 1.69 mmol) and $PhCO(OMe)$ (1.69 mmol, 0.230 g) in THF (5 mL) was added a suspension of anhydrous KOH (0.010 g, 0.178 mmol) in THF (5 mL) under an inert atmosphere. The reaction mixture was stirred for 24 h at room temperature and only the signal assigned to $MesP(SiMe_3)_2$ ($\delta = -162.6$) was observed by ^{31}P NMR spectroscopy, suggesting no reaction had occurred.

Preparation of $Li[Z-2] \cdot THF$

To a stirred solution of $MesP(SiMe_3)_2$ (0.474 g, 1.60 mmol) in THF (10 mL) was added MeLi (1 mL, 1.6 M, 1.60 mmol) in diethyl ether. The solution was monitored by ^{31}P NMR spec-

troscopy until the signal assigned to $\text{MesP}(\text{SiMe}_3)_2$ was completely consumed (*ca.* 5 h), then phenyl benzoate (0.317 g, 1.60 mmol) in THF (5 mL) was added. The reaction mixture was stirred for 16 h. After removal of volatiles *in vacuo*, the yellow amorphous solid was washed with pentane (3×2 mL). The product was purified by slow diffusion of pentane into a saturated THF solution of $\text{Li}[\text{Z}-2]\cdot\text{THF}$ producing yellow crystals (0.455, 85%).

^{31}P NMR ($\text{THF}-d_8$, 162 MHz): δ 58.2. ^1H ($\text{THF}-d_8$, 400 MHz): δ 7.96–7.92 (m, 2H), 7.11–7.04 (m, 3H), 6.70 (s, 2H), 3.63–3.59 (m, 4H), 2.42 (s, 6H), 2.17 (s, 3H), 1.78–1.75 (m, 4H); $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{THF}-d_8$, 100 MHz): δ 211.9 (d, $^1J_{\text{CP}} = 69$ Hz), 149.5 (d, $^1J_{\text{CP}} = 48$ Hz), 143.4 (d, $^2J_{\text{CP}} = 6$ Hz), 142.0 (d, $^2J_{\text{CP}} = 44$ Hz), 134.4, 127.8, 127.5 (d, $^4J_{\text{CP}} = 4$ Hz), 127.4, 125.6 (d, $^3J_{\text{CP}} = 19$ Hz), 68.3, 26.4, 23.6 (d, $^3J_{\text{CP}} = 9$ Hz), 21.3; LRMS (–ESI): m/z 1042, 1041 $\{[\text{Li}_3(2)_4]^-$, 3%, 3%, 782, 781, 780, 779 $\{[\text{Li}_2(2)_3]^-$, 2, 9, 42, 100}, 519, 518, 517 $\{[\text{Li}(2)_2]^-$, 2, 11, 26}, 255 $\{[2]^-$, 1%}. Elemental anal. calcd for $\text{C}_{20}\text{H}_{24}\text{POLi}$: C, 71.85; H, 7.2; found: C, 69.2; H, 7.2. Satisfactory elemental analyses could not be obtained despite apparently clean NMR spectra.

Preparation of $\text{Na}[\text{Z}-2]\cdot\text{THF}$

This procedure follows a similar procedure to that previously reported for $\text{Na}[\text{PhP}=\text{C}(\text{O})\text{Mes}]$ except that the present procedure employed THF at 25 °C instead of toluene at 0 °C.⁴⁹ In the present experiment, using toluene as solvent produced lower yields of $\text{Na}[\text{Z}-2]\cdot\text{THF}$. To a stirred solution of MesPH_2 (0.152 g, 1.00 mmol) in THF (5 mL) was added a suspension of NaOt-Bu (0.192 g, 2.00 mmol) in THF (5 mL). After the reaction mixture was stirred for 30 minutes, a solution of benzoyl chloride (0.141 g, 1.00 mmol) in THF (5 mL) was added. The reaction mixture was stirred for 2 h at room temperature, filtered, and the solvent was removed *in vacuo*. The crude product was purified by slow diffusion of pentane into a saturated THF solution of $\text{Na}[\text{Z}-2]$ affording yellow crystals (0.175, 50%).

^{31}P NMR ($\text{THF}-d_8$, 162 MHz): δ 57.4. ^1H ($\text{THF}-d_8$, 400 MHz): δ 7.98–7.95 (m, 2H), 7.11–7.04 (m, 3H), 6.76 (s, 2H), 3.63–3.59 (m, 4H), 2.43 (s, 6H), 2.19 (s, 3H), 1.79–1.75 (m, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{THF}-d_8$, 100 MHz): δ 212.8 (d, $^1J_{\text{CP}} = 69$ Hz), 149.3 (d, $^1J_{\text{CP}} = 48$ Hz), 143.3 (d, $^2J_{\text{CP}} = 6$ Hz), 141.8 (d, $^2J_{\text{CP}} = 47$ Hz), 134.9, 128.2, 127.7 (d, $^4J_{\text{CP}} = 4$ Hz), 127.6, 125.3 (d, $^3J_{\text{CP}} = 19$ Hz), 68.2, 26.4, 23.5 (d, $^3J_{\text{CP}} = 9$ Hz), 21.3; LRMS (–ESI): m/z 1091, 1090, 1089 $\{[\text{Na}_3(2)_4]^-$, 2%, 5%, 8%, 814, 813, 812, 811 $\{[\text{Na}_2(2)_3]^-$, 2, 12, 52, 100}, 535, 534, 533 $\{[\text{Na}(2)_2]^-$, 2, 11, 32}, 256, 255 $\{[2]^-$, 1, 8}.

Reaction of $\text{Li}[\text{Z}-2]\cdot\text{THF}$ and Me_3SiCl to afford $\text{MesP}=\text{C}(\text{OSiMe}_3)\text{Ph}$ (*E/Z-1a'*)

To a solution of $\text{Li}[\text{Z}-2]\cdot\text{THF}$ (0.020 g, 0.030 mmol) in 1 mL of THF in an NMR tube was added three drops of Me_3SiCl (*ca.* 0.020 g, 0.180 mmol). The NMR tube was capped and lightly shaken until the clear yellow solution became faintly cloudy and colourless (*ca.* 30 s). ^{31}P NMR spectroscopy of the reaction mixture revealed the signal assigned to $\text{Li}[\text{Z}-2]\cdot\text{THF}$ was no longer present. Two new signals had appeared which were

assigned to *Z-1a'* and *E-1a'* (*ca.* 99:1).¹² No attempts were made to isolate this product.

Reaction of $\text{MesP}(\text{SiMe}_3)_2$ and $\text{PhCO}(\text{OPh})$ in the presence of AlCl_3 to afford $\text{MesP}=\text{C}(\text{OSiMe}_3)\text{Ph}$ (*E/Z-1a'*)

To a stirred suspension of anhydrous AlCl_3 (0.450 g, 3.37 mmol) in CH_2Cl_2 (5 mL) was added $\text{MesP}(\text{SiMe}_3)_2$ (1.00 g, 3.37 mmol) and $\text{PhCO}(\text{OPh})$ (0.668 g, 3.37 mmol) in CH_2Cl_2 (5 mL). The reaction mixture was monitored by ^{31}P NMR spectroscopy until the signal assigned to $\text{MesP}(\text{SiMe}_3)_2$ was no longer present (1–3 h). Upon consumption of $\text{MesP}(\text{SiMe}_3)_2$, 10 mL of hexanes was added to the reaction mixture, producing a brown precipitate. The suspension was filtered, and the solvent was removed *in vacuo*. The mixture was washed with hexane (3×2 mL) and the washings were combined and filtered. The solvent was again removed *in vacuo* to afford a red oil (0.336 g, 30%). The data below suggested that the oil consisted of a mixture of *Z-1a* and *E-1a* (*ca.* 90:10).¹² It was not purified further.

^{31}P NMR (CDCl_3 , 162 MHz): δ 145.6 (93%, *Z-1a'*), 141.6 (7%, *E-1a'*).

Reaction of $\text{MesP}(\text{SiMe}_3)_2$ and $\text{PhCO}(\text{OMe})$ in the presence of AlCl_3 to afford $\text{MesP}=\text{C}(\text{OSiMe}_3)\text{Ph}$ (*E/Z-1a'*)

To a stirred suspension of anhydrous AlCl_3 (0.450 g, 3.37 mmol) in CH_2Cl_2 (5 mL) was added $\text{MesP}(\text{SiMe}_3)_2$ (1.00 g, 3.37 mmol) and $\text{PhCO}(\text{OMe})$ (0.459 g, 3.37 mmol) in CH_2Cl_2 (5 mL). The reaction mixture was monitored by ^{31}P NMR spectroscopy until the signal assigned to $\text{MesP}(\text{SiMe}_3)_2$ was no longer present (1–3 h). The reaction mixture displayed ^{31}P NMR spectroscopy signals consistent with *Z-1a'* and *E-1a'*.¹² It was not purified further.

Reaction of $\text{MesP}(\text{SiMe}_3)_2$ and $\text{PhCO}(\text{OCy})$ in the presence of AlCl_3 to afford $\text{MesP}=\text{C}(\text{OSiMe}_3)\text{Ph}$ (*E/Z-1a'*)

To a stirred suspension of anhydrous AlCl_3 (0.450 g, 3.37 mmol) in CH_2Cl_2 (5 mL) was added $\text{MesP}(\text{SiMe}_3)_2$ (1.00 g, 3.37 mmol) and $\text{PhCO}(\text{OCy})$ (0.689 g, 3.37 mmol) in CH_2Cl_2 (5 mL). The reaction mixture was monitored by ^{31}P NMR spectroscopy until the signal assigned to $\text{MesP}(\text{SiMe}_3)_2$ was no longer present (1–3 h). The reaction mixture displayed ^{31}P NMR spectroscopy signals consistent with *Z-1a'* and *E-1a'*.¹² It was not purified further.

Reaction of $\text{MesP}(\text{SiMe}_3)_2$ and $\text{PhCO}(\text{Ot-Bu})$ in the presence of AlCl_3 to afford $\text{MesP}=\text{C}(\text{OSiMe}_3)\text{Ph}$ (*E/Z-1a'*)

To a stirred suspension of anhydrous AlCl_3 (0.450 g, 3.37 mmol) in CH_2Cl_2 (5 mL) was added $\text{MesP}(\text{SiMe}_3)_2$ (1.00 g, 3.37 mmol) and $\text{PhCO}(\text{Ot-Bu})$ (0.601 g, 3.37 mmol) in CH_2Cl_2 (5 mL). The reaction mixture was monitored by ^{31}P NMR spectroscopy until the signal assigned to $\text{MesP}(\text{SiMe}_3)_2$ was no longer present (1–3 h). The reaction mixture displayed ^{31}P NMR spectroscopy signals consistent with *Z-1a'* and *E-1a'*.¹² It was not purified further.

Reaction of MesP(SiMe₃)₂ with ε-caprolactone in the presence of AlCl₃ to afford (MesPH)₂

To a stirred suspension of anhydrous AlCl₃ (0.112 g, 0.843 mmol) in CH₂Cl₂ (2 mL) was added MesP(SiMe₃)₂ (0.250 g, 0.843 mmol) and ε-caprolactone (0.096 g, 0.843 mmol) in CH₂Cl₂ (2 mL). The reaction mixture was stirred for 1 h at room temperature. ³¹P NMR spectroscopy of an aliquot from the reaction mixture showed no resonances in the expected phosphalkene region and only those assigned to (MesPH)₂ by comparison to the literature.⁵⁵ No attempts were made to isolate this product. ³¹P NMR (CH₂Cl₂, 162 MHz): δ −111.3 [m, *D*-/*L*-(MesPH)₂], −118.8 [m, *meso*-(MesPH)₂] were identical to those described in the literature.⁵⁵

Preparation of 3a–c

To a stirred suspension of anhydrous AlCl₃ (0.450 g, 3.37 mmol) in CH₂Cl₂ (5 mL) was added RP(SiMe₃)₂ (3.37 mmol) and ε-thiocaprolactone (0.439 g, 3.37 mmol) in CH₂Cl₂ (5 mL). The reaction was monitored by ³¹P NMR spectroscopy and after 1 h the solution was concentrated *in vacuo* leaving a bright red solution. The product was crystallized at −35 °C, producing colourless crystals suitable for single crystal X-ray diffraction. The product was further purified by recrystallization from hexanes.

3a: (0.705 g, 79%). ³¹P NMR (CDCl₃, 162 MHz): δ 180.0 (t, ³J_{PH} = 21 Hz). ¹H (CDCl₃, 400 MHz): δ 6.90 (s, 2H), 3.04 (dt, ³J_{HP} = 21 Hz, ³J_{HH} = 5 Hz, 2H), 2.79 (t, ³J_{HH} = 5 Hz, 2H), 2.37 (s, 6H), 2.28 (s, 3H), 1.87 (m, 2H), 1.83 (m, 2H), 1.72 (m, 2H). ¹³C {¹H} NMR (CDCl₃, 100 MHz): δ 193.6 (d, ¹J_{CP} = 54 Hz), 140.7 (d, ²J_{CP} = 6 Hz), 138.6, 135.3 (d, ¹J_{CP} = 39 Hz), 128.5, 39.9 (d, ²J_{CP} = 39 Hz), 33.0 (d, ³J_{CP} = 2 Hz), 32.0 (d, ⁴J_{CP} = 2 Hz), 31.0 (d, ³J_{CP} = 13 Hz), 29.8, 21.4 (d, ³J_{CP} = 8 Hz), 21.2; LRMS (FD): *m/z* 266, 265, 264 {[3a]⁺, 8%, 21%, 100%}. Elemental anal. calcd for C₁₅H₂₁PS: C, 68.15; H, 8.0; found: C, 68.0; H, 8.0.

3b: (0.843 g, 95%). ³¹P NMR (CDCl₃, 162 MHz): δ 179.2 (t, ³J_{PH} = 21 Hz). ¹H (CDCl₃, 400 MHz): δ 7.17 (t, ³J_{HH} = 7 Hz, 1H), 7.06 (d, ³J_{HH} = 7 Hz, 2H), 3.05 (dt, ³J_{HP} = 21 Hz, ³J_{HH} = 5 Hz), 2.79 (t, ³J_{HH} = 5 Hz, 2H), 2.41 (s, 6H), 1.87 (m, 2H), 1.81 (m, 2H), 1.70 (m, 2H); ¹³C {¹H} NMR (CDCl₃, 100 MHz): δ 193.4 (d, ¹J_{CP} = 53 Hz), 140.7 (d, ²J_{CP} = 6 Hz), 138.9 (d, ¹J_{CP} = 40 Hz), 128.7, 127.5, 40.0 (d, ²J_{CP} = 39 Hz), 33.1 (d, ³J_{CP} = 2 Hz), 32.0 (d, ⁴J_{CP} = 2 Hz), 31.0 (d, ³J_{CP} = 13 Hz), 29.8, 21.5 (d, ³J_{CP} = 8 Hz); LRMS (FD): *m/z* 502, 501, 500 {[3b]₂⁺, 2%, 5%, 15%}, 252, 251, 250 {[3b]⁺, 6, 16, 100}. Elemental anal. calcd for C₁₄H₁₉PS: C, 67.2; H, 7.65; found: C, 67.4; H, 7.5.

3c: (0.939 g, 80%). ³¹P NMR (CDCl₃, 162 MHz): δ 179.8 (t, ³J_{PH} = 21 Hz); ¹H (CDCl₃, 400 MHz): δ 7.03 (s, 2H), 3.40 (m, 2H), 3.05 (dt, ³J_{HP} = 21 Hz, ³J_{HH} = 5 Hz), 2.90 (sept, 1H), 2.79 (t, ³J_{HH} = 5 Hz, 2H), 1.86 (m, 2H), 1.81 (m, 2H), 1.69 (m, 2H), 1.29 (d, ³J_{HH} = 7 Hz, 6H), 1.27 (d, ³J_{HH} = 7 Hz, 6H), 1.20 (d, ³J_{HH} = 7 Hz, 6H); ¹³C {¹H} NMR (CDCl₃, 100 MHz): δ 193.1 (d, ¹J_{CP} = 53 Hz), 151.5 (d, ²J_{CP} = 5 Hz), 149.9, 133.8 (d, ¹J_{CP} = 39 Hz), 121.1, 40.1 (d, ²J_{CP} = 39 Hz, 34.4, 33.4, 33.3 (d, ³J_{CP} = 2 Hz), 32.2 (d, ⁴J_{CP} = 2 Hz), 31.3 (d, ³J_{CP} = 13 Hz), 30.0, 24.8 (d, ³J_{CP} = 7 Hz), 24.1; LRMS (FD): *m/z* 350, 349, 348 {[3c]⁺, 7%, 24%, 100%}.

Elemental anal. calcd for C₂₁H₃₃PS: C, 72.4; H, 9.5; found: C, 72.0; H, 9.4.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article has been included as part of the SI. Supplementary information: figures of spectra for new compounds. See DOI: <https://doi.org/10.1039/d5dt01781e>.

CCDC 2475807–2475811 (Li[Z-2], Na[Z-2], **3a**, **3b** and **3c**) contain the supplementary crystallographic data for this paper.^{68a–e}

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References

- 1 R. Appel and R. Zimmermann, *Tetrahedron Lett.*, 1983, **24**, 3591–3594.
- 2 K. Issleib, E. Leissring and H. Schmidt, *Phosphorus Sulfur Relat. Elem.*, 1983, **18**, 15–18.
- 3 J. Grobe, D. L. Van, J. Schulze and J. Szameitat, *Phosphorus Sulfur Relat. Elem.*, 1986, **28**, 239–252.
- 4 C.-W. Tsang, B. Baharloo, D. Riendl, M. Yam and D. P. Gates, *Angew. Chem., Int. Ed.*, 2004, **43**, 5682–5685.
- 5 B. W. Rawe, C. P. Chun and D. P. Gates, *Chem. Sci.*, 2014, **5**, 4928–4938.
- 6 K. Dück, B. W. Rawe, M. R. Scott and D. P. Gates, *Angew. Chem., Int. Ed.*, 2017, **56**, 9507–9511.
- 7 M. Li, A. A. Mitchell, T. Zhang, B. O. Patrick, M. D. Fryzuk and D. P. Gates, *J. Am. Chem. Soc.*, 2024, **146**, 25912–25917.
- 8 P. Gupta, H.-J. Drexler, R. Wingad, D. Wass, E. Baráth, T. Beweries and C. Hering-Junghans, *Inorg. Chem. Front.*, 2023, **10**, 2285–2293.
- 9 S. T. Clausen, D. Morales Salazar and A. Orthaber, *Inorg. Chim. Acta*, 2020, **513**, 119958.
- 10 A. Ziółkowska, T. Kruczyński, D. Gudat and Ł. Ponikiewski, *Dalton Trans.*, 2024, **53**, 19107–19111.
- 11 G. Becker, *Z. Anorg. Allg. Chem.*, 1976, **423**, 242–254.
- 12 V. A. Wright, B. O. Patrick, C. Schneider and D. P. Gates, *J. Am. Chem. Soc.*, 2006, **128**, 8836–8844.
- 13 V. A. Wright and D. P. Gates, *Angew. Chem., Int. Ed.*, 2002, **41**, 2389–2392.

- 14 G. Becker, W. Becker and O. Mundt, *Phosphorus Sulfur Relat. Elem.*, 1983, **14**, 267–283.
- 15 R. Pietschnig, E. Niecke, M. Nieger and K. Airola, *J. Organomet. Chem.*, 1997, **529**, 127–133.
- 16 G. Becker, O. Mundt and G. Uhl, *Z. Anorg. Allg. Chem.*, 1984, **517**, 89–102.
- 17 I. F. Lutsenko, V. L. Foss, Y. A. Veits, E. G. Neganova and A. A. Borisenko, *J. Organomet. Chem.*, 1987, **333**, C45–C47.
- 18 T. Allspach, M. Regitz, G. Becker and W. Becker, *Synthesis*, 2002, 31–36.
- 19 G. Becker, O. Mundt, M. Rössler and E. Schneider, *Z. Anorg. Allg. Chem.*, 1978, **443**, 42–52.
- 20 G. Becker, *Z. Anorg. Allg. Chem.*, 1981, **480**, 21–37.
- 21 M. Slany and M. Regitz, *Synthesis*, 2002, 1262–1266.
- 22 E. A. Ishmaeva, D. V. Chachkov, A. Z. Alimova, Y. A. Vereshchagina and V. I. Galkin, *Russ. J. Gen. Chem.*, 2012, **82**, 1951–1953.
- 23 A. Orthaber and R. Pietschnig, *Phosphorus, Sulfur Silicon Relat. Elem.*, 2013, **188**, 128–131.
- 24 A. Orthaber, F. Belaj and R. Pietschnig, *Inorg. Chim. Acta*, 2011, **374**, 211–215.
- 25 C. Moser, A. Orthaber, M. Nieger, F. Belaj and R. Pietschnig, *Dalton Trans.*, 2006, 3879–3885.
- 26 A. Orthaber, R. H. Herber and R. Pietschnig, *J. Organomet. Chem.*, 2012, **719**, 36–40.
- 27 T. Wiesner, D. Neshchadin, G. Glotz, Z. Gfader, E. Schrader, S. Christen, R. C. Fischer, A.-M. Kelterer, G. Gescheidt, H. Grützmacher and M. Haas, *Chem. – Eur. J.*, 2023, **29**, e202302535.
- 28 J. Grobe, D. L. Van and J. Nientiedt, *Z. Naturforsch., B*, 1986, **41**, 149–161.
- 29 J. Grobe, D. L. Van, U. Althoff and G. Lange, *Chem. Ber.*, 1992, **125**, 567–570.
- 30 J. Grobe, D. L. Van and G. Lange, *Z. Naturforsch., B: J. Chem. Sci.*, 1993, **48**, 58–67.
- 31 J. Grobe and D. Le Van, *Angew. Chem.*, 1984, **96**, 716–717.
- 32 A. M. Borys, E. F. Rice, G. S. Nichol and M. J. Cowley, *J. Am. Chem. Soc.*, 2021, **143**, 14065–14070.
- 33 S. Ito and M. Yoshifuji, *Chem. Lett.*, 1998, **27**, 651–652.
- 34 S. Ito, S. Kimura and M. Yoshifuji, *Bull. Chem. Soc. Jpn.*, 2003, **76**, 405–412.
- 35 S. Ito and M. Yoshifuji, *Chem. Lett.*, 2000, **29**, 1390–1391.
- 36 R. Appel, J. Hünnerbein and N. Siabalis, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 779–780.
- 37 P. Royla, K. Schwedtmann, Z. Han, J. Fidelius, D. P. Gates, R. M. Gomila, A. Frontera and J. J. Weigand, *J. Am. Chem. Soc.*, 2023, **145**, 10364–10375.
- 38 P. Royla, K. Schwedtmann, R. M. Gomila, A. Frontera and J. J. Weigand, *Angew. Chem., Int. Ed.*, 2025, **64**, e202419502.
- 39 P. Gupta, T. Taeufer, J.-E. Siewert, F. Reiß, H.-J. Drexler, J. Pospech, T. Beweries and C. Hering-Junghans, *Inorg. Chem.*, 2022, **61**, 11639–11650.
- 40 C.-W. Tsang, C. A. Rohrick, T. S. Saini, B. O. Patrick and D. P. Gates, *Organometallics*, 2002, **21**, 1008–1010.
- 41 J. I. Bates, B. O. Patrick and D. P. Gates, *New J. Chem.*, 2010, **34**, 1660.
- 42 M. Yam, J. H. Chong, C.-W. Tsang, B. O. Patrick, A. E. Lam and D. P. Gates, *Inorg. Chem.*, 2006, **45**, 5225–5234.
- 43 S. Shah and J. D. Protasiewicz, *Chem. Commun.*, 1998, 1585–1586.
- 44 K. Esfandiarfard, A. I. Arkhypchuk, A. Orthaber and S. Ott, *Dalton Trans.*, 2016, **45**, 2201–2207.
- 45 A. Ziółkowska, N. Szykiewicz and Ł. Ponikiewski, *Inorg. Chem. Front.*, 2021, **8**, 3851–3862.
- 46 L. C. Moores, D. Kaur, M. D. Smith and J. S. Poole, *J. Org. Chem.*, 2019, **84**, 3260–3269.
- 47 G. Becker, W. Uhl and H. Wessely, *Z. Anorg. Allg. Chem.*, 1981, **479**, 41–56.
- 48 H. Grützmacher, P. Murer, J.-P. Wolf, S. Boulmaaz, R. H. Sommerlade, H. Schönberg, T. Ott, D. Stein, J. Geier and T. Ulrich, *Chimia*, 2008, **62**, 18–18.
- 49 H. Grützmacher and G. Müller, World Intellectual Property Organization, *Patent Application*, WO2014/053455A1, 2014.
- 50 D. W. N. Wilson, A. Hinz and J. M. Goicoechea, *Angew. Chem., Int. Ed.*, 2018, **57**, 2188–2193.
- 51 S. J. Urwin and J. M. Goicoechea, *Chem. – Eur. J.*, 2023, **29**, e202203081.
- 52 G. Becker, M. Birkhahn, W. Massa and W. Uhl, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 741–742.
- 53 K. M. Szkop, M. B. Geeson, D. W. Stephan and C. C. Cummins, *Chem. Sci.*, 2019, **10**, 3627–3631.
- 54 M. Regitz and O. J. Scherer, *Multiple bonds and low coordination in phosphorus chemistry*, G. Thieme Verlag, Thieme Medical Publishers, Stuttgart, New York, 1990.
- 55 S. Kurz, H. Oesen, J. Sieler and E. Hey-Hawkins, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1996, **117**, 189–196.
- 56 D. R. Lide, in *CRC Handbook of Chemistry and Physics*, CRC Press, Boca Raton, Florida, 97th edn, 2003.
- 57 D. D. Perrin, *Purification of laboratory chemicals*, Pergamon Press, Oxford, New York, 3rd edn, 1988.
- 58 D. Dey and D. Chopra, *Cryst. Growth Des.*, 2017, **17**, 5117–5128.
- 59 F. Tamaddon, M. A. Amrollahi and L. Sharafat, *Tetrahedron Lett.*, 2005, **46**, 7841–7844.
- 60 T. J. Bannin and M. K. Kiesewetter, *Macromolecules*, 2015, **48**, 5481–5486.
- 61 B. W. Rawe, A. M. Priegert, S. Wang, C. Schiller, S. Gerke and D. P. Gates, *Macromolecules*, 2018, **51**, 2621–2629.
- 62 Y. van den Winkel, H. M. M. Bastiaans and F. Bickelhaupt, *J. Organomet. Chem.*, 1991, **405**, 183–194.
- 63 *Software for the Integration of CCD Detector System Bruker Analytical X-ray Systems*, Bruker AXS LLC, Madison, WI, 2017–2024.
- 64 L. Krause, R. Herbst-Irmer, G. M. Sheldrick and D. Stalke, *J. Appl. Crystallogr.*, 2015, **48**, 3–10.
- 65 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv.*, 2015, **71**, 3–8.
- 66 G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, **71**, 3–8.
- 67 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.

- 68 (a) A. A. Mitchell, P. A. Heine, J. Chang, A. De Paolis, B. O. Patrick and D. P. Gates, CCDC 2475807: Experimental Crystal Structure Determination, 2025, DOI: [10.5517/ccdc.csd.cc2p38rv](https://doi.org/10.5517/ccdc.csd.cc2p38rv); (b) A. A. Mitchell, P. A. Heine, J. Chang, A. De Paolis, B. O. Patrick and D. P. Gates, CCDC 2475808: Experimental Crystal Structure Determination, 2025, DOI: [10.5517/ccdc.csd.cc2p38sw](https://doi.org/10.5517/ccdc.csd.cc2p38sw); (c) A. A. Mitchell, P. A. Heine, J. Chang, A. De Paolis, B. O. Patrick and D. P. Gates, CCDC 2475809: Experimental Crystal Structure Determination, 2025, DOI: [10.5517/ccdc.csd.cc2p38tx](https://doi.org/10.5517/ccdc.csd.cc2p38tx); (d) A. A. Mitchell, P. A. Heine, J. Chang, A. De Paolis, B. O. Patrick and D. P. Gates, CCDC 2475810: Experimental Crystal Structure Determination, 2025, DOI: [10.5517/ccdc.csd.cc2p38vy](https://doi.org/10.5517/ccdc.csd.cc2p38vy); (e) A. A. Mitchell, P. A. Heine, J. Chang, A. De Paolis, B. O. Patrick and D. P. Gates, CCDC 2475811: Experimental Crystal Structure Determination, 2025, DOI: [10.5517/ccdc.csd.cc2p38wz](https://doi.org/10.5517/ccdc.csd.cc2p38wz).