

# A Lewis acid-mediated synthesis of P-alkyl-substituted phosphaaalkenes†‡§

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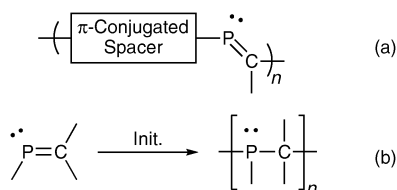
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Treating an equimolar mixture of  $R^1P(SiMe_3)_2$  ( $R^1 = 'Bu, Ad, Mes, Me_3Si$ ;  $Ad = 1\text{-adamantyl}$ ,  $Mes = 2,4,6\text{-trimethylphenyl}$ ) and  $R^2C(O)R^3$  ( $R^2:R^3 = 'Bu:H, Ph:Ph, 'Bu:'Bu, 'Bu:Ph, 'Bu:Me$ ) with  $AlCl_3$  (1 equiv.) affords the corresponding phosphaaalkenes  $R^1P=CR^2R^3$  as monitored by  $^{31}P$  NMR spectroscopy. This new method was applied to the multigram synthesis of  $R^1P=CR^2R^3$  [**1a**:  $R^1 = 'Bu, R^2 = 'Bu, R^3 = H$ ; **2a**:  $R^1 = Ad, R^2 = 'Bu, R^3 = H$ ; **3a**:  $R^1 = Mes, R^2 = 'Bu, R^3 = H$ ; **3b**:  $R^1 = Mes, R^2 = R^3 = Ph$ ] in good isolated yields (**1a**: 80%; **2a**: 57%; **3a**: 63%; **3b**: 76%). Previously unknown **2a** has been fully characterized. The reactivity of **1a** and **2a** with group 13 Lewis acids was performed in an effort to probe their reactivity and provide a means to structurally characterize these P-alkyl phosphaaalkenes. The X-ray crystal structures of **1a**· $AlCl_3$ , **1a**· $GaCl_3$  and **2a**· $GaCl_3$  reveal that the  $'Bu$  substituents are configured in a *trans* arrangement and the  $P=C$  bond lengths are as expected (avg. 1.64 Å).

## Introduction

Possessing a formal  $(3p-2p)\pi$  bond between phosphorus and carbon, the chemistry of phosphaaalkenes ( $RP=CR_2$ ) often more closely resembles that of olefins ( $R_2C=CR_2$ ) than imines ( $RN=CR_2$ ).<sup>1–3</sup> Although the  $P=C/C=C$  analogy is common in molecular chemistry, there has recently been considerable interest in extending this analogy to polymer science.<sup>4</sup> Examples include the development of  $\pi$ -conjugated polymers containing  $P=C$  bonds<sup>5–8</sup> and the addition polymerization of  $P=C$  bonds to afford poly(methylenephosphine)s, PMPs (Scheme 1).<sup>9</sup>

We have been interested in exploring substituent-effects in the polymerization of phosphaaalkene monomers as a means of evaluating the scope of this new reaction. Moreover, the ability to vary substituents is critical to gaining an understanding of structure–property relationships in PMPs and to tune the donor properties of these macromolecular ligands.



**Scheme 1** Examples illustrating the use of  $P=C$  bonds in polymer science: (a)  $\pi$ -conjugated polymers; (b) addition polymerization of  $P=C$  bonds.

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† In memory of Professor Pascal LeFloch and his contributions to the field of phosphorus chemistry.

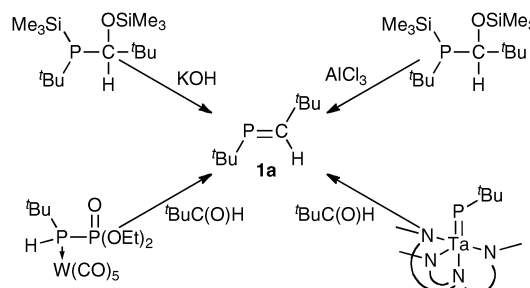
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Such studies require access to simple and convenient methods to prepare isolable phosphaaalkenes bearing a variety of different substituents.

Although many methods for the assembly of  $P=C$  bonds are known, the phosphaa-Peterson reaction<sup>10–19</sup> is attractive due to its versatility as a route to  $Mes-P$ -substituted phosphaaalkenes.<sup>20,21</sup> The reaction involves treating ketones or aldehydes with either  $RP(SiMe_3)_2$  and a catalyst (*e.g.*  $KOH$ ) or  $RP(SiMe_3)Li$  alone. While this method is very effective for the preparation of P-aryl-substituted phosphaaalkenes, it is less suitable when P-alkyl-substituents are desired due to the difficulty in generating the alkylsilylphosphide intermediates.<sup>20</sup> For example, the preparation of  $'BuP=CH'Bu$  (**1a**) from  $'BuP(SiMe_3)_2$  and  $'BuC(O)H$  using  $KOH$  as a catalyst requires *ca.* 11 weeks.<sup>22</sup>

We were intrigued with compound **1a** because it is a rather rare example of an isolable P-alkyl-substituted phosphaaalkene and is a precursor to novel  $P_2C$  and  $P_2C_2$  heterocycles.<sup>23</sup> Clearly, a less time-consuming route to that described above is desirable. Alternative phosphaa-Wittig strategies to **1a** or **1a**· $W(CO)_5$  are known (Scheme 2).<sup>24,25</sup> We also noted that treating  $'BuP(SiMe_3)CH(OSiMe_3)'Bu$ , derived from  $'BuP(SiMe_3)_2$  and  $'BuC(O)H$ , with  $AlCl_3$  afforded high yields



**Scheme 2** Known synthetic routes to the  $'Bu-P$ -substituted phosphaaalkene **1a** or **1a**· $W(CO)_5$ .

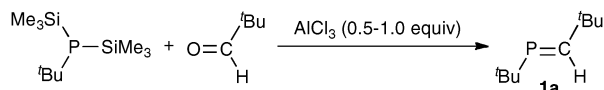
of **1a** (86%).<sup>22</sup> Strikingly, no timeframe is specified for this reaction nor was the direct reaction of <sup>t</sup>BuP(SiMe<sub>3</sub>)<sub>2</sub> and <sup>t</sup>BuC(O)H in the presence of AlCl<sub>3</sub> mentioned. Interestingly, recent work has shown that Lewis acids can catalyze the coupling of silylphosphines and aldehydes to give α-siloxyalkylphosphines.<sup>26</sup> If such an acid mediated approach could be applied to the synthesis of **1a**, it may provide a convenient route to P-alkyl-substituted phosphalkenes for further study.

Herein, we report a simple one-pot synthesis of phosphalkenes from RP(SiMe<sub>3</sub>)<sub>2</sub>, a ketone or aldehyde, and AlCl<sub>3</sub>. In addition, the preparation and molecular structures of the phosphalkene–Lewis acid adducts, (Cl<sub>3</sub>Al)<sup>t</sup>BuP=CH<sup>t</sup>Bu, (Cl<sub>3</sub>Ga)<sup>t</sup>BuP=CH<sup>t</sup>Bu and (Cl<sub>3</sub>Ga)AdP=CH<sup>t</sup>Bu (Ad = 1-adamantyl), are also reported.

## Results and discussion

To assess the feasibility of a Lewis acid-mediated synthesis of phosphalkenes, an equimolar mixture of <sup>t</sup>BuP(SiMe<sub>3</sub>)<sub>2</sub> and <sup>t</sup>BuC(O)H in dichloromethane was treated with AlCl<sub>3</sub> (1 equiv.). Analysis of an aliquot removed from the reaction mixture by <sup>31</sup>P NMR spectroscopy revealed that the signal assigned to <sup>t</sup>BuP(SiMe<sub>3</sub>)<sub>2</sub> (δ = −108) was replaced by a new signal assigned to **1a** (δ = 273).<sup>22</sup> The separation of **1a** from the side-products, Me<sub>3</sub>SiCl and [Cl<sub>2</sub>AlOSiMe<sub>3</sub>]<sub>2</sub>, may be accomplished through the use of reduced pressures to first remove the solvent and Me<sub>3</sub>SiCl (25 °C, 200 mmHg). Subsequently, the phosphalkene **1a** can be distilled (bp = 75 °C, 60 mmHg). This separation must be performed carefully in order to avoid contamination of **1a** with volatile [Cl<sub>2</sub>AlOSiMe<sub>3</sub>]<sub>2</sub>. The liquid product **1a** is isolated in 80% yield and its purity was confirmed by NMR spectroscopy and elemental analysis.

Given the difficulty in separating [Cl<sub>2</sub>AlOSiMe<sub>3</sub>]<sub>2</sub> from **1a**, we sought methods to minimize the production of Al-containing species. Thus, <sup>t</sup>BuP(SiMe<sub>3</sub>)<sub>2</sub> and <sup>t</sup>BuC(O)H in dichloromethane were treated with substoichiometric amounts of AlCl<sub>3</sub>. Monitoring by <sup>31</sup>P NMR spectroscopy revealed that <sup>t</sup>BuP(SiMe<sub>3</sub>)<sub>2</sub> could be transformed quantitatively to **1a** in the presence of 0.5 to 1.0 equiv. of AlCl<sub>3</sub>. The reaction times were substantially longer when less AlCl<sub>3</sub> is used. When 0.8 equiv. AlCl<sub>3</sub> was employed, the isolated yield of **1a** was ca. 70–80%. When 0.33 equiv. of AlCl<sub>3</sub> was employed, a 2 : 1 mixture of product **1a** and intermediate, <sup>t</sup>BuP(SiMe<sub>3</sub>)CH(OSiMe<sub>3</sub>)<sup>t</sup>Bu, were observed. Although it appears possible to use reduced quantities of AlCl<sub>3</sub>, in the following studies stoichiometric quantities were employed since this gives the most rapid reaction.



To assess the generality of the AlCl<sub>3</sub>-mediated synthesis of phosphalkenes, we performed a series of NMR scale reactions involving the mixing of equimolar quantities of R<sup>1</sup>P(SiMe<sub>3</sub>)<sub>2</sub> (R<sup>1</sup> = <sup>t</sup>Bu, Ad, Mes), aldehyde/ketone and AlCl<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub>. In most instances, the phosphalkene product is rapidly and quantitatively formed as suggested by <sup>31</sup>P NMR spectroscopy

**Table 1** Selected <sup>31</sup>P NMR data (CH<sub>2</sub>Cl<sub>2</sub>) for phosphalkenes prepared following AlCl<sub>3</sub>-mediated procedure

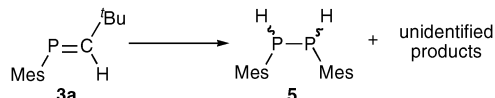
R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	Product	<sup>31</sup> P NMR (δ)
<sup>t</sup> Bu	<sup>t</sup> Bu	H	<b>1a</b>	273
<sup>t</sup> Bu	Ph	Ph	<b>1b</b>	292
<sup>t</sup> Bu	<sup>t</sup> Bu	<sup>t</sup> Bu	<b>1c</b>	295
<sup>t</sup> Bu	<sup>t</sup> Bu	Ph	<b>1d</b>	277
<sup>t</sup> Bu	<sup>t</sup> Bu	Me	<b>1e</b>	270
Ad	<sup>t</sup> Bu	H	<b>2a</b>	268
Mes	<sup>t</sup> Bu	H	<b>3a</b>	224
Mes	Ph	Ph	<b>3b</b>	234
SiMe <sub>3</sub>	<sup>t</sup> Bu	H	<b>4a</b>	240

(Table 1). Although phosphalkene **1b** initially forms cleanly, the previously reported 1,2-diphosphetane is observed on standing.<sup>27</sup> In the case of the extremely hindered 2,2,4,4-tetramethylpentan-3-one, its reaction with <sup>t</sup>BuP(SiMe<sub>3</sub>)<sub>2</sub> to form **1c** required prolonged heating (>100 °C for 12 h). Although the C–Me phosphalkene **1e** could be detected by <sup>31</sup>P NMR spectroscopy, this species was present in low quantities (ca. 25% of total P). Given that <sup>t</sup>BuPH<sub>2</sub> was present in the reaction mixture (δ = −80, t), it is likely that the readily enolizable ketone, <sup>t</sup>BuC(O)Me, provided acidic protons for reaction with <sup>t</sup>BuP(SiMe<sub>3</sub>)<sub>2</sub>. Interestingly, this methodology is amenable to the preparation of a P-silyl-phosphalkene as illustrated by the quantitative formation of **4a** from P(SiMe<sub>3</sub>)<sub>3</sub> and pivaldehyde.

In addition to **1a**, three other phosphalkenes have been isolated on a preparative scale (**2a**, **3a** and **3b**) following this new methodology. The procedure described above for **1a** was followed in each case and analysis of the reaction mixtures by <sup>31</sup>P NMR spectroscopy suggested quantitative conversion of RP(SiMe<sub>3</sub>)<sub>2</sub> to phosphalkene. The separation of the heavier phosphalkenes from the aluminium-containing byproduct proved impossible by fractional distillation due to the very similar volatility of these compounds. Instead, [Cl<sub>2</sub>AlOSiMe<sub>3</sub>]<sub>2</sub> can be removed by extracting a solution of the crude product with a degassed mixture of aqueous NaOH (~5 M) and hexanes. The use of hexanes is critical to keep salts out of the organic layer. Remarkably, the organic layer contained the unhydrolyzed phosphalkene product free from Al-containing impurities. Final purification was accomplished through vacuum sublimation (**2a**), distillation (**3a**) or recrystallization from hexanes (**3b**). To our knowledge, the only other isolable P–Ad substituted phosphalkene is the Becker phosphalkene, AdP=C(<sup>t</sup>Bu)OSiMe<sub>3</sub>.<sup>28</sup> We have previously observed AdP=CPh<sub>2</sub> by <sup>31</sup>P NMR spectroscopy (δ = 286), however only the head-to-head dimeric 1,2-diphosphetane, [AdP–CPh<sub>2</sub>]<sub>2</sub>, could be isolated.<sup>20</sup>

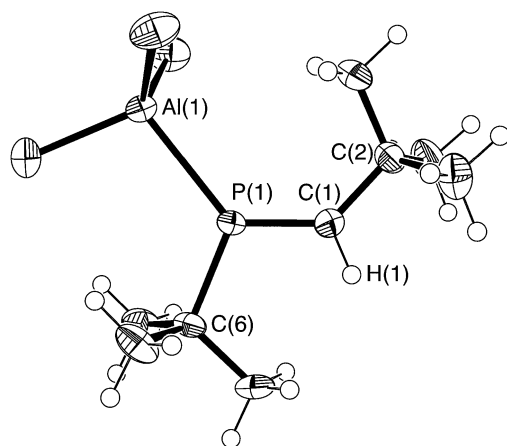
Although, pure **3a** can be isolated as a colorless oil, after several days in a sealed vial under inert atmosphere, colorless crystals precipitate from the oil. Surprisingly, these crystals were determined to be the diphosphine **5** after analysis using NMR spectroscopy and X-ray diffraction. Compound **5** had previously been isolated and crystallographically characterized

from the reaction of LiPHMes and 1,2-dibromoethane,<sup>29</sup> and has been detected in solution in several other instances.<sup>30</sup> Whether this transformation is caused by the presence of a trace impurity or is a consequence of some inherent instability of **3a** has not been ascertained. However, it should be noted that the analogous crystals of **5** are isolated each time **3a** is prepared.

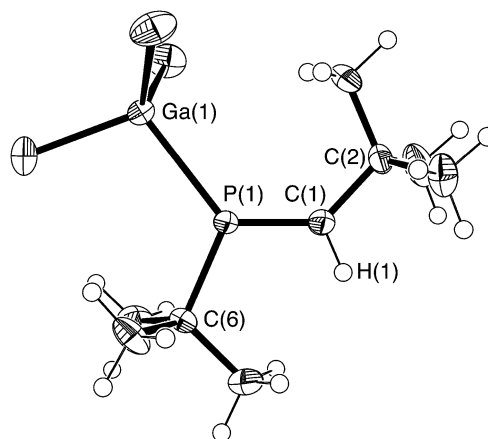


As a means to probe their reactivity and to structurally characterize P-alkyl phosphalkenes, the potential formation of adducts of **1a** and **2a** with group 13 Lewis acids was explored. We have previously reported that treating **3b** with group 13 Lewis acids affords the simple P-adduct (Cl<sub>3</sub>Ga)MesP=CPh<sub>2</sub> (**3b**·GaCl<sub>3</sub>).<sup>31</sup> In contrast, evidence of C-addition of GaCl<sub>3</sub> was observed with bulkier Mes\*P=CH<sub>2</sub> (Mes\* = 2,4,6-tri-*tert*-butylphenyl) to afford fleeting phosphonium zwitterion Mes\*P=CH<sub>2</sub>GaCl<sub>3</sub>.<sup>31</sup> Therefore, an investigation of the reactions of **1a** and **2a** with GaCl<sub>3</sub> and AlCl<sub>3</sub> was conducted. Prior studies had shown that the reaction of **1a** with sources of H<sup>+</sup> or Me<sup>+</sup> affords novel diphosphiranium or diphosphetanium cations, respectively.<sup>23</sup>

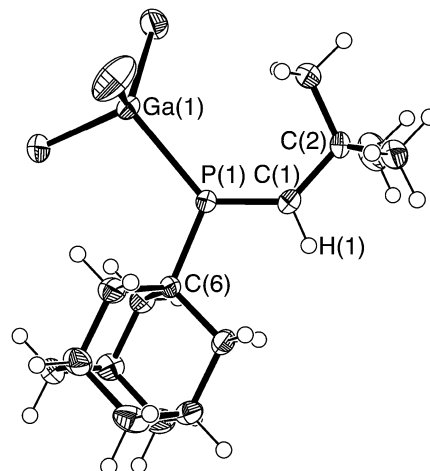
Analysis of a solution of phosphalkene **1a** and AlCl<sub>3</sub> (1 equiv.) in CH<sub>2</sub>Cl<sub>2</sub> by <sup>31</sup>P NMR spectroscopy revealed that the signal for **1a** (δ = 273) was not present and a new singlet resonance was observed (δ = 199.8). The chemical shift is consistent with that reported previously for **1a**·AlCl<sub>3</sub> (δ = 200.5 in C<sub>7</sub>D<sub>8</sub>).<sup>22</sup> Furthermore, the <sup>1</sup>H and <sup>13</sup>C NMR spectra of crystals obtained from the reaction solution were also consistent with adduct formation. Analysis of the crystals by X-ray diffraction confirmed the adduct formation and the *trans* arrangement of the <sup>t</sup>Bu substituents in *Z*-**1a**·AlCl<sub>3</sub> (Fig. 1). Perhaps this indicates that the bulky alkyl substituent imposes a larger steric demand than the Lewis acid. Similarly,



**Fig. 1** ORTEP view of a molecule of **1a**·AlCl<sub>3</sub>. Displacement ellipsoids are shown at the 50% probability level. Selected bond distances (Å) and angles (°) are as follows. P(1)–C(1) 1.652(3), P(1)–C(6) 1.866(3), P(1)–Al(1) 2.4516(11), C(1)–C(2) 1.502(4), C(6)–P(1)–C(1) 111.96(14), C(1)–P(1)–Al(1) 128.52(11), C(6)–P(1)–Al(1) 119.46(10), P(1)–C(1)–C(2) 132.5(2), C(6)–P(1)–C(1)–C(2) 179.2(3).



**Fig. 2** ORTEP view of a molecule of **1a**·GaCl<sub>3</sub>. Displacement ellipsoids are shown at the 50% probability level. Selected bond distances (Å) and angles (°) are as follows. P(1)–C(1) 1.655(3), P(1)–C(6) 1.862(2), P(1)–Ga(1) 2.4164(7), C(1)–C(2) 1.502(3), C(6)–P(1)–C(1) 113.30(12), C(1)–P(1)–Ga(1) 127.77(9), C(6)–P(1)–Ga(1) 118.84(8), P(1)–C(1)–C(2) 132.7(2), C(6)–P(1)–C(1)–C(2) 179.2(2).



**Fig. 3** ORTEP view of a molecule of **2a**·GaCl<sub>3</sub>. Displacement ellipsoids are shown at the 50% probability level. Selected bond distances (Å) and angles (°) are as follows. P(1)–C(1) 1.647(4), P(1)–C(6) 1.842(3), P(1)–Ga(1) 2.4178(10), C(1)–C(2) 1.503(5), C(6)–P(1)–C(1) 112.56(17), C(1)–P(1)–Ga(1) 129.74(14), C(6)–P(1)–Ga(1) 117.30(11), P(1)–C(1)–C(2) 131.7(3), C(6)–P(1)–C(1)–C(2) 179.8(4).

the new adducts *Z*-**1a**·GaCl<sub>3</sub> and *Z*-**2a**·GaCl<sub>3</sub> were isolated and crystallographically characterized (Fig. 2 and 3, respectively).

Interestingly, the <sup>31</sup>P{<sup>1</sup>H} NMR spectra (300 MHz, 298 K) of the Ga and Al adducts show very broad resonances. For example, the full width at half-height (fwhh) for **1a**·GaCl<sub>3</sub> (233 Hz) is much larger than that for uncomplexed **1a** (9 Hz). We speculate that a fluxional process, such as equilibration between coordinated and free phosphalkene, may be taking place in solution. Evidence for weak binding of Lewis acids to **1a** has been alluded to previously since AlCl<sub>3</sub> is readily displaced from **1a**·AlCl<sub>3</sub> in the presence of Et<sub>2</sub>O.<sup>22</sup>

There are very few other η<sup>1</sup> complexes of phosphalkenes to p-block metals. We have previously reported the molecular structure of **3b**·GaCl<sub>3</sub> and detected (Cl<sub>3</sub>Ga)Mes\*P=CH<sub>2</sub> at

low-temperature ( $-80\text{ }^{\circ}\text{C}$ ). It has also been reported that the inversely polarized phosphalkene  $[\text{Cp}^*(\text{CO})_2\text{Fe}]\text{P}=\text{C}(\text{NMe}_2)_2$  will form  $\eta^1$  complexes with  $\text{MMe}_3$  ( $\text{M} = \text{Al}, \text{Ga}, \text{In}$ ), however crystallographic analysis revealed significant pyramidalization of the phosphorus atoms ( $\sim 340^{\circ}$ ) and lengthening of the P–C bonds suggests little double bond character in these species.<sup>32</sup> In **1a**· $\text{AlCl}_3$ , **1a**· $\text{GaCl}_3$ , and **2a**· $\text{GaCl}_3$  the sum of the angles at phosphorus are  $360^{\circ}$ , consistent with retention of the P=C bond upon complexation.

Analysis of the metrical parameters reveals that the P=C bond lengths in **1a**· $\text{AlCl}_3$  [1.652(3) Å], **1a**· $\text{GaCl}_3$  [1.655(3) Å] and **2a**· $\text{GaCl}_3$  [1.647(4) Å] are similar in length. These P=C bond lengths lie at shorter end of the range associated with P=C bonds (1.61–1.71 Å),<sup>1</sup> but are comparable to  $(\text{CO})_5\text{W}[\text{C}(\text{H}_2\text{CH}_2\text{C})(1\text{-cyclohexene})]\text{P}=\text{CH}^t\text{Bu}$  (1.649 Å)<sup>33</sup> and  $(\text{CO})_5\text{W}^t(\text{Bu})\text{P}=\text{CH}^t\text{Pr}$  (1.652 Å),<sup>25</sup> and are consistent with the retention of multiple-bond character upon adduct formation. The P=C bond length in **3b**· $\text{GaCl}_3$  [1.687(3) Å] is slightly longer than that for **1a**· $\text{GaCl}_3$  and **2a**· $\text{GaCl}_3$  which likely results from  $\pi$ -delocalization between the P=C bond and the aryl moiety in the former.

The P– $\text{C}_{\text{alkyl}}$  bond lengths in **1a**· $\text{AlCl}_3$  [1.866(3) Å], **1a**· $\text{GaCl}_3$  [1.862(2) Å] and **2a**· $\text{GaCl}_3$  [1.842(3) Å] lie towards the shorter end of the range typical of P– $\text{C}_{\text{alkyl}}$  bonds (range: 1.85–1.90).<sup>34</sup> Interestingly, the P– $\text{C}_{\text{rBu}}$  bonds are significantly longer than the P– $\text{C}_{\text{Ad}}$  bond. Presumably this reflects the lower steric demand of the cyclic Ad substituent. The P–Ga bond lengths in **1a**· $\text{GaCl}_3$  [2.4164(7) Å] and **2a**· $\text{GaCl}_3$  [2.4178(10) Å] are comparable to that in **3b**· $\text{GaCl}_3$  [2.3938(7) Å] and are typical of P–Ga bonds.

## Conclusions

The  $\text{AlCl}_3$ -mediated reaction of bis(silyl)phosphines and aldehydes or ketones provides a useful one-pot route to phosphalkenes. The acid-mediated method is preferable to base-mediated routes when the preparation of P-alkyl-substituted phosphalkenes is desired. A series of phosphalkenes bearing P- $t\text{Bu}$  and P-Ad substituents have been prepared and isolated following this new methodology. The adducts  $Z-(\text{Cl}_3\text{Ga})^t\text{BuP}=\text{CH}^t\text{Bu}$  (**1a**· $\text{GaCl}_3$ ),  $Z-(\text{Cl}_3\text{Al})^t\text{BuP}=\text{CH}^t\text{Bu}$  (**1a**· $\text{AlCl}_3$ ), and  $Z-(\text{Cl}_3\text{Ga})\text{AdP}=\text{CH}^t\text{Bu}$  (**2a**· $\text{GaCl}_3$ ) are rare examples of phosphalkene complexes of a group 13 Lewis acid and provide a means to investigate the structural features of P-alkyl-substituted phosphalkenes.

## Experimental

All manipulations were performed under an atmosphere of nitrogen. Hexanes, dichloromethane and diethyl ether were deoxygenated with nitrogen and dried by passing through a column containing activated alumina. Distilled water was degassed prior to use.  $\text{C}_6\text{D}_6$  was stored over molecular sieves before use and ampules of  $\text{CD}_2\text{Cl}_2$  were used as received from CIL. Benzophenone (Aldrich) was sublimed before use. Pivaldehyde, 3,3-dimethylbutan-2-one and  $\text{AlCl}_3$  were used as received from Aldrich. NaOH and anhydrous  $\text{MgSO}_4$  were purchased from Fisher and used as received. 2,2,4,4-Tetramethylpentan-3-one,<sup>35</sup> 2,2-dimethyl-1-phenylpropan-1-one,<sup>36</sup>

$^t\text{BuP}(\text{SiMe}_3)_2$ ,<sup>37</sup>  $\text{AdP}(\text{SiMe}_3)_2$ ,<sup>20,38</sup>  $\text{MesP}(\text{SiMe}_3)_2$ <sup>37</sup> and  $\text{P}(\text{SiMe}_3)_3$ <sup>39</sup> were prepared following literature procedures.  $^1\text{H}$ ,  $^{31}\text{P}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded at room temperature on Bruker Avance 300 or 400 MHz spectrometers. Chemical shifts are reported relative to residual  $\text{C}_6\text{HD}_5$  or  $\text{CHDCl}_2$  ( $\delta = 7.16$  or  $5.32$  for  $^1\text{H}$ , respectively), 85%  $\text{H}_3\text{PO}_4$  as an external standard ( $\delta = 0.0$  for  $^{31}\text{P}$ ), and  $\text{C}_6\text{D}_6$  or  $\text{CD}_2\text{Cl}_2$  ( $\delta = 128$  or  $53.8$  for  $^{13}\text{C}$ , respectively). Mass spectra were recorded on a Kratos MS 50 instrument in EI mode (70 eV).

## General procedure for NMR scale reactions

To a small vial charged with  $\text{AlCl}_3$  (33 mg, 0.25 mmol), dichloromethane ( $\sim 2$  mL) and a small magnetic stir-bar was added a solution of  $\text{RP}(\text{SiMe}_3)_2$  (0.25 mmol) and aldehyde/ketone (0.25 mmol) in dichloromethane ( $\sim 2$  mL). The mixture was stirred for 10 min and then an aliquot removed and analyzed by  $^{31}\text{P}$  NMR spectroscopy. The presence of phosphalkene is indicated by a diagnostic signal in the respective NMR spectra ( $\delta > 200$ ).

### $^t\text{BuP}=\text{CH}^t\text{Bu}$ (**1a**)

To a suspension of  $\text{AlCl}_3$  (5.6 g, 42 mmol) in dichloromethane (100 mL) was added a mixture of  $^t\text{BuP}(\text{SiMe}_3)_2$  (10.0 g, 43 mmol) and pivaldehyde (3.8 g, 44 mmol) in dichloromethane (50 mL). The resulting mixture was stirred until quantitative conversion to **1a** was observed from  $^{31}\text{P}$  NMR spectroscopy ( $\sim 30$  min). Volatiles (dichloromethane and  $\text{ClSiMe}_3$ ) were removed at reduced pressure (200 Torr). A reduced pressure distillation ( $75\text{ }^{\circ}\text{C}/60$  Torr) affords **1a** as a pale yellow oil (5.4 g, 80%).  $^{31}\text{P}$ ,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra confirmed the formation of **1**:  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  275.7, lit. ( $\text{CDCl}_3$ )  $\delta$  278.2.<sup>22</sup> Found: C, 68.14; H, 12.03%.  $\text{C}_9\text{H}_{11}\text{P}$  requires C, 68.32; H, 12.10%.

### $\text{AdP}=\text{CH}^t\text{Bu}$ (**2a**)

To a suspension of  $\text{AlCl}_3$  (4.3 g, 32 mmol) in dichloromethane (100 mL) was added a mixture of  $\text{AdP}(\text{SiMe}_3)_2$  (10.0 g, 32 mmol) and pivaldehyde (2.8 g, 33 mmol) in dichloromethane (50 mL). The resulting mixture was stirred for 1 h and then the volatiles (dichloromethane and  $\text{ClSiMe}_3$ ) were removed at reduced pressure (200 Torr). The crude product was dissolved in diethyl ether (100 mL) and added dropwise to a stirred mixture of degassed 5 M NaOH(aq.) (200 mL) and hexanes (100 mL). The organic fraction was separated and the aqueous fraction washed with hexanes ( $3 \times 30$  mL). The combined organic fractions were dried with anhydrous  $\text{MgSO}_4$ , filtered, and evaporated to dryness. The crude solid was vacuum distilled and sublimed ( $100\text{ }^{\circ}\text{C}/2$  mmHg) to afford an analytically pure colorless solid (4.3 g, 57%).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  268.4.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  8.65 (d,  $^2J_{\text{PH}} = 24.9$  Hz, 1H), 1.98 (m, 3H), 1.80 (m, 6H), 1.75 (m, 6H), 1.13 (d,  $^4J_{\text{PH}} = 1.8$  Hz, 9H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  194.6 (d,  $^1J_{\text{PC}} = 46.2$  Hz), 42.6 (d,  $^2J_{\text{PC}} = 8.4$  Hz), 38.4 (d,  $^2J_{\text{PC}} = 11.8$  Hz), 37.3, 36.1 (d,  $^1J_{\text{PC}} = 34.0$  Hz), 31.2 (d,  $^3J_{\text{PC}} = 12.9$  Hz), 29.7 (d,  $^3J_{\text{PC}} = 6.6$  Hz). MS (EI):  $m/z$  [%] 135, 136 [100, 15,  $\text{Ad}^+$ ], 236, 237 [18, 3,  $\text{M}^+$ ]. Found: C, 76.56; H, 10.89%.  $\text{C}_{15}\text{H}_{25}\text{P}$  requires C, 76.23; H, 10.66%.

### MesP=CH'Bu (3a)

To a suspension of AlCl<sub>3</sub> (1.7 g, 13 mmol) in dichloromethane (40 mL) was added a mixture of MesP(SiMe<sub>3</sub>)<sub>2</sub> (4.0 g, 13 mmol) and pivaldehyde (1.1 g, 13 mmol) in dichloromethane (25 mL). The resulting mixture was stirred for 1 h and then the volatiles (dichloromethane and ClSiMe<sub>3</sub>) were removed at reduced pressure (200 Torr). The crude product was dissolved in diethyl ether (100 mL) and added dropwise to a stirred mixture of degassed 5 M NaOH(aq.) (200 mL) and hexanes (100 mL). The organic fraction was separated and the aqueous fraction washed with hexanes (3 × 30 mL). The combined organic fractions were dried with anhydrous MgSO<sub>4</sub>, filtered, and evaporated to dryness. The crude product was purified by vacuum distillation (1.9 g, 63%). <sup>31</sup>P and <sup>1</sup>H NMR spectra confirmed the formation of **3a**: <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 224.6, lit. (C<sub>6</sub>D<sub>6</sub>) δ 228.4.<sup>40,41</sup> After several days, crystals of **5** precipitate from the liquid **3a**: <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ -111.9 (60%), -119.1 (40%), lit. (C<sub>6</sub>D<sub>6</sub>) δ -109.9 (60%), -117.1 (40%).<sup>29</sup>

### MesP=CPh<sub>2</sub> (3b)

To a suspension of AlCl<sub>3</sub> (2.2 g, 17 mmol) in dichloromethane (50 mL) was added a mixture of MesP(SiMe<sub>3</sub>)<sub>2</sub> (5.0 g, 16 mmol) and benzophenone (3.1 g, 17 mmol) in dichloromethane (50 mL). The resulting mixture was stirred for 1 h and then the volatiles (dichloromethane and ClSiMe<sub>3</sub>) were removed *in vacuo*. The crude product was dissolved in diethyl ether (100 mL) and added dropwise to a stirred mixture of degassed 5 M NaOH(aq.) (200 mL) and hexanes (100 mL). The organic fraction was separated and the aqueous fraction washed with hexanes (3 × 30 mL). The combined organic fractions were dried with anhydrous MgSO<sub>4</sub>, filtered, and evaporated to dryness. The crude product was purified by

vacuum distillation and then recrystallization from hexanes to afford yellow crystals of **3b** (4.1 g, 76%). <sup>31</sup>P, <sup>1</sup>H and <sup>13</sup>C NMR spectra confirmed the formation of **3b**: <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>) δ 234.6, lit. (CDCl<sub>3</sub>) δ 233.<sup>42</sup> Found: C, 83.17; H, 6.62%. C<sub>22</sub>H<sub>21</sub>P requires C, 83.52; H, 6.69%.

### Z-(Cl<sub>3</sub>Al)'BuP=CH'Bu (1a·AlCl<sub>3</sub>)

To a solution of AlCl<sub>3</sub> (0.266 g, 2 mmol) in dichloromethane (2 mL) was added a solution of **1a** (0.316 g, 2 mmol) in dichloromethane (1 mL). Upon the reaction mixture was layered 1 mL of hexanes. The mixture was stored at -40 °C for 24 h at which point crystals of **1a**·AlCl<sub>3</sub> suitable for X-ray crystallography were harvested (0.25 g, 43%). <sup>31</sup>P and <sup>1</sup>H spectra confirmed the formation of **1a**·AlCl<sub>3</sub>: <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) δ 198.6, lit. (C<sub>7</sub>D<sub>8</sub>) δ 200.5.<sup>22</sup>

### Z-(Cl<sub>3</sub>Ga)'BuP=CH'Bu (1a·GaCl<sub>3</sub>)

To a solution of GaCl<sub>3</sub> (0.350 g, 2 mmol) in dichloromethane (2 mL) was added a solution of **1a** (0.316 g, 2 mmol) in dichloromethane (1 mL). Upon the reaction mixture was layered 1 mL of hexanes. The mixture was stored at -40 °C for 24 h at which point crystals of **1a**·GaCl<sub>3</sub> suitable for X-ray crystallography were collected (0.48 g, 72%). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 194.4; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 8.74 (d, <sup>2</sup>J<sub>PH</sub> = 24.3 Hz, 1H), 1.60 (d, <sup>3</sup>J<sub>PH</sub> = 16.8, 9H), 1.38 (d, <sup>4</sup>J<sub>PH</sub> = 1.8 Hz, 9H). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 190.8 (d, <sup>1</sup>J<sub>PC</sub> = 20.6 Hz), 40.9, 40.7 (d, <sup>1</sup>J<sub>PC</sub> = 4.9 Hz), 31.5 (d, <sup>2</sup>J<sub>PC</sub> = 12.9 Hz), 29.9. Found: C, 32.40; H, 5.89%. C<sub>9</sub>H<sub>19</sub>PGaCl<sub>3</sub> requires C, 31.82; H, 5.73%.

### Z-(Cl<sub>3</sub>Ga)AdP=CH'Bu (2a·GaCl<sub>3</sub>)

To a solution of GaCl<sub>3</sub> (0.200 g, 1.1 mmol) in dichloromethane (1 mL) was added a solution of **2a** (0.260 g, 1.1 mmol) in

**Table 2** Crystallographic data for **1a**·AlCl<sub>3</sub>, **1a**·GaCl<sub>3</sub> and **2a**·GaCl<sub>3</sub>

	<b>1a</b> ·AlCl <sub>3</sub>	<b>1a</b> ·GaCl <sub>3</sub>	<b>2a</b> ·GaCl <sub>3</sub>
Formula	C <sub>9</sub> H <sub>19</sub> PAIAlCl <sub>3</sub>	C <sub>9</sub> H <sub>19</sub> PGaAlCl <sub>3</sub>	C <sub>15</sub> H <sub>25</sub> PGaAlCl <sub>3</sub>
fw	291.54	334.28	412.39
Cryst syst	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
Color	Colorless	Colorless	Colorless
<i>a</i> /Å	11.0934(8)	11.0971(14)	10.5923(11)
<i>b</i> /Å	8.8646(6)	8.8556(12)	15.9466(17)
<i>c</i> /Å	16.1716(11)	16.184(2)	11.3326(13)
α/°	90	90	90
β/°	108.143(2)	108.247(5)	107.238(5)
γ/°	90	90	90
<i>V</i> /Å <sup>3</sup>	1511.23(18)	1510.5(3)	1828.2(3)
<i>T</i> /K	173(2)	173(2)	100(2)
<i>Z</i>	4	4	4
μ (MoKα)/cm <sup>-1</sup>	7.38	24.26	20.21
Cryst size/mm <sup>3</sup>	0.4 × 0.2 × 0.1	0.15 × 0.15 × 0.10	1.0 × 0.5 × 0.3
Calcd density/Mg m <sup>-3</sup>	1.281	1.470	1.498
2θ (max)/°	55.8	56.0	56.4
No. of reflns	18581	32228	39679
No. of unique data	3626	6868	7795
<i>R</i> <sub>int</sub>	0.0366	0.0505	0.0880
Refln/param ratio	27.26	51.25	42.14
<i>R</i> <sub>1</sub> <sup>a</sup>	0.0484; <i>I</i> > 2σ( <i>I</i> )	0.0377; <i>I</i> > 2σ( <i>I</i> )	0.0572; <i>I</i> > 2σ( <i>I</i> )
<i>wR</i> <sub>2</sub> (all data) <sup>b</sup>	0.1324	0.0887	0.1350
GOF	1.154	1.097	1.077

<sup>a</sup> *R*<sub>1</sub> = Σ||*F*<sub>o</sub>| - |*F*<sub>c</sub>||/Σ|*F*<sub>o</sub>|. <sup>b</sup> *wR*<sub>2</sub>(*F*<sup>2</sup> [all data]) = {Σ[*w*(*F*<sub>o</sub><sup>2</sup> - *F*<sub>c</sub><sup>2</sup>)]/Σ[*w*(*F*<sub>o</sub><sup>2</sup>)]}<sup>1/2</sup>.

dichloromethane (1 mL). The mixture layered with hexanes (2 mL) and was stored at  $-40\text{ }^{\circ}\text{C}$  for 24 h from which crystals of **2a**·GaCl<sub>3</sub> suitable for X-ray crystallography were grown (0.34 g, 75%). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  189.3; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  8.60 (d, <sup>2</sup>J<sub>PH</sub> = 23.7 Hz, 1H), 2.24 (m, 6H), 2.15 (m, 3H), 1.81 (m, 6H), 1.37 (d, <sup>4</sup>J<sub>PH</sub> = 1.8, 9H). <sup>13</sup>C{<sup>1</sup>H} (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  189.8 (d, <sup>1</sup>J<sub>PC</sub> = 24.1 Hz), 45.1, 41.0, 40.5, 36.1, 31.5 (d, <sup>3</sup>J<sub>PC</sub> = 9.6 Hz), 29.4 (d, <sup>3</sup>J<sub>PC</sub> = 7.1 Hz). Found: C, 43.67; H, 5.95%. C<sub>15</sub>H<sub>25</sub>PGaCl<sub>3</sub> requires C, 43.68; H, 6.11%.

### X-Ray crystallography

Crystals suitable for diffraction were immersed in Paratone-N oil and mounted on a glass fiber. Data for **1a**·GaCl<sub>3</sub> were collected on a Bruker X8 APEX diffractometer and for both **1a**·AlCl<sub>3</sub> and **2a**·GaCl<sub>3</sub> on a Bruker X8 APEX II diffractometer with graphite-monochromated MoK $\alpha$  radiation. Data were collected and integrated using the Bruker SAINT<sup>43</sup> software package and corrected for absorption effects using SADABS<sup>44</sup> (**1a**·AlCl<sub>3</sub>) or TWINABS<sup>45</sup> (**1a**·GaCl<sub>3</sub> and **2a**·GaCl<sub>3</sub>). **1a**·GaCl<sub>3</sub> crystallizes as a two-component twin with the two components (major : minor  $\approx$  3 : 1) related by a 180° rotation about the (0 0 1) reciprocal axis. **2a**·GaCl<sub>3</sub> crystallizes as a two-component twin with the two components (major : minor  $\approx$  2 : 1) related by a 180° rotation about the (1 0 0) reciprocal axis. All data sets were corrected for Lorentz and polarization effects. All structures were solved by direct methods<sup>46</sup> and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms using the SHELXTL<sup>47</sup> crystallographic software package from Bruker-AXS. H-atoms were included in calculated positions (riding model). Compounds **1a**·AlCl<sub>3</sub> and **1a**·GaCl<sub>3</sub> are isomorphous and were refined using the same origin (Table 2). CCDC 768435 (**1a**·AlCl<sub>3</sub>), 768436 (**1a**·GaCl<sub>3</sub>) and 768437 (**2a**·GaCl<sub>3</sub>).†

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