Accessing Cationic α-Silylated and α-Germylated Phosphorus Ylides

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Dedicated to Prof. Holger Braunschweig on the occasion of his 60th birthday.

Abstract: The synthesis and full characterization of α-silylated (α-SiCPs; 1–7) and α-germylated (α-GeCPs; 11–13) phosphorus ylides bearing one chloride substituent R[PC(R')E-(Cl)R'2]2 (R = Ph; R' = Me, Et, Pr; R'' = Me, Et, iPr, Mes; E = Si, Ge) is presented. The molecular structures were determined by X-ray diffraction studies. The title compounds were applied in halide abstraction studies in order to access cationic species. The reaction of Ph3PC(Me)Si(Cl)Me2 (1) with Na[B(C6F5)4] furnished the dimeric phosphonium-like dication [Ph3PC(Me)SiMe]2[B(C6F5)4] (8). The highly reactive, mesityl- or iPr-substituted cationic ylides [Ph3PC(MeSiMes)2][B(C6F5)4] (9) and [Ph3PC(Et)SiPr2][B(C6F5)4] (10) could be characterized by NMR spectroscopy. Carrying out the halide abstraction reaction in the sterically demanding ether iPr2O afforded the protonated α-SiCP [Ph3PC(ethyl)Si(Cl)]Pr2][B(C6F5)4] (6 dec) by sodium-mediated basic ether decomposition, whereas successfully synthesized [Ph3PC(Et)SiPr2][B(C6F5)4] (10) readily cleaves the F–C bond in fluorobenzene. Thus, the ambiphilic character of α-SiCPs is clearly demonstrated. The less reactive germanium analogue [Ph3PC(Me)GeMes]2[B(C6F5)4] (11) was obtained by treating 11 with Na[B(3,5-(CF3)2C6H4)4] and fully characterized including by X-ray diffraction analysis. Structural parameters indicate a strong C(Ph)Ge interaction with high double bond character, and consequently the C–E (E = Si, Ge) bonds in 9, 10 and 14 were analyzed by NBO and AIM methods.

Introduction

Frustrated Lewis pairs (FLPs) have been studied in great detail in recent years.[1] Most commonly, a combination of a sterically hindered Lewis acid and a Lewis base are applied, leading to “frustration” by preventing Lewis acid/base adduct formation. The majority of known FLP systems use group 13 element-based Lewis acids with electron-withdrawing substituents in order to increase the Lewis acidity, as in the landmark example I (Scheme 1) by the Stephan group.[2] Phosphine and amine derivatives are the most common Lewis basic counterparts. Combination of stronger Lewis acidic cationic silicon compounds and phosphines or amines is much less common.[3]

Moreover, so-called hidden FLPs were reported,[3] which seem to be not frustrated at first glance, as a bond between acidic and basic site is formed. However, ring strain or steric strain can still enable dissociation of the acidic and basic site.

Scheme 1. Selected examples of FLPs, hidden FLPs and ambiphilic ylides.

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for the electron pair on the Lewis basic carbon center. In order to further extend our activities in this area, we intended to access cationic α-silylated and α-germylated phosphorus ylides (Scheme 1).

π-Stabilized silicon cations are of fundamental interest. Komatsu published the first π-stabilized silylium ion in 2000, which, however, could only be characterized in solution.[7] Greb and co-workers recently reported on a dimeric tris(dimethylamino)silylium cation.[8] A surprisingly high fluoride ion affinity (FIA) of 809.6 kJ mol$^{-1}$ for the hypothetical monomer was reported. The Lewis acidity of silicon and germanium cations as well as their versatile chemistry has been well examined.[9,9a,b,10] Gessner and co-workers recently reported on stabilized ylide-substituted dinuclear cationic germanium analogue of a vinyl cation [Ph$_3$PC(TolSO$_2$)Ge$_2$][SnCl$_4$], which can be described as germylene stabilized Ge$^{II}$ cation.[11] Nonstabilized phosphorus ylide-substituted silicon and germanium cations are, to the best of our knowledge, not yet known in the literature.[10a,12,13] but their reactivity can be expected to resemble that of the highly reactive C=E (E=Si, Ge) double bonds in silenes and germanenes.[14] Herein we report on the syntheses and characterization of new α-silylated and germaylated phosphorus ylides bearing one chloride substituent on the group 14 element, including studies on cation formation by halide abstraction (Scheme 3).

**Results and Discussion**

α-Substituted phosphorus ylides are readily available by transylidation (Scheme 3).[10a,15] Thus, our synthetic strategy to α-silylated (α-SiCPs) and α-germylated (α-GeCPs) phosphorus ylides followed this route. Three different groups R$_1$ (R$_1$=Me, Et, Ph) were chosen as substituent for the ylidic carbon atom due to the ready availability of the corresponding starting materials. The phosphonium salts [Ph$_3$PC(H$_2$)$_2$][SnCl$_4$] were straightforwardly converted to the ylides Ph$_3$PC[H$_2$] by deprotonation.[16] Subsequent treatment of the ylides Ph$_3$PC[H$_2$] by dichlorosilanes in a 2:1 stoichiometric ratio resulted in trans-ylidation and formation of the silylated phosphorus ylides $1–7$. In these novel phosphorus ylides, the substituents on the heavier tetrels R$_2$ were either Me, Et, iPr or Mes to study effects of steric strain (Table 1). These reactions for the synthesis of $1–7$ were carried out in toluene followed by filtration and extraction with boiling hexane (reaction conditions and yields for $1–7$ are given in Table 4 in the Experimental Section). Crystals suitable for X-ray analysis were obtained by recrystallization from hexane. The crystal structure of 1 is exemplarily shown in Figure 1 (crystal structures of $2–7$ and all other crystallographic parameters are...
attributed to ionic contributions or to hyperconjugative 
average C\( \alpha \) bonds are noticeably shorter (8–10 pm) than the calculated 
in Ph\( \text{Me} \) [8].

Table 2. Calculated dimerization energies of potential \( \alpha \)-Si\( \alpha \)+CPs (dimer with \( R^1 = \text{Me}, \text{R}^2 = \text{Mes} \) could not be converged)

| \( R^1 \) | \( R^2 \) | \( \Delta E \) [kJ mol\(^{-1}\)] |
|---|---|---|
| Me | Me | –111.51 |
| Et | Et | –92.92 |
| Ph | Me | –70.26 |
| Ph | Et | –22.49 |
| Ph | Ph | + 3.80 |
| Me | iPr | + 32.39 |
| Et | iPr | + 98.88 |
| Ph | iPr | + 104.57 |
| Me | Mes | – |
| Mes | Mes | + 113.49 |
| Mes | Et | + 145.59 |

Figure 1. Molecular structure of 1; ellipsoids are drawn at the 30 % probability level. Hydrogen atoms are omitted for clarity. Selected distances [Å] and angles [°] of P1–C1–Si1 are given in Section S3 in the Supporting Information). Selected bond lengths and angles of 1–7 are shown in Table 1.

The P1–C1 bonds in 1–7 are 2–3 pm shorter than the bond in Ph\( \text{PC}(\text{Me})\text{Et}, \text{V}: 1, 1.717(3) \) Å, which can be attributed to less delocalization of the \( \pi \)-electron density towards the \( \alpha \) acceptor orbitals of the Si moiety compared to the \( \beta \) fragment featuring a proper \( \pi \)-acceptor orbital.[16] The C1–Si1 bonds are noticeably shorter (8–10 pm) than the calculated average C–Si single bond radii of 1.88 Å.[17] This can be attributed to ionic contributions or to hyperconjugative effects.[18] The angles P1–C1–Si1 are 1–7° wider than the ideal angle on sp\(^2\) carbon atoms of 120°.

Back in 1991, Grützmacher and co-workers showed that cationic \( \alpha \)-stannylium ylides ([Ph\( \text{PC} \beta \text{SiBu}, ]^{+} \) [BF\(_4 \)]) tend to dimerize.[19] Prior to employing the starting materials 1–7 in halide abstraction reaction in order to generate cationic \( \alpha \)-silylium ylides (denoted \( \alpha \)-Si\( \alpha \)+CPs hereafter), DFT calculations at the TPSS/def2-TZVP level of theory including D3BJ dispersion correction were performed. The dimerization energies of eleven potential cationic \( \alpha \)-Si\( \alpha \)+CPs were investigated and the results are compiled in Table 2.

As expected, the dimerization energies strongly depend on the substituent pattern. For the model compound [Ph\( \text{PC} \beta \text{Me} \)Si\( \text{Me}_2 \)]\(^{+} \) (entry 1) featuring small substituents on both the ylidic carbon atom (\( R^1 \)) and the silicon center (\( R^2 \)) the dimer is favored by 112 kJ mol\(^{-1}\). Upon increasing the steric bulk to \( R^1 = \text{Et} \), \( R^2 = \text{Et} \) (entry 2), Ph/Me (entry 3) and Ph/Et (entry 4), the dimer becomes increasingly disfavored. Once iso-propyl groups are considered as \( R^1 = \text{Me} \), \( R^2 = \text{Et} \) (entry 8) and \( R^1 = \text{Me} \), \( R^2 = \text{Et} \) (entry 9) the dimer is favored by 112 kJ mol\(^{-1}\). Upon increasing the steric bulk to \( R^1 = \text{Et} \), \( R^2 = \text{Et} \) (entry 8) and \( R^1 = \text{Me} \), \( R^2 = \text{Et} \) (entry 9) the dimer is favored by 112 kJ mol\(^{-1}\). Upon increasing the steric bulk to \( R^1 = \text{Et} \), \( R^2 = \text{Et} \) (entry 8) and \( R^1 = \text{Me} \), \( R^2 = \text{Et} \) (entry 9) the dimer is favored by 112 kJ mol\(^{-1}\). Upon increasing the steric bulk to \( R^1 = \text{Et} \), \( R^2 = \text{Et} \) (entry 8) and \( R^1 = \text{Me} \), \( R^2 = \text{Et} \) (entry 9) the dimer is favored by 112 kJ mol\(^{-1}\). Upon increasing the steric bulk to \( R^1 = \text{Et} \), \( R^2 = \text{Et} \) (entry 8) and \( R^1 = \text{Me} \), \( R^2 = \text{Et} \) (entry 9) the dimer is favored by 112 kJ mol\(^{-1}\). Upon increasing the steric bulk to \( R^1 = \text{Et} \), \( R^2 = \text{Et} \) (entry 8) and \( R^1 = \text{Me} \), \( R^2 = \text{Et} \) (entry 9) the dimer is favored by 112 kJ mol\(^{-1}\). Upon increasing the steric bulk to \( R^1 = \text{Et} \), \( R^2 = \text{Et} \) (entry 8) and \( R^1 = \text{Me} \), \( R^2 = \text{Et} \) (entry 9) the dimer is favored by 112 kJ mol\(^{-1}\). Upon increasing the steric bulk to \( R^1 = \text{Et} \), \( R^2 = \text{Et} \) (entry 8) and \( R^1 = \text{Me} \), \( R^2 = \text{Et} \) (entry 9) the dimer is favored by 112 kJ mol\(^{-1}\). Upon increasing the steric bulk to \( R^1 = \text{Et} \), \( R^2 = \text{Et} \) (entry 8) and \( R^1 = \text{Me} \), \( R^2 = \text{Et} \) (entry 9) the dimer is favored by 112 kJ mol\(^{-1}\). Upon increasing the steric bulk to \( R^1 = \text{Et} \), \( R^2 = \text{Et} \) (entry 8) and \( R^1 = \text{Me} \), \( R^2 = \text{Et} \) (entry 9) the dimer is favored by 112 kJ mol\(^{-1}\). Upon increasing the steric bulk to \( R^1 = \text{Et} \), \( R^2 = \text{Et} \) (entry 8) and \( R^1 = \text{Me} \), \( R^2 = \text{Et} \) (entry 9) the dimer is favored by 112 kJ mol\(^{-1}\). Upon increasing the steric bulk to \( R^1 = \text{Et} \), \( R^2 = \text{Et} \) (entry 8) and \( R^1 = \text{Me} \), \( R^2 = \text{Et} \) (entry 9) the dimer is favored by 112 kJ mol\(^{-1}\). Upon increasing the steric bulk to \( R^1 = \text{Et} \), \( R^2 = \text{Et} \) (entry 8) and \( R^1 = \text{Me} \), \( R^2 = \text{Et} \) (entry 9) the dimer is favored by 112 kJ mol\(^{-1}\). Upon increasing the steric bulk to \( R^1 = \text{Et} \), \( R^2 = \text{Et} \) (entry 8) and \( R^1 = \text{Me} \), \( R^2 = \text{Et} \) (entry 9) the dimer is favored by 112 kJ mol\(^{-1}\). Upon increasing the steric bulk to \( R^1 = \text{Et} \), \( R^2 = \text{Et} \) (entry 8) and \( R^1 = \text{Me} \), \( R^2 = \text{Et} \) (entry 9) the dimer is favored by 112 kJ mol\(^{-1}\). Upon increasing the steric bulk to \( R^1 = \text{Et} \), \( R^2 = \text{Et} \) (entry 8) and \( R^1 = \text{Me} \), \( R^2 = \text{Et} \) (entry 9) the dimer is favored by 112 kJ mol\(^{-1}\)}.
showed that 8 consists of trans and cis isomers in the ratio 1.7:1.

Crystals suitable for X-ray diffraction were obtained by slow concentration of a methylene chloride solution of 8 (Figure 2).

The P1–C1 bond in 8 is elongated by 11 pm compared to 1 indicating less double bond character. The angles P1–C1–Si1 = 119.73(8)° is relatively obtuse due to the steric demand of the PPh3 moieties. The Si1–C1 bond is elongated by 6 pm compared to the calculated Si–C bond length of 1.89 Å based on single bond radii.[17]

Because of the poor solubility of the oily reaction products in aromatic solvents after chloride abstraction with Na[B(C6F5)4], a series of sodium salts with other WCAs were checked in order to increase the solubility. 7 showed no reaction towards NaX (X = [PF6]−, [BF4]−, [SbF6]3−, [BPh4]+, and OTf−) in benzene, even at 90 °C for 24 h. The reaction of 7 with Ag[Al(OC(CF3)3)4] resulted in a deep purple, insoluble oil and elementary metal, indicating a redox reaction instead of halide abstraction. Due to the poor solubility, further synthesis was carried out in CH2Cl2 or THF. It quickly turned out that 8 represents the only isolable compound under these conditions and that 2, 4, 5 and 7 readily decompose to [Ph3PC(R)H2][B(C6F5)4]. Even ortho-dichlorobenzene (o-DCB), which is a common solvent in silicon cation chemistry,[10f] showed poor stability towards intermediary formed cationic species. This underlines the amphiphilic character and high reactivity of the cationic α-Si+CPs. Nevertheless, reaction of 3 with Na[B(C6F5)4] in benzene leads to discoloration of the formerly yellow solution (Scheme 6).

Although the cationic compound [Ph3PC(Me)SiMes][B(C6F5)4] (9) could not be crystallized or isolated due to decomposition, we found clear indications for its formation by NMR spectroscopy (Figure 3). Due to poor solubility of the salt,
a mixture of benzene and fluorbenezene (4:1) was used. In the
$^{31}$P(1H) NMR spectra (Figure 3a), an expected downfield shift of
$+0.7$ ppm could be detected, indicating the more electron-
withdrawing nature of the cationic (SiMes$_2$) fragment (as
compared to (SiMes$_3$)Cl in 3). Furthermore, the $\alpha$-BCP Ph$_3$PC
-(Me)BEt$_2$ (V.1) showed hindered rotation of the C$_{\text{Si}}$-B bond
due to double bond character leading to discrete NMR
resonances for the ethyl groups of the (BEt$_2$) entity.$^{[5a]}$ In the
$^1$H NMR spectra of 3, a broad signal for the ortho-methyl groups of
the mesityl substituent were detected (Figure 3b). Formation of
the cation 9 results in clear separation of mesityl group resonances.
$^{29}$Si NMR measurements were performed using
INEPTRD (no proton coupling) and INEPTND (with proton
coupling) protocols. The INEPTRD experiments (Figure 3c) show
that the $J_{\text{SiC}}$ coupling constant of 21 Hz for 9 is considerably
smaller as compared to 3 (37 Hz). This may be caused by the
reduction of ylene character. Also, the $J_{\text{SiC}}$ coupling constant of
the phosphorus atom to the ylidic CH$_3$ group decreases from
19.5 to 19 Hz, while the $J_{\text{SiH}}$ coupling constant simultaneously
increases. In the $^1$H NMR spectrum of 9, silicon satellites with a
coupling constant of 10.5 Hz were observed, which are not
observed in the $^1$H NMR spectra of 3 (below 6 Hz baseline of
the signal). This Si-H J coupling is also observed in the $^{29}$Si
INEPTND experiments (Figure 3d). In the $^{29}$Si NMR spectra, one
signal at $\delta(^{29}$Si$)=136.3$ ppm could be detected. The free silylium
cation Me$_3$Si$^+$ shows a $^{29}$Si NMR chemical shift of $\delta(^{29}$Si$)=
225.5$ ppm.$^{[10c]}$ Such a strong downfield shifting is not expected
due to the electron density provided by the ylide substituent.
The $\pi$-conjugated silylium ion of Komatsu displays a more similar
electronic situation to $\alpha$-SiH$\neq$CP and, correspondingly, its
$^{29}$Si NMR shift was observed at $\delta(^{29}$Si$)=142.9$ ppm.$^{[2]}$ In
addition, DFT calculations at the TPSS/TZVP level of theory for
the chemical shielding of 9 were performed. The calculated $^{29}$Si
NMR shift for the $\alpha$-SiH$\neq$CP of $\delta(^{29}$Si)$_{\text{calc.}}=141$ ppm is in good
agreement with experimental findings.

Furthermore, the fluoride ion affinity (FIA) including
solvent correction (FIA$_{\text{solv.}}$) of 9 was calculated (TPSS/TZVP)
towards the isodesmic reaction of the Me$_3$Si$^+$/Me$_3$SiF system
(further details are given in Section S4). The FIA of 691 kJ mol$^{-1}$
(FIA$_{\text{solv.}}=589$ kJ mol$^{-1}$) is significantly higher compared to iso-
electronic $\alpha$-BCP Ph$_3$PC(B$_2$C$_6$F$_5$)$_2$ (qB, 271 kJ mol$^{-1}$; FIA$_{\text{solv.}}=
225$ kJ mol$^{-1}$) and the hypothetical aluminium analogue Ph$_3$PC
-(Me)AlMes$_2$ (qAl, 360 kJ mol$^{-1}$; FIA$_{\text{solv.}}=256$ kJ mol$^{-1}$; Figure 4).

Still higher FIA of 735 kJ mol$^{-1}$ (FIA$_{\text{solv.}}=659$ kJ mol$^{-1}$) was
obtained by changing the substituent pattern at the silicon
center from aromatic to aliphatic (R$^1$=Et, R$^2$=iPr). The reaction of 6 with Na[B(C$_6$F$_5$)$_2$] in benzene results in the formation of an
insoluble yellow oil (Scheme 7) that could not be purified or
solidified. Unlike 9, the formed cationic species 10 undergoes
decomposition when adding PhF, which is consistent with the
large calculated FIA. In order to record NMR spectra of the
insoluble oily residue, it was layered with perfluorohexane to
position the sample at the correct level of the measurement
window. For internal reference, a capillary with Cd$_2$ was
inserted (Figure S39). The $^{29}$Si and $^{31}$P NMR spectra obtained in
this way clearly indicated the formation of the cation [Ph$_3$PC
-(Et)SiPr$_2$]$\neq$[B(C$_6$F$_5$)$_2$] (10). The $^{29}$Si NMR resonance at $\delta(^{29}$Si$)=
164.3$ ppm is shifted downfield by 28 ppm with respect to 9.
In the $^{31}$P(1H) NMR spectra, the detected resonance at $\delta(^{31}$P$)=
26.8$ ppm is also shifted 3.8 ppm downfield compared to 9. This
is in good agreement with less electron-donating properties of
the isopropyl groups compared to mesityl, and the accompanying
higher electron-withdrawing character of the (SiR$_3$) fragment.
Due to the fact that the cationic species are not stable
compared to (SiMes$_3$)$^+$, the sterically demanding disopro-
propyl ether $\neq$Pr$_2$O was tested as potential solvent. Reaction of 6
with Na[B(C$_6$F$_5$)$_2$] surprisingly lead to the protonated silicon
ylide 6dec (Scheme 8).

It appears reasonable to assume that the product is formed by
sodium-mediated basic ether splitting forming NaOPr and
propene.$^{[20]}$ These results corroborate the amphiphilic character of
silylated ylides. Colorless crystals suitable for X-ray analysis

![Figure 4](image-url)

**Figure 4.** Comparison of the FIA of 9 with its isoelectronic analogues qB and qAl.

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Chem. Eur. J. 2022, 28, e202103974 (S of 11)
were obtained by recrystallization from a mixture of iPr₂O and hexane (Figure 5).

The P1–C1 bond of 1.819(5) Å is elongated by 13 pm compared to 6, which would be in line with a smaller double bond character. This is further supported by the similarity to the P1–C1 bond length in the dimer 8 (1.807 Å). Elongation of the C1–Si1 distance of 1.947(5) by 14 pm as well shortening of d(Si1–C4) (1.862(6) Å) and d(Si1–C11) (2.0729(19) Å) by 3 and 7 pm, respectively, underline a lesser electron donation from the ylide to the silicon center.

Studies on α-germylated phosphorus ylides

After the promising generation of cationic silylium ylides, we focused on the synthesis of their germanium analogues. The starting materials 11–13 (R¹/R² = Me/Me (11), Ph/Me (12), Me/ Mes (13)) were synthesized by trans-ylidation followed by chloride abstraction with Na[B{3,5-(CF₃)₂C₆H₃}] (NaBAR², Scheme 9).

Crystals of 13 obtained from concentration of a toluene solution were analyzed by X-ray diffraction (Figure 6). The distance d(P1–C1) of 1.685(2) Å in 13 is 1.4 pm shorter compared to the silicon analogue 6, which indicates less stabilization of the ylide. In contrast, the Ge1–C1 bond of 1.878(2) Å is comparatively short in relation to the Ge1–C3(aryl) bond length (1.993(2) Å), indicating a strong negative hyper-conjugation of electron density from the ylidic carbon to the germanium center. The additional elongation of the Ge1–C1 bond (2.22615(8) Å) underscores this assumption (cf. Mes₂GeCl₂ (d(Ge–Cl) = 2.179 Å); structural data of Mes₂GeCl₂ are shown in Section S3). The behavior of 13 in solution is quite similar to 3. The ortho-methyl groups show large broadening in the ¹H NMR signals. The doublet of the ylidic methyl group at δ(¹H) = 2.34 ppm possesses a coupling constant of 18.8 Hz, which was found to be slightly smaller than in 3 (19.5 Hz). The ³¹P(¹H) resonance of δ(³¹P) = 21.8 ppm is less downfield-shifted than in 3 (23.2 ppm).

The reaction of 13 with NaBAR² in toluene followed by extraction in CH₂Cl₂ gave 14 as light yellow crystalline solid in 30% yield (Scheme 9). Crystals suitable for X-ray diffraction were obtained by slow concentration of a CH₂Cl₂ solution of 14 at room temperature (Figure 7).

The P1–C1 distance of 1.739(4) Å is elongated by 5.4 pm as compared to 13. This indicates a weak P–C₁₂β interaction. The germanium carbon bond length of 1.808(4) Å (C1–Ge1) is

![Molecular structure of 6dec](image1.png)

**Figure 5.** Molecular structure of 6dec; ellipsoids are drawn at the 10% probability level. Only the cationic part is shown; hydrogen atoms (except H1) are omitted for clarity. Selected distances [Å] and angles [°]: P1–C1 = 1.819(5); C1–Si1 = 1.947(5); Si1–C4 = 1.862(6); Si1–C11 = 2.0729(19); P1–C1–Si1 = 118.8(2).

![Scheme 9](image2.png)

**Scheme 9.** Synthesis of 14. a) toluene, 90 °C, 2 h; b) toluene, RT.

![Molecular structure of 13](image3.png)

**Figure 6.** Molecular structure of 13; ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected distances [Å] and angles [°]: P1–C1 = 1.685(2); C1–Ge1 = 1.878(2); Ge1–C3 = 1.993(2); Ge1–C11 = 2.22615(8); C1–C2 = 1.528(3); P1–C1–Ge1 = 126.85(11).

![Molecular structure of 14](image4.png)

**Figure 7.** Molecular structure of 14; ellipsoids are drawn at the 30% probability level. Only the cationic part is shown; hydrogen atoms are omitted for clarity. Selected distances [Å] and angles [°]: P1–C1 = 1.739(4); C1–C2 = 1.5216(6); Ge1–C1 = 1.808(4); Ge1–C3 = 1.931(5); P1–C1–Ge1 = 1.248(2); C2–C2–Ge1–C3 = 17.0(4).
comparable to the short Ge–C bonds in a germabenzene or germananaphthalene published by Tokitoh.[21,22] This structural feature clearly underlines the double bond character in the germanium ylide. The closely related germenes Mes2Ge=CR1(CR2) (CR1 = fluorenylidene) possess Ge–C distances of 1.803 and 1.806 Å. Only a slightly longer (1.827 Å) Ge–C distance was reported for a diboryl-stabilized germene.[24] Thus, the germanium ylide 14 can clearly be regarded as a germe ne bearing a cationic phosphonium substituent.[14a,25] The small C2–C1–Ge–C3 dihedral angle of 17° supports these findings. The Ge1–C3 bond length of 1.931(5) Å is in the expected range of Ge–C single bonds.[24]

The double-bond character in the respective cationic silicon and germanium ylides 9, 10, and 14 is also corroborated by NBO and AIM analyses.[27] For comparison, the silene Me2C=SiMe2 and silane Me2C–SiMe2 were investigated (Table 3). The three cationic ylides show typical characteristics of double bonds, with π-bond occupations between 1.82 and 1.85 e, bond ellipticities between 0.28 and 0.45, as well as Wiberg Bond Indices of greater than 1, between 1.25 and 1.30. Compared to properties of Me2C=SiMe2, all of these indicators are comparable but slightly smaller, which indicates less covalent character in the cationic double bonds. However, the bond polarization in the cationic ylides is considerably larger, with a negative charge between −1.12 and −1.20 on C and a positive charge between +1.64 and +1.87 e on Si or Ge, respectively. These charges are larger than in the tetramethyl silene Me2C=SiMe2 (−0.62, +1.42 e). Therefore, the C–Si and C–Ge interactions in 9, 10 and 14 can be interpreted as strongly polarized double bond systems. In accord with this interpretation, the depicted HOMO and LUMO of the converged structural model (TPSS/def2-TZVP) of 9 show the polarized orbital contributions (Figure 8).

Similar to the silicon derivative 9, the FIA in the gas phase was calculated, furnishing a FIA of 624 kJ mol⁻¹ (FIAα = 522 kJ mol⁻¹) for 14. The observed weakening of 66.5 kJ mol⁻¹ compared to 9 can be attributed to the less electropositive character of Ge. Unfortunately, the Gutmann-Beckett-Method[28] could not be applied due to dynamic processes in solution. Initial reactivity studies revealed that 14 shows no reactivity towards H2, CO and CO2, which might be a result of steric shielding.

Conclusion

In this work, the synthesis and full characterization of α-silylated (1–7) and α-germylated (11–13) phosphorus ylides of the general formula R1PC(R2)Br are reported. The title compounds were fully characterized, including determination of their molecular structures by X-ray diffraction. We report the reactivity towards the abstraction of the chloride with sodium salts of the weakly coordination anions Na[B(CxFy)] and Na[B(3,5-(CF3)x,CH3y)]+. The reaction of Ph3PC(Me)Si(Ci)Me2 (1) with Na[B(C6F5)2] furnished the dimeric phosphonium-like dication Ph3PC(Me)SiMe2][B(C6F5)2]+ (8). To determine the organic auxiliary to prevent dimerization of the polarized C/Si π-bonds in the cationic α-Si±CPs, DFT calculations on 11 potential systems were performed. Mesityl- and iPr-substituted derivatives were found to be suitable targets to access monomeric species. The highly reactive compounds [Ph4PC(Me)SiMes3][B(3,5-(CF3)x,CH3y)] (9) and [Ph4PC(Et)SiPr3][B(C6F5)2]+ (10) could be characterized by NMR spectroscopy and decompose in polar solvents. The less reactive germanium analogue [Ph3PC(Me)GeMes2][B(3,5-(CF3)x,CH3y)] (14) was obtained by the reaction of 11 with Na[Bar]+. Whereas 9 and 10 decompose rapidly in methylene chloride, 14 could be crystallized from this solvent and was fully characterized including X-ray diffraction analysis. Structural parameters in accord with NBO and AIM analyses provide clear evidence of a strong Cβ–Ge interaction with high double bond character. Studies in our lab continue to further explore the reactivity on neutral and cationic species of this type.

Experimental Section

General methods: All operations were carried out under dry argon using standard Schlenk and glovebox techniques. The phosphonium salts Ph3PC(R)HBr were used as purchased from Sigma–Aldrich. The ylides Ph3PC(R)H (R = Me, Et, Ph) were synthesized according to literature procedures[13,16] as well as Mes2GeCl2[19] sodium salts Na[B(CxFy)2][20] and Na[Bar]+.[31] Solvents were dried over Na/K and rigorously degassed before use. NMR spectra were recorded on Bruker AV 300 and 400 spectrometers in dry degassed deuterated solvents. 1H, 13C{1H} and 29Si chemical shifts where reported against TMS and 29Si{1H} against H2PO4. Coupling constants (J) are given in Hertz as positive values, regardless of their real individual signs. The multiplicity of the signals is indicated as s, d, q, sept, or m for singlet, doublet, quartet, septet, or multiplet, respectively. The assignments were confirmed, as necessary, with the use of 2D NMR correlation experiments. IR spectra were measured on a Bruker Alpha spectrometer using the attenuated reflectione technique (ATR) and the data are quoted in wave-
numbers [cm⁻¹]. The intensity of the absorption band is indicated as vw (very weak), w (weak), m (medium), s (strong), vs (very strong), and br (broad). Melting points were measured with a Thermo Fischer melting point apparatus and are not corrected.

Elemental analyses were carried out in the institutional technical laboratories of the Karlsruhe Institute of Technology (KIT). No satisfactory elemental analyses could be obtained for 11 and 12, due to their sensitivity towards air and moisture, and for 8 and 14, due to high fluorine content of the samples.

**Computational details:** For the calculations we used the ORCA 4.2 program. The DFT calculations were carried out with the functional TPS23 and the basis set def-TZVP23. Calculations were done with the following settings of calculation parameters: grid size24, 4, threshold for SCF energy change 10⁻⁶; convergence thresholds for the structure optimization: energy change 10⁻⁶ gradient norm 10⁻⁶. Natural bond orbital (NBO) analysis was performed with the NBO 6.0 program13 interfaced with Gaussian 09.25 The programs AIMAll26 and Multiwfn27 were used for QTAIM analysis.

**Synthesis of 1–7:** To a solution of 2 equiv. ylide Ph₂PC(=CHPh) (R = Me, Et, Ph) in toluene 1 equiv. of the appropriate dichloroamine R₂SiCl₂ (R = Me, Et, Pr, Mes) was added at room temperature. The reaction mixture, heated for several hours to days (Table 4), after filtration and evaporation of the solvent the crude product was recrystallized from hot hexane to afford 1–7 as yellow crystalline solids in yields of 30–83% (Table 4).

| Comp. | R on C(toluene) (R²) | R on E (R²) | T (°C) | t (h) | Yield [%] |
|-------|----------------------|-------------|--------|------|-----------|
| 1     | Me                   | Me          | 95     | 96   | 96        |
| 2     | Et                   | Et          | 110    | 48   | 52        |
| 3     | Me                   | Mes         | 90     | 120  | 48        |
| 4     | Et                   | Et          | 85     | 24   | 30        |
| 6     | Et                   | ipr         | 70     | 18   | 83        |
| 9     | Ph                   | Me          | 60     | 48   | 49        |

**Table 4. Reaction conditions and yields for the syntheses of 1–7. With R at the α-carbon atom and R at the silicon atom.**
Synthesis of 6dec: In a glovebox, a vial was charged with 6 (100 mg, 0.22 mmol) and Na[B(C₃F₇)₃] (155 mg, 0.22 mmol) and iPr₂O (5 mL). After stirring overnight, the light-yellow suspension was filtered and washed with hexane (10 mL). After 5 days, the supernatant was removed and the remaining sticky solid was washed with 5 mL toluene. Drying under high vacuum yielded (30 mg, 12%) pure 6dec as colorless sticky crystals. Crystals suitable for XRD were obtained by layering a solution of 6dec in iPr₂O with hexane.

Synthesis of 8: A Schlenk tube was charged with 3 (260 mg, 0.68 mmol) and Na[B(C₃F₇)₃] (477 mg, 0.68 mmol) and toluene (18 mL). After stirring overnight, the resulting colorless suspension was filtered and the remaining solid was washed with CH₂Cl₂ (10 mL). After a second filtration and concentration the solution was stored at 4°C for 3 days. Removing the supernatant and drying under high vacuum yielded 8 (98 mg, 14 mmol, 21% as colorless crystals, 0.6:1). Crystals suitable for XRD were obtained by slow concentration of a CH₂Cl₂ solution of 8. Trans isomer: ¹H NMR (300 MHz, 298 K, CDCl₃): δ = 7.92–7.82 (m, H₄ ortho, 12H), 7.74–7.62 (m, H₄ ortho, 24H), 7.47–7.30 (m, H₄ meta, 24H), 1.56 (δ, 1H, J = 20.7 Hz, H₂ meta, 6H). 0.32 ppm (s, H₂ ortho, 12H). ¹³C NMR (75 MHz, 298 K, CDCl₃): δ = 136.6 (s, C ortho, 131.4 (brs, C meta, overlap with trans isomer), 131.6 (m, C meta, overlap with trans isomer), 21.9 (s, C ortho, 2.2 ppm (s, C meta, overlap with trans isomer), 31P H NMR (121 MHz, 298 K, CDCl₃): δ = 35.5 (s). ¹³C NMR (60 MHz, 298 K, CDCl₃): δ = 24.3 ppm (t, J = 41.1 Hz, Cis isomer). ¹H NMR (300 MHz, 298 K, CDCl₃): δ = 7.92–7.82 (m, H₄ ortho, 12H), 7.74–7.62 (m, H₄ meta, 24H), 7.47–7.30 (m, H₄ meta, 24H), 1.85 (δ, 1H, J = 20.6 Hz, H₂ meta, 6H). 0.93 ppm (s, H₂ ortho, 12H). 0.05 ppm (s, H₂ ortho, 12H). Synthesis of 13: Mes₃GeCl (1.00 g, 2.62 mmol) and Ph₃PC(Me)H (1.52 g, 5.24 mmol) were dissolved in 10 mL toluene. After heating the mixture for 2 h to 90°C, a colorless precipitate was formed and the color changed from orange to yellow. After filtration, evaporation of the solvent and recrystallization from a small amount of toluene the supernatant layer was removed. Drying in high vacuum yielded pure 13 (812 mg, 49%) as yellow crystalline solid. Crystals suitable for XRD were obtained from saturated toluene solution of 13 (M.p. (decmp.): 236°C). ¹H NMR (300 MHz, 298 K, CDCl₃): δ = 7.71–7.64 (m, H₄ ortho, 6H), 7.00–6.89 (m, H₄ meta, 9H), 6.53 (brs, H₄ meta, 9H). 1H NMR (96 K, 298 K, CDCl₃): δ = 167.3 ppm (s, B(C₃F₇)₂Cl). ¹³C NMR (298 MHz, 298 K, CDCl₃): δ = 133.0 (m, B(C₃F₇)₂Cl). 167.7 ppm (t, J = 28.8 Hz, B(C₃F₇)₂Cl). 1H NMR (96 K, 298 K, CDCl₃): δ = 167.3 ppm (m, J = 28.8 Hz, B(C₃F₇)₂Cl). 167.7 ppm (m, J = 28.8 Hz, B(C₃F₇)₂Cl).
404 (vw), 386 (vw). Elemental analysis (%): C_{20}H_{17}ClGeP calculated. C 71.79, H 6.34; meas. C 71.49, H 5.99.

Synthesis of 14: To a solution of 13 (300 mg, 0.47 mmol) in toluene (10 mL) Na[B(3,5-(CF_3)-C_6H_4)] (418 mg, 0.47 mmol) was added. After short stirring, two phases formed. Removing the solvent in vacuo and storing the resulting oil at −40 °C overnight again two phases formed. The remaining toluene was quickly evaporated. CHCl_3 (1 mL) and pentane (5 mL) were added to the oily residue. The solvent was removed by syringe and the remaining solid was dried in high vacuum. Recrystallization from CHCl_3, by slow concentration of the solution yielded 14 (200 mg, 30%) in pure form as light-yellow crystals suitable for XRD. M.p.: 158 °C. 1H NMR (300 MHz, 298 K, CDCl_3): δ = 8.41 (s, H_s, 2H), 7.64 (s, H_s, 4H), 7.21–7.14 (m, H_m, 6H), 6.99–6.93 (m, H_m, 3H), 6.90–6.82 (m, H_m, 6H), 6.64 (s, H_m, 2H), 6.15 (s, H_m, 2H), 2.12 (s, H_n, 2H), 2.03 (s, H_n, 2H), 1.87 (s, H_n, 2H), 1.77 ppm (d, δ = 8.2 Hz, H_ortho 3H), 13C[H] NMR (75 MHz, 298 K, C, D), and PhF): δ = 162.8 (q, δ = 49.7 Hz, C_m, 6H), 143.0 (s, C_m, 60H), 142.2 (s, C_ortho-Mes), 142.1 (s, C_ortho-Mes), 140.5 (s, C_ortho-Mes), 135.5 (br, s, C_ortho-Bn), 134.2 (d, J = 2.8 Hz, C_ortho-Pol), 133.5 (d, J = 9.7 Hz, C_ortho-Pol), 129.6 (s, C_ortho-Mes), 129.6 (d, J = 12.2 Hz, C_ortho-Mes), 128.9 (s, C_ortho-Mes), 125.3 (q, J = 273 Hz, C_s), 120.9 (d, J = 60.7 Hz, C_s, C_s), 118.0 (br, s, C_ortho-Bn), 24.6 (s, C_ortho-Mes), 23.4 (s, C_ortho-Mes), 20.9 (s, C_ortho-Mes), 20.6 (s, C_ortho-Mes), 17.6 (s, C_Visad), 11.80 ppm (d, J = 62.2 ppm). The resonance for meta-C of BaR could not be detected due to overlap with Ph. 11B NMR (96 MHz, 298 K, C, D): δ = –5.9 ppm (s). 19F NMR (282 MHz, 298 K, C, D): δ = –24.6 ppm (s). IR (ATR, cm⁻¹): ν = 1607 (vwr), 1439 (vs), 1352 (s), 1275 (vs), 1161 (m), 1118 (vs), 1104 (vs), 1028 (vw), 999 (vw), 929 (vw), 885 (m), 854 (vw), 838 (w), 744 (w), 713 (m), 693 (w), 681 (m), 668 (m), 595 (vw), 575 (w), 566 (vv), 547 (w), 515 (m), 447 (vw), 382 (w). Elemental analysis: due to the high fluorine content no appropriate elemental analysis was obtained.

Crystallographic details: Deposition Numbers (2098527 for 1), 2098528 (for 2), 2098529 (for 3), 2098530 (for 4), 2098531 (for 5), 2098532 (for 6), 2098533 (for 6dec), 2098534 (for 7), 2098535 (for 8), 2098536 (for 11), 2098537 (for 12), 2098538 (for 13), 2098539 (for 14), 2098540 (for Mes,GeCl_3) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the Joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.
