

A "Push–Pull" Phosphasilene and Phosphagermene and Their **Anion-Radicals**

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Summary: Phosphasilene 1a and phosphagermene 1b, featuring unprecedented substitution patterns (donors on Si or Ge and acceptor on P), were synthesized utilizing a one-step synthetic approach: direct coupling of dilithiosilane/dilithiogermane and dichlorophosphine. The structural features of both 1a and 1b based on their NMR and X-ray crystal data are discussed, as well as their one-electron reduction forming persistent phosphasilene and phosphagermene anion-radicals.

Multiple bonding between the main group elements heavier than the elements of the second row is one of the main themes in contemporary heteroatomic and organometallic chemistry. Being well established in the case of homonuclear derivatives of the types $-E_{13}=E_{13}-$, $>E_{14}=E_{14}<$, or $-E_{15}=E_{15}-(E_{13}, E_{14}, \text{ or } E_{15} = \text{ group } 13, 14, \text{ or } 15$ elements),¹ the chemistry of heteronuclear combinations, particularly those of different group elements of the types $-E_{13}=E_{15}-$, $-E_{13}=E_{14}<$, and $>E_{14}=E_{15}-$, is much less developed.¹ Of the heavy doubly bonded derivatives of the main group elements, those of group 14 and group 15 elements are particularly interesting, since they contain two reactive sites in one molecule: an $E_{14}=E_{15}\pi$ -bond and lone electron pair on the E_{15} element.² Several compounds of the

type $> E_{14} = E_{15}$ have been reported, including phosphasilenes > Si=P-, phosphagermenes > Ge=P-, phosphastannenes > Sn=P-, and arsasilenes > Si=As-.³ The double bond between silicon/germanium and phosphorus is polar-ized, $>E^{\delta+}=P^{\delta-}-(E = \text{Si or Ge})$, because of the difference in electronegativity between Si (or Ge) and P atoms: 1.90 (or 2.01) vs 2.19 (Pauling scale). Such bond polarization results in the enhanced reactivity of both > Si=P- and > Ge=P-. Using substituents with opposing electronic effects on the > E=P- bond (E = Si or Ge), namely, electron-donating groups (D) on silicon/germanium and electron-accepting groups (A) on phosphorus ("push-pull" substitution pattern), one can expect that such double-bond polarization would be decreased or even reversed as in $D_2 E^{\delta^-} = P^{\delta^+} - A$. However, this interesting synthetic challenge, directed toward a changed electron distribution in the group 14-15 element double bonds, has not yet been achieved experimentally.²

In this communication, we report the synthesis of phosphasilene and phosphagermene derivatives with such a substitution pattern (electron-releasing silvl substituents on Si or Ge and an electron-withdrawing aryl group on P). The onestep procedure used takes advantage of the high and selective reactivity of $({}^{t}Bu_{2}MeSi)_{2}ELi_{2}$ (E = Si, Ge) reagents. The structural features of these phosphasilene and phosphagermene compounds, based on their structures as determined by X-ray crystallography and their NMR and UV spectroscopic data, are discussed, and their reduction with potassium graphite to form persistent anion-radical species is described.

Previously reported phosphasilenes and phosphagermenes are typically prepared employing a two-step procedure: initial coupling of phosphorus and silicon/germanium units to form a > E(X)-P(H)-(E = Si, Ge) bond followed by reductive dehydrohalogenation to form a > E=P-(E =Si or Ge) bond.^{2,3a-3k} We applied a one-step coupling of a dihalophosphine with a dilithiosilane/dilithiogermane to effect the direct formation of the >E=P- (E = Si or Ge) double bond. Thus, reaction of Mes*PCl₂⁴ (Mes* = 2,4,6-tri-*tert*-butylphenyl) with (^{*t*}Bu₂MeSi)₂SiLi₂⁵ (or (^{*t*}Bu₂MeSi)₂GeLi₂)⁶ in THF produced the phosphasilene (^{*t*}Bu₂MeSi)₂Si=PMes* (1a) and phosphagermene $({}^{t}Bu_{2}MeSi)_{2}Ge=PMes^{*}$ (1b),

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isolated as orange crystals in 34% and 40% yield, respectively (Scheme 1).⁷

In the ¹H NMR spectra of both **1a** and **1b**, the resonances of the methyl groups of the two ^tBu₂MeSi substituents were observed in distinctly different regions: -0.40 and 0.50 ppm ($\Delta \delta = 0.90$ ppm) for **1a**, -0.30 and 0.55 ppm $(\Delta \delta = 0.85 \text{ ppm})$ for **1b**. Such a difference can be explained by the nonequivalent spatial arrangement of these methyl groups, one of which is directed toward the shielding area of the aromatic ring of the Mes* substituent, which results in the remarkable shift of its resonance to higher magnetic field. The ²⁹Si and ³¹P NMR spectra of **1a** and **1b** are particularly informative in elucidating the structures in solution. Thus, in the ²⁹Si NMR spectrum of **1a**, three signals were observed, each split into a doublet by coupling to the phosphorus nucleus: 13.5 (d, ${}^{2}J({}^{29}\text{Si}-{}^{31}\text{P}) = 25.2$ Hz), 19.3 (d, ${}^{2}J$ - $(^{29}\text{Si}-^{31}\text{P}) = 6.9 \text{ Hz}$, and 201.2 (d, $^{1}J(^{29}\text{Si}-^{31}\text{P}) = 171.3$ Hz) ppm. The latter resonance due to the central Si atom, observed in the diagnostic low-field region, exhibits a very large ${}^{1}J({}^{29}\text{Si}-{}^{31}\text{P})$ coupling constant.⁸ This clearly testifies to its sp²-hybridization, confirming the presence of a > Si=Pdouble bond. In agreement, the resonance of the P atom was found in extremely low-field region at 389.3 ppm, being by far more deshielded than the P atoms of other phosphasilenes reported to date (from -33.0 to 292.5 ppm).^{3a-3h} Expectedly, the doubly bonded phosphorus atom in 1b is more deshielded, being observed at 416.3 ppm. Such an extreme low-field shift of the doubly bonded phosphorus resonance can be attributed in part to the electron-withdrawing effect of the aromatic substituent. However, one should recognize the σ -donating effect of the silvl substituents bonded to the central Si atom as the other, even more important, contributor to the overall deshielding of the doubly bonded atoms. Such a phenomenon, well known in the chemistry of disilenes > Si=Si < , resulting from a paramagnetic contribution,⁹ can also be seen in the great deshielding of the central Si atom in 1a (201.2 ppm). This markedly exceeds the range of most other known phosphasilenes.^{3a-3h} The paramagnetic contribution, responsible for the overall low-field isotropic chemical shift, stems from the paramagnetic currents induced by the applied magnetic field.

It is determined by the Ramsey formula¹⁰ and is inversely proportional to the energy difference between the interacting occupied and vacant molecular orbitals, which are coupled by the external magnetic field.⁹ In the case of phosphasilenes, the most relevant molecular orbitals under consideration are $n_{\rm P}$ (occupied) and $\pi^*_{\rm Si=P}$ (vacant) orbitals. In the case of silyl-substituted phosphasilenes, appreciable $n_{\rm P} - \pi^*_{\rm Si=P}$ orbital mixing can be promoted by the remarkable lowering of the π^* energy level, resulting in the overall decrease of the n- π^* energy gap. Given the fact that, according to our computations on the model (Me₃Si)₂Si=PMes (Mes = 2,4,6trimethylphenyl) compound 1a', the *n* and π^* orbitals represent the HOMO and LUMO, respectively, such a paramagnetic contribution should be responsible not only for the extreme deshielding of the doubly bonded Si and P atoms in **1a** but also for the notable red shift in its UV spectrum.¹¹ Indeed, the longest wavelength absorption of 1a was found to be markedly red-shifted compared with those of phosphasilenes featuring aryl groups on the doubly bonded Si atom: 461 nm vs 331-343 nm.3f In accord with such observations, our computations on a series of differently substituted phosphasilenes (from σ -accepting alkyl/aryl to σ donating silvl groups on the doubly bonded silicon atom) revealed the general tendencies of significant deshielding of doubly bonded atoms taking place on decreasing the $n-\pi^*$ energy gap upon the successive introduction of silvl substituents on the sp²-Si center ($\Delta E(n-\pi^*)$ in eV, ²⁹Si NMR in ppm, ³¹P NMR in ppm): 4.33, 186.0, 85.4 ['Bu₂Si=PMes]; 3.97, 205.2, 189.6 $[(E)^{-t}Bu(Me_3Si)Si=PMes]$; 3.73, 236.1, 322.6 [(Me₃Si)₂Si=PMes].¹¹

The crystal structures of 1a and 1b are shown in Figures 1 and 2.7 The most important structural feature of both 1a and **1b** is the length of the double bond: 2.1114(7) Å (Si1=P1 in 1a) and 2.1748(14) Å (Ge1=P1 in 1b). Although these two values are greater than those of other reported phosphasilenes $(2.062(1)-2.094(5) \text{ Å})^{1,3b,3c,3f}$ and phosphagermenes $(2.138(3)-2.144(3) \text{ Å})^{3j}$ because of the appreciable steric congestion around the double bonds in **1a**,**b**, they are smaller than the sum of the covalent radii of Si and P (2.27 Å) or Ge and P $(2.32 \text{ Å})^{12}$ by ca. 6–7%, suggesting > E=P- (E = Si or Ge) double-bond character.¹³ The > E=P - (E = Si or)Ge) double bonds exhibited no kind of distortion, being neither pyramidalized (both Si1 and Ge1 centers in 1a and 1b are perfectly planar, with the sum of the bond angles around them being 360°) nor twisted (torsional angles C19-P1-Si1-Si2 and C19-P1-Ge1-Si1 in 1a and 1b are 178.8° and 178.9°, respectively).⁷ One should note that the overall geometry of both 1a and 1b is mainly dictated by the degree of steric interactions. Thus, 'Bu2MeSi substituents facing bulky Mes* groups are bent away from them because of the steric repulsions: 128.05(3)° (P1-Si1-Si3) vs 104.83(3)° (P1-Si1-Si2) in 1a; 127.50(6)° vs 104.88(5)° in 1b.

In the context of structural discussion, it is interesting to mention that the tendencies seen in both 1a and 1b are reminiscent of those of the well-studied silenes > Si=C <. Thus, quite similar to the case of 1a and 1b, Apeloig's silene

⁽⁷⁾ For the experimental procedures and spectral and X-ray crystal data of **1a** and **1b**, see the Supporting Information.

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⁽¹³⁾ Calculated values of the >Si=P- and >Ge=P- bond lengths in the model (Me₃Si)₂Si=PMes (1a') and (Me₃Si)₂Ge=PMes (1b') are 2.113 and 2.163 Å, respectively.



Figure 1. ORTEP drawing of 1a (30% thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Si1-P1 = 2.1114(7), Si1-Si2 = 2.3855(8), Si1-Si3 = 2.4100(8), P1-C19 = 1.863(2). Selected bond angles (deg): P1-Si1-Si2 = 104.83(3), P1-Si1-Si3 = 128.05(3), Si2-Si1-Si3 = 127.12(3), Si1-P1-C19 = 110.66(7).



Figure 2. ORTEP drawing of **1b** (30% thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Ge1-P1 = 2.1748(14), Ge1-Si1 = 2.4297(14), Ge1-Si2 = 2.4406(16), P1-C19 = 1.854(5). Selected bond angles (deg): P1-Ge1-Si1 = 104.88(5), P1-Ge1-Si2 = 127.50(6), Si1-Ge1-Si2 = 127.59(6), Ge1-P1-C19 = 109.90(16).

Me₃Si(^{*i*}BuMe₂Si)Si=Ad (Ad = adamantylidene)¹⁴ with the substitution pattern Si₂Si=CC₂, which favors relaxation of the natural bond polarity >Si^{$\delta+$}=C^{$\delta-$} < due to the inductive effect of the substituents, featured a relatively long >Si=C < bond (1.741(2) Å).¹⁵ In marked contrast, Wiberg's silene Me₂Si=C(SiMe^{*i*}Bu₂)SiMe₃¹⁶ with the opposite substitution pattern C₂Si=CSi₂, enhancing the intrinsic >Si^{$\delta+$}=C^{$\delta-$} < bond polarity by the substituent effect, manifested a remarkably short >Si=C < bond (1.702-(5) Å).¹⁵ Likewise, silyl substitution at the Si atom of the >Si=C < bond resulted in the notable red shifts in their UV spectra, ^{1h} similar to the situation observed in **1a** and **1b**.

Scheme 2. One-Electron Reduction of 1a and 1b with KC₈ in THF to Form the Potassium Salts of the Corresponding Anion-Radicals



The electrochemical reduction of 1a,b under cyclic voltammetry conditions (vs Ag/Ag⁺, THF, rt, 0.1 M ["Bu₄N]-ClO₄) revealed reversible one-electron reduction waves with the reduction potentials $E_{1/2}(\text{red}) = -1.78 \text{ V}$ (for 1a) and $E_{1/2}$ (red) = -1.75 V (for 1b). As expected, these values are just in between those of ('Bu2MeSi)2Si=Si(SiMe'Bu2)2 $(-1.47 \text{ V})^{17}$ and Mes*P=PMes* (-1.93 V).¹⁸ Given the reversibility of the electrochemical reduction, one can suggest the stability (and hence accessibility) of the resulting phosphasilene/phosphagermene anion-radical species. We have therefore undertaken the chemical reduction of 1a and 1b with an equimolar amount of potassium graphite. In both cases, one-electron reduction resulted in immediate change of the orange color of the starting 1a and 1b to the dark green color of their anion-radicals [1a]^{-•} and [1b]^{-•} (Scheme 2).⁷

Both anion-radicals were persistent at room temperature, which allowed their characterization by EPR spectroscopy. Thus, in THF solution the EPR spectrum of the phosphasilene anion-radical $[1a]^{-\bullet}$ showed a doublet resulting from coupling to the phosphorus nucleus ($a(^{31}P) = 5.4 \text{ mT}$) with a *g*-factor of 2.0083, accompanied by a pair of silicon satellites ($a(^{29}Si) = 5.0 \text{ mT}$) (Figure 3).

Although the value of the hyperfine coupling constant (hfcc) $a(^{29}\text{Si})$ of $[1a]^{\bullet}$ is close to those of silyl-substituted silyl radicals (5.6–6.4 mT),¹⁹ the value of $a(^{31}\text{P})$ hfcc is remarkably lower than that of phosphorus-centered radicals (9.2–10.8 mT),²⁰ being very close to those of delocalized diphosphene anion-radicals (4.1–5.5 mT).²¹ Likewise, the EPR spectrum of the phosphagermene anion-radical $[1b]^{-\bullet}$ contained a doublet resonance with the very characteristic set of 10 satellite signals (⁷³Ge coupling) with the following EPR parameters: g-factor = 2.0161, $a(^{31}\text{P}) = 5.6 \text{ mT}, a(^{73}\text{Ge}) = 2.5 \text{ mT}$. The EPR spectrum pattern of $[1a]^{-\bullet}$ dramatically changed upon changing the solvent from polar THF to

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Figure 3. EPR spectrum of the potassium salt of phosphasilene anion-radical $[1a]^{-} \cdot [K^+]$ in THF.

nonpolar benzene.²² The value of $a({}^{31}\text{P})$ hfcc of the central doublet (g = 2.0076) was significantly decreased to 1.5 mT, whereas that of $a({}^{29}\text{Si})$ hfcc was increased to 6.5 mT. Overall, such a decrease in the $a({}^{31}\text{P})$ hfcc and simultaneous increase in the $a({}^{29}\text{Si})$ hfcc in the EPR spectrum of $[1a]^{-1}$ upon the

THF \rightarrow benzene solvent exchange can be explained in terms of a more delocalized structure of the anion-radical in THF and a more localized (unpaired electron on Si and negative charge on P) structure in benzene. In nonpolar benzene the anionic phosphorus center can be stabilized by the bonding interaction to the potassium counterion (contact ion pair), thus favoring unpaired electron-negative charge localization and separation, whereas in polar THF such cationanion interaction is, apparently, broken down because of solvation effects, thus leading to a more delocalized structure.

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Supporting Information Available: The experimental procedures and spectral data for compounds 1a, 1b, and their anionradicals, CV charts of 1a and 1b, tables of crystallographic data including atomic positional and thermal parameters for 1a and 1b (PDF/CIF), and computational details (tables of atomic coordinates for optimized geometries of the model compounds 1a' and 1b' and values of their total energies). This material is available free of charge via the Internet at http://pubs.acs.org.

⁽²²⁾ Such a change is reversible, and by replacing benzene with THF again, we were able to recover the original structure exhibiting the EPR spectrum shown in Figure 3.