Isolation of Elusive Phosphinidene-Chlorotetrylenes: The Heavier Cyanogen Chloride Analogues

Ekta Nag,[a] Maria Francis,[a] Sridhar Battuluri,[a] Bhavya Bini Sinu,[a] and Sudipta Roy*[a]

Dedicated to Professor Oliver Reiser on the occasion of his 60th birthday

Abstract: The elusive phosphinidene-chlorotetrylenes, [PGeCl] and [PSiCl] have been stabilized by the hetero-bileptic cyclic alkyl(amino) carbene (cAAC), N-heterocyclic carbene (NHC) ligands, and isolated in the solid state at room temperature as the first neutral monomeric species of this class with the general formulae (L)P-ECl(L') (E = Ge, **3a–3c**; E = Si, **6**; L = cAAC; L' = NHC). Compounds **3a–3c** have been synthesized by the reaction of cAAC-supported potassium phosphinidenides [cAAC=PK(THF)$_x$]$_n$ (**1a–1c**) with the adduct NHC:→GeCl$_2$ (**2**). Similarly, compound **6** has been synthesized via reaction of **1a** with NHC:→SiCl$_2$ adduct (**4**). Compounds **3a–3c**, and **6** have been structurally characterized by single-crystal X-ray diffraction, NMR spectroscopy and mass spectrometric analysis. DFT calculations revealed that the heteroatom P in **3** bears two lone pairs; the non-bonding pair with 67.8% of s- and 32% of p character, whereas the other lone pair is involved in π backdonation to the C$_{cAAC}$-N π* of cAAC. The Ge atom in **3** contains a lone pair with 80% of s character, and slightly involved in the π backdonation to C$_{NHC}$. EDA-NOCV analyses showed that two charged doublet fragments {(cAAC)(NHC)}$^+$, and {PGeCl}$^-$ prefer to form one covalent electron-sharing σ bond, one dative σ bond, one dative π bond, and a charge polarized weak π bond. The covalent electron-sharing σ bond contributes to the major stabilization energy to the total orbital interaction energy of **3**, enabling the first successful isolations of this class of compounds (**3**, **6**) in the laboratory.

Introduction

Cyanogen chloride [N≡C–Cl] is a stable volatile compound, utilized in various organic synthesis.[1] In contrast, chlorophosphagermyne [P≡Ge–Cl], and chloro-phosphasilyne [P≡Si–Cl], the elusive heavier analogues of cyanogen chloride are expected to be highly unstable due to the presence of weaker P≡E triple bond (E = Ge, Si) because of the participation of significantly diffused 3s/3p and 4s/4p orbitals with internal nodes and Pauli repulsion energy, leading to the huge deviation from compact overlap of these orbitals of P and E atoms.[2] The predicted lower thermodynamic stability of the heavier analogues of cyanogen halides can be attributed to the dramatically decreased ability of these heavier group 15/14 elements to form the multiple bonds,[3] which in turn potentially increases the contribution of the phosphinidene-tetrylene[4] type isomer **B** to the ground state of the molecule (Figure 1). Such species has been theoretically predicted to be stabilized by using significantly bulky alkyl or aryl substituents, where the stability of the multiple bonded linear form of [:P≡ER] (**A**, E = heavier group 14 elements, for example, Si, Ge, etc.) is much higher compared to

the corresponding bent structure **C** [RP=E:] with an electronegative R group (R = Cl, F) at the group 14 atom (E).[5] However, none of the experimental attempts to synthesize these molecules have been successful so far, except the approach, where the sterically demanding amido ligands have been employed to stabilize the phosphinidene-tetrylene dimer **D**,[6d] and the monomer **G**[6f] (Figure 1).[6]

Although, the syntheses and reactivity of main group higher analogues of alkenes, alkynes and nitriles have attracted huge attention for past few decades,[7] the stabilization of the higher analogues of cyanogen chloride as the neutral, monomeric, low coordinate phosphorus-(chloro)-germanium/silicon compounds has been rarely explored due to the high synthetic challenges caused by the lower thermodynamic stability and tendency to oligomerise. Although, a few groups have reported the isolation of the corresponding non-halogenated analogues in the dimeric forms, for example, the phosphagermylyne dimers **D** [LGeP]$_2$ (Figure 1),[8] synthesis of the donor base-stabilized corresponding chloro substituted species, i.e., the phosphinidene-chlorotetrylenes [(L)P≡ECl(L'); E = Ge, Si; L = L' = donor base ligands] could not be achieved so far. In recent past, a phosphorus containing digermanium species[2b] and a germylene-P=C=O[2c] have been reported. A decade ago, Ge–P containing clusters have been isolated by reaction of BuLi with GeCl$_2$(dioxane).[2d] The interconversion of donor base ligand free P≡Si–Cl and Si=P–Cl species have been theoretically studied by Chu et al.[5a] The first phosphasilene R–P=Si(R$_2$) was characterized in 1984 by Bickelhaupt et al.[2e] and such class of compound was first structurally characterized by Niecke et al.[2f] Since then,

Chemistry–A European Journal

Research Article
doi.org/10.1002/chem.202201242

Chemistry Europe
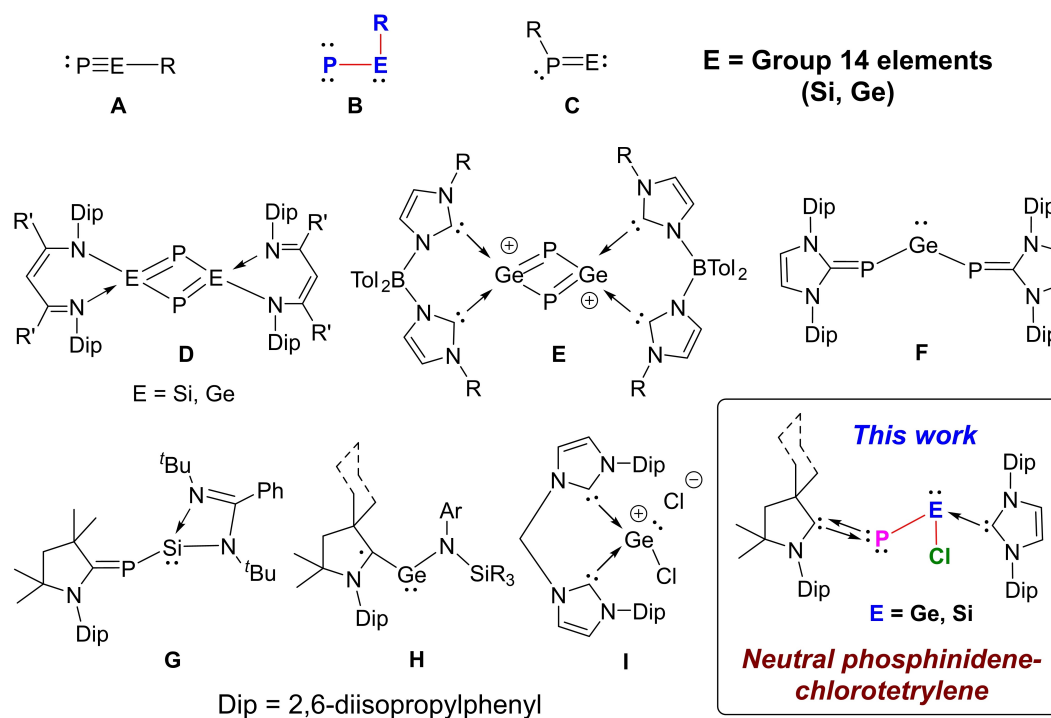European Chemical
Societies Publishing

Figure 1. Representative heavier analogues of cyanide (**A**–**H**) and carbene-stabilized low coordinate germanium halide (**I**).

a large number of phosphasilenes have been synthesized, isolated and characterized by different techniques.[2g–h]

Since the discovery of N-heterocyclic carbenes (NHCs) in 1991[9] by the group of Arduengo, and cyclic alkyl(amino) carbenes (cAACs) in 2005[10] by the group of Bertrand, NHCs and cAACs have been hugely employed as Lewis base donor ligands to stabilize a variety of otherwise unstable exotic main group compounds with low coordinate main-group elements.[11] However, the chemistry of low coordinate exotic germanium-based compounds are still scarce in the literature. Recently, the group of Roesky reported the cAAC-stabilized neutral germanium(I) radicals **H** (Figure 1).[12] The stabilization of heterodiatomic group 14/15 compounds with low coordinate group 14/15 elements stabilized by donor base ligands has been of significant interest during the past few decades.[13] NHCs have been employed for the stabilization of low coordinate, cationic phosphorus-germanium compound **E**,[14] and the chlorogermyliumylidene chloride **I**.[15] Recently, phosphinidenes, the reactive group 15 analogues of carbenes with two lone pairs of electrons on phosphorus have gained considerable attention for stabilizing main group exotic species. One such example is the bis-NHC-phosphinidenide-stabilized tetrylene **F** (Figure 1).[16] Lappert et al. reported the possible stabilization of such species by utilizing a variety of anionic ligands, for example, the bulky amido ligands (−NR$_2$) due to the effective p$_\pi$-p$_\pi$ interaction between the lone pair of electrons at N atom and the vacant p orbital at the heavier group 14 elements.[17] However, the synthetic viability of phosphinidene-stabilized chlorotetrylenes, more precisely the phosphinidene-chlorogermylenes, and phosphinidene-chlorosilylenes are not

explored till date. In this context, it is worth mentioning that recently, we have theoretically predicted that the laboratory isolation of the elusive homo- and hetero-bileptic chloro-phosphasilynes or the corresponding positional isomers, the phosphinidene-chlorosilylenes would be feasible by using homo- or hetero-bileptic donor base ligands, such as, carbenes (NHCs or cAACs).[18] Inspired by these predictions, we attempted the syntheses of such species along with the corresponding germanium analogues, i.e., the elusive chloro-phosphagermylynes or the phosphinidene-chlorogermylenes. Herein, we report on the successful syntheses of room temperature stable, neutral, monomeric, hetero-bileptic phosphinidene-chlorogermylenes **3a**–**3c** with general formula (L)P-GeCl(L') [L' = NHC (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene); L = Cy-cAAC = (:C(N-2,6-^{i}Pr$_2$C$_6$H$_3$)(C$_6$H$_{10}$)(CMe$_2$)(CH$_2$)) (**3a**), Et$_2$-cAAC = (: C(N-2,6-^{i}Pr$_2$C$_6$H$_3$)(CEt$_2$)(CMe$_2$)$_2$(CH$_2$)) (**3b**), Me$_2$-cAAC = (:C(N-2,6-^{i}Pr$_2$C$_6$H$_3$)(CMe$_2$)$_2$(CH$_2$)) (**3c**)], and phosphinidene-chlorosilylene **6** with general formula (L)P-SiCl(L') (L' = NHC; L = Me$_2$-cAAC) using cAACs and NHC as stabilizing ligands. The compounds **3a**–**3c**, and **6** have been further structurally characterized in the solid state by single-crystal X-ray diffraction, NMR spectroscopy and mass spectrometric analysis.

Results and Discussion

The reaction of 1:1 molar ratio of cAAC-stabilized potassium phosphinedenides [cAAC=PK(THF)$_x$]$_n$[19] (**1a**–**1c**) ((Cy-cAAC=PK-(THF)$_x$)$_n$, **1a**; (Et$_2$-cAAC=PK(THF)$_x$)$_n$, **1b**; (Me$_2$-cAAC=PK(THF)$_x$)$_n$, **1c**), and NHC-stabilized dichlorogermanium NHC:→GeCl$_2$ (**2**)

Chem. Eur. J. **2022**, e202201242 (2 of 9)

© 2022 Wiley-VCH GmbH

(NHC = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) in anhydrous THF at −78 °C resulted in a dark brownish-red solution. The temperature of the reaction mixture was then slowly raised to room temperature over 1 h and further kept at that temperature with constant stirring for 2 h until the color of the reaction mixture changes to orange-red. THF was then completely removed under reduced pressure and the orange-red crystalline solid was extracted in anhydrous hexane. The hexane solution was then filtered to remove the salt (KCl), and the dark red filtrate was concentrated under reduced pressure to 1–2 mL and kept for crystallization. The orange-red block or rod shaped crystals of compounds **3a–3c** [cAAC: $\rightleftharpoons$:P—Ge(Cl): $\leftarrow$:NHC] [cAAC = Cy-cAAC (**3a**), Et₂-cAAC (**3b**), and Me₂-cAAC (**3c**)] were obtained in 40–48% yields from the concentrated hexane solutions kept at −40 °C (Scheme 1).

A longer reaction time led to the dissociation of the free NHC along with the formation of the NHC salt (confirmed by ^{1}H, and ^{13}C NMR spectra). To study the reaction progress with time, we have recorded the ^{31}P NMR spectra of the reaction mixture at room temperature in a regular time interval. The ^{31}P spectrum recorded after 5 min of the addition of NHC:→GeCl₂ (**2**) to a pre-cooled THF-D₈ solution of (Me₂-cAAC=PK(THF)ₓ)ₙ (**1c**) at −110 °C exhibited a broad singlet at 207.5 ppm corresponding to the potassium phosphinidenide **1c**.[19] The ^{31}P spectrum of the same reaction mixture recorded after 30 min showed the appearance of a sharp singlet at the upfield region of 90.5 ppm with the disappearance of the characteristic resonance, of **1c**. No further changes were observed when the ^{31}P spectrum was recorded after 1 h.

The control of the reaction temperature was found to be critical for the increased yields of the products **3a–3c**. When the reaction was carried out at room temperature or there was a sudden increase in the reaction temperature, the formation of a tetraphosphinidenide-anchored Ge(IV) compound (cAACP)₄Ge (**4**) was isolated as a light yellow crystalline by-product, which was characterized by single-crystal X-ray diffraction, and NMR spectroscopic analysis (see Supporting Information). The formation of compound **4** [(Me₂-cAACP)₄Ge] was found to be more significant in case of the less bulky Me₂-cAAC ligand. A concentrated hexane solution kept at −40 °C afforded the light yellow block shaped crystals of **4** after 2–3 days. Several attempts to grow single crystals of **4**, suitable for X-ray diffraction always produced very weakly diffracting crystals for
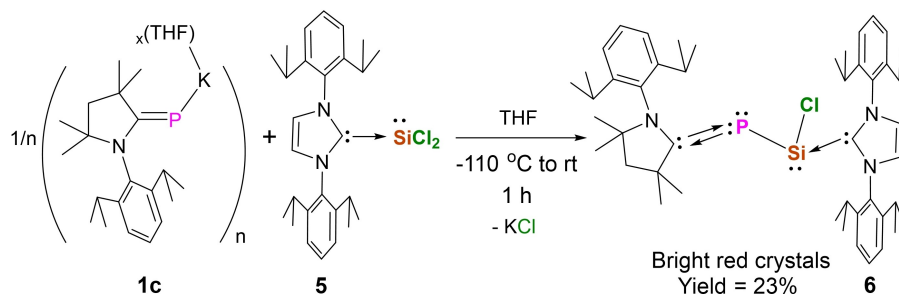
which the data quality was poor (see Supporting Information for the molecular structure of **4**, given only for the atom connectivity and not for comparing the experimental bond parameters). The ^{31}P NMR spectrum of **4** in C₆D₆ exhibited a singlet at 37.7 ppm.

A similar synthetic approach to isolate the corresponding phosphinidene-chlorosilylene **6** became successful when the cAAC-stabilized potassium phosphinedenide ((Me₂-cAAC=PK-(THF)ₓ)ₙ, **1c** and NHC-stabilized dichlorosilylene NHC:→SiCl₂ (**5**) reacted in 1:1 molar ratio in THF at −110 °C. The temperature of the reaction mixture was slowly raised to 0 °C over 30 min, and further stirred at that temperature for additional 30 min to obtain a dark brownish-red solution. The dark-red crystalline solid obtained upon evaporation of the THF was extracted in hexane and filtered. The dark red filtrate was concentrated under reduced pressure to 1–2 mL and kept for crystallization. The bright red plates of compound **6** [Me₂-cAAC: $\rightleftharpoons$:P− : Si(Cl)← :NHC] was obtained in 23% yield from the concentrated hexane solution, kept at −40 °C after three weeks (Scheme 2). Recently, the bonding and stability of the donor base stabilized (L)PSi–Cl(L′) (**6**) have been theoretically predicted by the groups of Roy and Mondal.[18]

Compounds **3a–3c**, **6** were found to be extremely air and moisture sensitive. Exposure of the orange-red crystals of **3a–3c** under air for 5 min led to the decomposition of the compounds to the colorless solid of the carbene salts, while the dark red crystals of **6** decomposed immediately after exposure to air. The solutions of **3a–3c**, **6** in hexane were stable at −40 to 0 °C for several months (**3**) under an inert atmosphere. However, an exposure to air, turned the solution to light yellow to colorless within 1–2 min. The crystals of **3a–3c** are stable at room temperature for more than 6 months and those of **6** for several days under an inert atmosphere. **3a–3c** melt above 200 (**3a**), 182–184 (**3b**), 163–165 °C (**3c**). The ^{31}P NMR spectra of the respective C₆D₆ solutions of **3a–3c**, and THF-D₈ solution of **6** showed sharp singlets at 87.8, 79.8, 86.7, and 75.7 ppm, respectively, which are much upfield shifted when compared with those of the corresponding cAAC=PK (**1a–1c**) (200–210 ppm, broad singlets).[19] The ^{29}Si NMR spectrum of **6** showed a doublet (due to coupling with ^{31}P nucleus with $I = \frac{1}{2}$) at −20.7 ppm, which is slightly upfield shifted when compared to that of the compound NHC→SiCl₂→P-Tip (−19.12 ppm).[20] The J_{Si-P} for compound **6** was found to be 219.2 Hz, which is higher
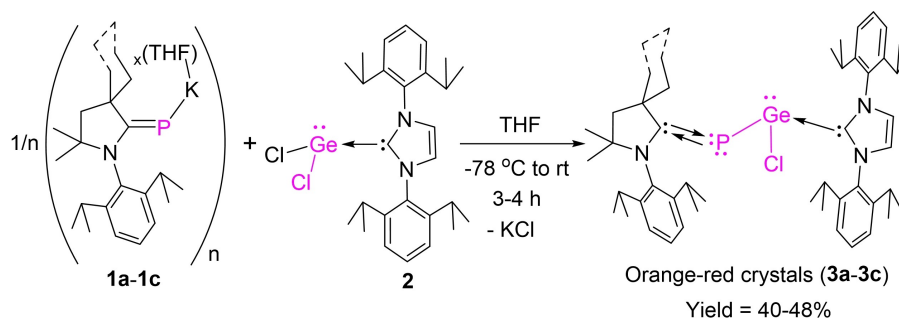
Scheme 1. Syntheses of cAAC and NHC-stabilized elusive phosphinidene-chlorogermylenes [(cAAC)P-GeCl(NHC) (**3a–3c**)].

Chem. Eur. J. **2022**, e202201242 (3 of 9)

© 2022 Wiley-VCH GmbH

Chemistry–A European Journal

Research Article
doi.org/10.1002/chem.202201242

Chemistry Europe
European Chemical
Societies Publishing

Scheme 2. Synthesis of cAAC and NHC-stabilized elusive phosphinidene-chlorosilylene [(cAAC)P–SiCl(NHC) (**6**)].

than that of NHC→SiCl$_2$→P-Tip (J_{Si-P} = 197.7 Hz).[20] This observation is in accordance with the previous prediction of the slight π electron delocalization between the silicon and phosphorus atoms in **6**, resulting in a stronger coupling between ^{29}Si and ^{31}P nuclei.[18] The ^{13}C resonances of **3a–3c** for C$_{cAAC}$ were observed as doublets in the range of 213.8–212.5 ppm with J_{C-P} in the range of 83.0–86.0 Hz, which are slightly downfield shifted when compared with those of the corresponding [cAAC=PK-(THF)$_x$]$_n$ (**1a–1c**) (202–208 ppm),[19] but upfield shifted when compared with those of the corresponding free carbenes (309.4 and 304.2 ppm for Cy-cAAC and Me$_2$-cAAC, respectively).[21] The ^{13}C NMR spectrum of **6** showed a comparatively downfield shifted doublet at 221.9 ppm (J_{C-P} = 112.1 Hz). The UV-vis spectra of **3a–3c** were recorded in hexane under an inert atmosphere, which showed broad (300–500 nm) band with an absorption maxima (λ_{max}) at 428 nm for **3a**, 369 nm for **3b**, and 360 nm for **3c** (see Supporting Information for details).

Single crystal X-ray structure determinations of compounds **3a–3c**, and **6** revealed that all the compounds have similar molecular structures (Figures 2 and 3), and therefore, the structural aspects of only compound **3a** are described herein (for structural details of **3b–3c**, and **6** see Supporting Information).

Compound **3a** crystallizes in the triclinic space group *P*-1 (Figure 2). The molecular structure of (Cy-cAAC)P-GeCl(NHC) (**3a**) exhibits bent geometry at phosphorus atom which is bound to one carbene (Cy-cAAC) and one chlorogermanium (GeCl) unit, which is further bonded to the NHC.

The germanium atom adopts a trigonal pyramidal geometry (sum of the bond angles at Ge1 is 279.67°), indicating the presence of a lone pair of electrons. Ge/Si atom is 1.11 Å above the plane containing PClC atoms. The Cy-cAAC and the NHC units of **3a** are oriented in a *trans*-position (*E*) (C1–P1–Ge1–C2 torsion angle 151.52°) with respect to the central P-GeCl moiety.

The phosphorus atom in **3a** is bound to one germanium atom with the Ge1–P1 bond length of 2.3872(5) Å, which is comparable with the Ge–P electron-sharing single bond [2.3823(12) Å] in the diphosphidogermylene [(Ar$_2$P)$_2$Ge:],[22] but much shorter than the P→Ge donor-acceptor type interaction [2.525(3), 2.612(3) Å] in the dimeric phosphinoamido-chlorogermylene [Ph$_2$PN(Ar)GeCl]$_2$.[23] The Ge1-C2 bond length in **3a** is 2.0857(16) Å, which is shorter than that in NHC:→GeCl$_2$
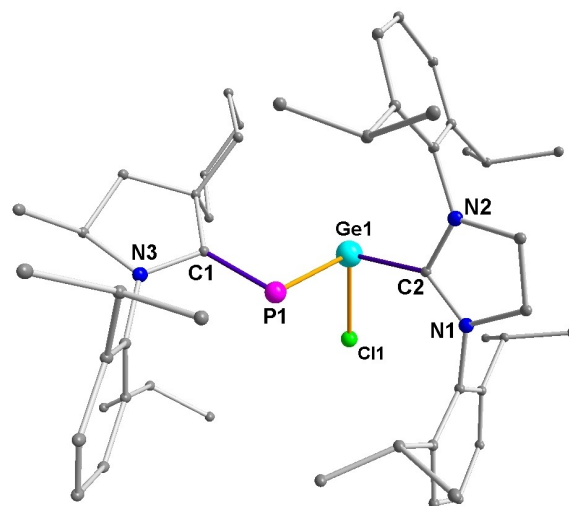

Figure 2. Molecular structure of compound (Cy-cAAC)P-GeCl(NHC) (**3a**). H atoms are omitted for clarity. Selected bond lengths [Å] and bond angles (°): N3–C1 [1.371(2)], C1–P1 [1.7240(17)], P1–Ge1 [2.3872(5)], Ge1–Cl1 [2.3222(5)], Ge1–C2 [2.0857(16)], C2–N1 [1.348(2)], C2–N2 [1.359(2)], N3–C1–P1 [119.95(13)], C1–P1–Ge1 [105.479(6)], P1–Ge1–Cl1 [93.886(18)], Cl1–Ge1–C2 [99.002(4)], Ge1–C2–N1 [137.438(9)], Ge1–C2–N2 [118.132(9)].

[2.112(2) Å],[24] but comparable with those [Ge1–C1: 2.058(3) Å, and Ge1–C2: 2.057(3) Å] of the Ge(II) salt in [bis(NHC)-GeCl]$^+$Cl$^-$, referring to a stronger chelating interaction of the C$_{NHC}$ to the Ge atom.[15] The Ge1–Cl1 bond distance in **3a** is 2.3222(5) Å, which is much longer than that in the adduct NHC:→GeCl$_2$ (**2**) (average 2.277 Å),[24] and in the related four-coordinate Ge(II) species 1,2,3,4-tetrakis(di-*tert*-butylmethylsilyl)-3,4-dichlorotetragermetene [2.248(1) Å],[25] but comparable [2.310(1) Å] with the Ge(II) salt in [bis(NHC)-GeCl]$^+$Cl$^-$.[15] The P1–C1 bond length in **3a** is 1.7240(17) Å, which is longer than that in cAAC=PK (**1a**) [1.702(3) Å][19] and in between those in Cy-cAAC$_2$P$_2$ [1.719(7) Å][26] and NHC$_2$P$_2$ [1.750(2) Å],[27] indicating a donor-acceptor type bond and the phosphinidene nature [cAAC: $\rightleftharpoons$: P:].

Several attempts to reduce compound **3** in the presence of various reducing agents, for example, K/Na/Na-C$_{10}$H$_8$ could not be successful, instead the corresponding cAAC-stabilized bis-phosphinidene cAAC$_2$P$_2$[28] was isolated each time. However, the *in situ* generation of the corresponding radical [(Et$_2$-cAAC)P–Ge-(NHC)]$^-$ (**3b-Cl**)$^-$ was confirmed by the EPR spectroscopic analysis
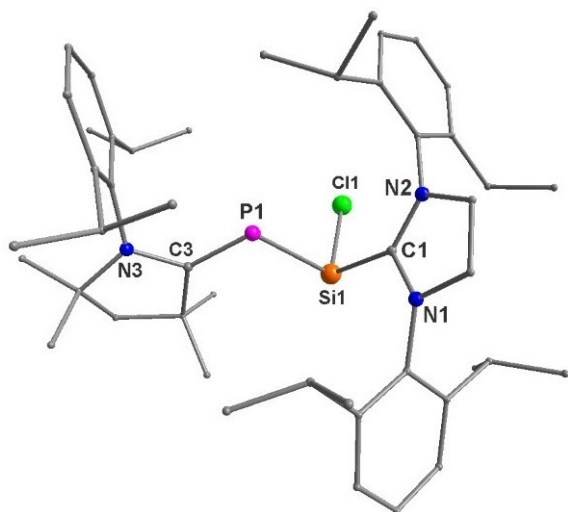
Chem. Eur. J. **2022**, e202201242 (4 of 9)

© 2022 Wiley-VCH GmbH

Chemistry–A European Journal

Research Article
doi.org/10.1002/chem.202201242

**Chemistry
Europe**
European Chemical
Societies Publishing

Figure 3. Molecular structure of compound (Me$_2$-cAAC)P-SiCl(NHC) (**6**). H atoms are omitted for clarity. Selected experimental bond lengths [Å] and bond angles [°]: N3–C3 1.379(6), C3–P1 1.713(5), P1–Si1 2.2951(18), Si1–Cl1 2.1857(17), C1–Si1 1.968(4), C1–N1 1.372(6), C1–N2 1.349(6), N3–C3–P1 122.0(3), C3–P1–Si1 107.32(16), P1–Si1–C1 87.02(14), P1–Si1–Cl1 98.84(7).

of the reaction mixture containing (Et$_2$-cAAC)P-GeCl(NHC) (**3 b**) and finely cut pieces of potassium metal in 1:1 molar ratio in THF at 293 K. The X-band EPR spectrum recorded for the above reaction mixture exhibited five hyperfine lines due to the coupling of the unpaired electron with two neighboring ^{14}N nuclei ($I = 1$), which have been further replicated two times due to the coupling with one neighboring ^{31}P nucleus ($I = 1/2$) (see Supporting Information).

The molecular structure of compound **6** is shown in Figure 3 (see Supporting Information for details), the structural features are very much similar to those of **3**, and hence not described here.

We have carried out density functional theory (DFT) calculations on a model compound **3 a**′, where the Dip (2,6-diisopropylphenyl) substituents at the cAAC and NHC donor moieties are replaced by the methyl groups (to save the computational time) in order to elucidate the electron densities distribution and bonding situation in compound **3 a**. We have optimized the geometry of **3 a**′ at the BP86/def2-TZVPP level of theory and then performed the natural bond orbital (NBO) analysis (see Supporting Information). The optimized bond lengths and bond angles of **3 a**′ are in good agreement with the experimental values obtained for **3 a** (see Supporting Information). The optimized geometry of the model compound **3 a**′ was found to be comparable to that of **3 a** (see Supporting Information). The natural bond orbital (NBO) analysis of **3 a**′ supports the bonding picture of the molecule in terms of the donor-acceptor interactions, depicted as cAAC: ⇌ :P–Ge(Cl): ⇌ :NHC. Figure 4 shows the relevant NBOs of **3 a**′ participating in bonding. The HOMO and HOMO-2 are the σ lone pair orbitals at P and Ge centres, respectively; whereas, the HOMO-3 is solely the σ lone pair orbital at P centre. HOMO-1 is the π bonding orbital of the C$_{cAAC}$=P bond, which is majorly polarised towards the P centre (58.9%). The lone pair on P has 67.8% of s character, and 32.0% of p character. Another lone pair on P is involved in π backdonation to the vacant orbital of cAAC (LUMO), which can be very well visualised in HOMO-1.

The Wiberg bond index (WBI = 1.51) and two bonding occupancies have been computed for the C$_{cAAC}$–P bond in **3 a**′ imply the presence of a partial double bond between C$_{cAAC}$ and P atoms of **3 a**′. The NBO analyses reveal the presence of a lone pair of electrons on Ge, which is 80.8% and 23.8% of s and p characters, respectively. HOMO of **3 a**′ suggests that there is a secondary bonding interaction between P–Ge single bond with C$_{cAAC/NHC}$. HOMO-2 shows the diffusion of electron densities on Ge towards P and C–P bond (Figure 4).

To study the topological features of the model compound **3 a**′, we have performed Bader's quantum theory of atoms in
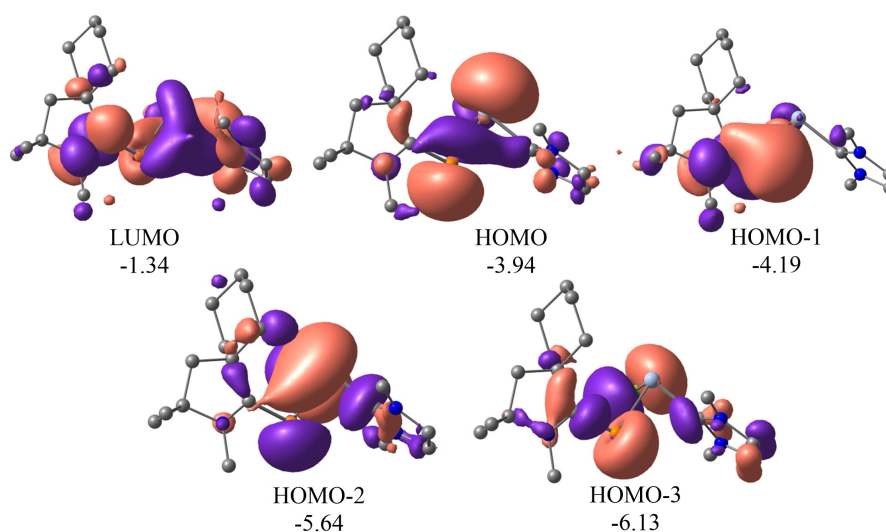

LUMO
-1.34

HOMO
-3.94

HOMO-1
-4.19

HOMO-2
-5.64

HOMO-3
-6.13

Figure 4. Representative NBOs of model compound **3**′ at BP86/def2-TZVPP level of theory. Hydrogen atoms are omitted for clarity. Energy values are in eV.
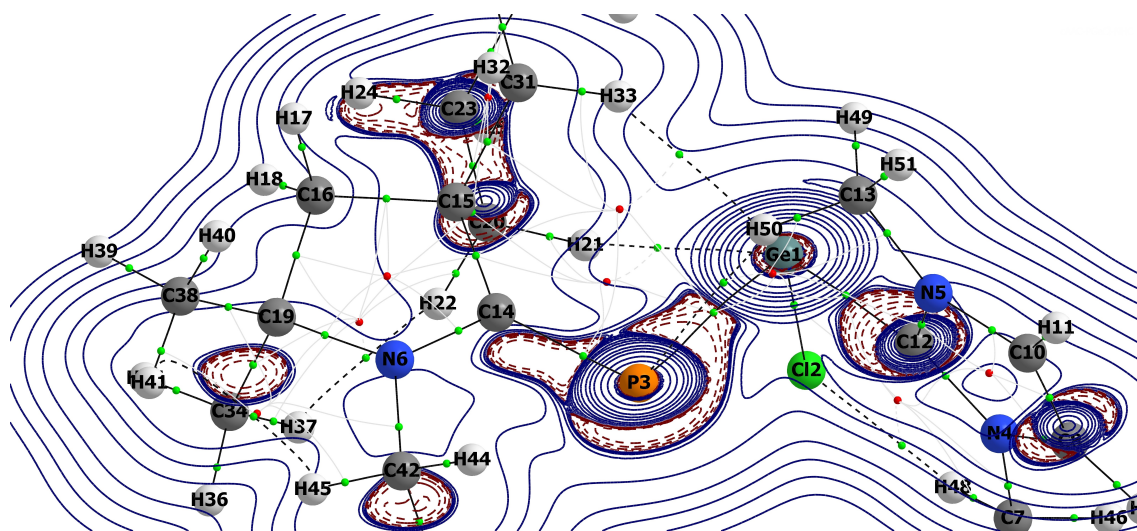
Chem. Eur. J. **2022**, e202201242 (5 of 9)

© 2022 Wiley-VCH GmbH

Chemistry–A European Journal

Research Article
doi.org/10.1002/chem.202201242

**Chemistry
Europe**

European Chemical
Societies Publishing

Figure 5. Contour plot of Laplacian distribution [$\nabla^2\rho(r)$] in the P3—Ge1—C12 plane of **3a'**. Solid blue lines indicate the areas of charge concentration ($\nabla^2\rho(r) < 0$), while dotted purple lines denote charge depletion ($\nabla^2\rho(r) > 0$). Solid lines connecting atomic nuclei (black) are the bond paths.

molecules (QTAIM).[29] The strength of a bond is echoed in the parameter, called the electron density at (3, −1) the bond critical point (BCP). The electron density, $\rho(r)$ of C_{cAAC}—P bond (0.16 a.u.) suggests a closed shell interaction, and more polarised towards the P centre (Figure 5; see Supporting Information). $\rho(r)$ for **3a'** was found to be comparatively lower for the bonds P—Ge and Ge—C_{NHC}, indicating a weaker closed-shell interaction. The positive values of $\nabla^2\rho(r)$[29d] for the bonds C_{cAAC}—P (0.16) and Ge—C_{NHC} (0.11) reveal the closed-shell interactions between them. A small negative value (−0.07) of $\nabla^2\rho(r)$ for the P—Ge bond implies that it may be a covalent electron-sharing bond. The ellipticity (ε) parameter of C_{cAAC}—P bond is 0.05 suggesting single or multiple bonding interactions between them. However, QTAIM cannot unambiguously predict the nature of chemical bond especially when heavier elements are involved.

To get a deeper insight into the bonding scenario between the ligand fragments (cAAC NHC) and PGeCl moiety, and the nature of the P—GeCl bond, we performed the energy decomposition analysis coupled with natural orbital for chemical valence (EDA-NOCV).[30] For the study of the bonding nature of (cAAC, NHC) and PGeCl fragments, we considered four different bonding possibilities by changing the charge and the multiplicity of the interacting fragments: (a) neutral (cAAC NHC)

Table 1. The EDA-NOCV results at the BP86-D3(BJ)/TZ2P level of theory for cAAC-PGe(Cl)-NHC bonds of cAAC–P-Ge(Cl)-NHC (**3a'**) using [(cAAC)(NHC)]$^+$ and [P–Ge(Cl)]$^-$ in the electronic doublet (D) states as interacting fragments. Energies are in kcal/mol.

Energy [kcal/mol]	Type of bonding interaction in **3'**	[(cAAC NHC)]$^+$ (D) + [P–Ge-(Cl)]$^{<m->}$ (D)
$\triangle E_{int}$		−239.5
$\triangle E_{Pauli}$		488.1
$\triangle E_{disp}$[a]		−23.4 (3.2%)
$\triangle E_{elstat}$[a]		−374.9 (51.5%)
$\triangle E_{orb}$[a]		−329.4 (45.2%)
$\triangle E_{orb(1)}$[b]	cAAC-PGe(Cl)-NHC σ electron-sharing	−161.7 (49.1%)
$\triangle E_{orb(2)}$[b]	cAAC→PGe(Cl)←NHC σ dative	−60.9 (18.5%)
$\triangle E_{orb(3)}$[b]	cAAC←PGe(Cl) π dative backdonation	−65.8 (20.0%)
$\triangle E_{orb(4)}$[b]	cAAC←PGe(Cl)→NHC charge po-larized π backdonation	−11.7 (3.5%)
$\triangle E_{orb(rest)}$		−29.3 (8.9%)

and PGeCl fragments in singlet state, interacting to form the dative bonds; (b) neutral (cAAC NHC) and PGeCl fragments in quintet state, implying the interaction to form electron-sharing covalent bond; (c) doubly charged fragments of [(cAAC NHC)]$^{2+}$ and [PGeCl]$^{2-}$ in triplet state, interacting to form σ electron-
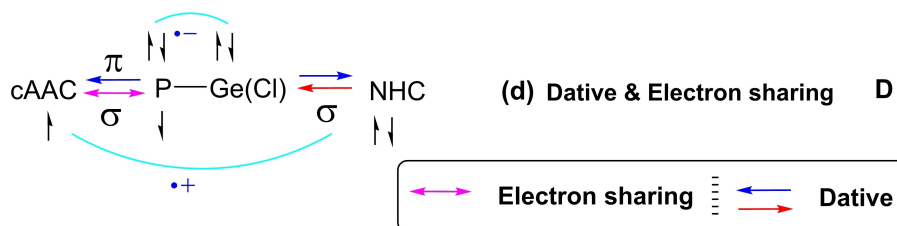
Scheme 3. Best bonding scenario in compound **3'**. The cAAC←P π-bond [$\triangle E_{orb(3)}$] is six time stronger than that (Ge→NHC) Ge—C_{NHC} bond [$\triangle E_{orb(4)}$, Figure 4].

Chem. Eur. J. **2022**, e202201242 (6 of 9)

© 2022 Wiley-VCH GmbH

Chemistry–A European Journal

Research Article
doi.org/10.1002/chem.202201242

Chemistry Europe
European Chemical
Societies Publishing

sharing and π dative bonds; and finally (d) singly charged fragments of [(cAAC NHC)]$^+$ and [PGeCl]$^-$ in doublet state, which would interact to form both electron-sharing and dative bonds (Scheme S5).
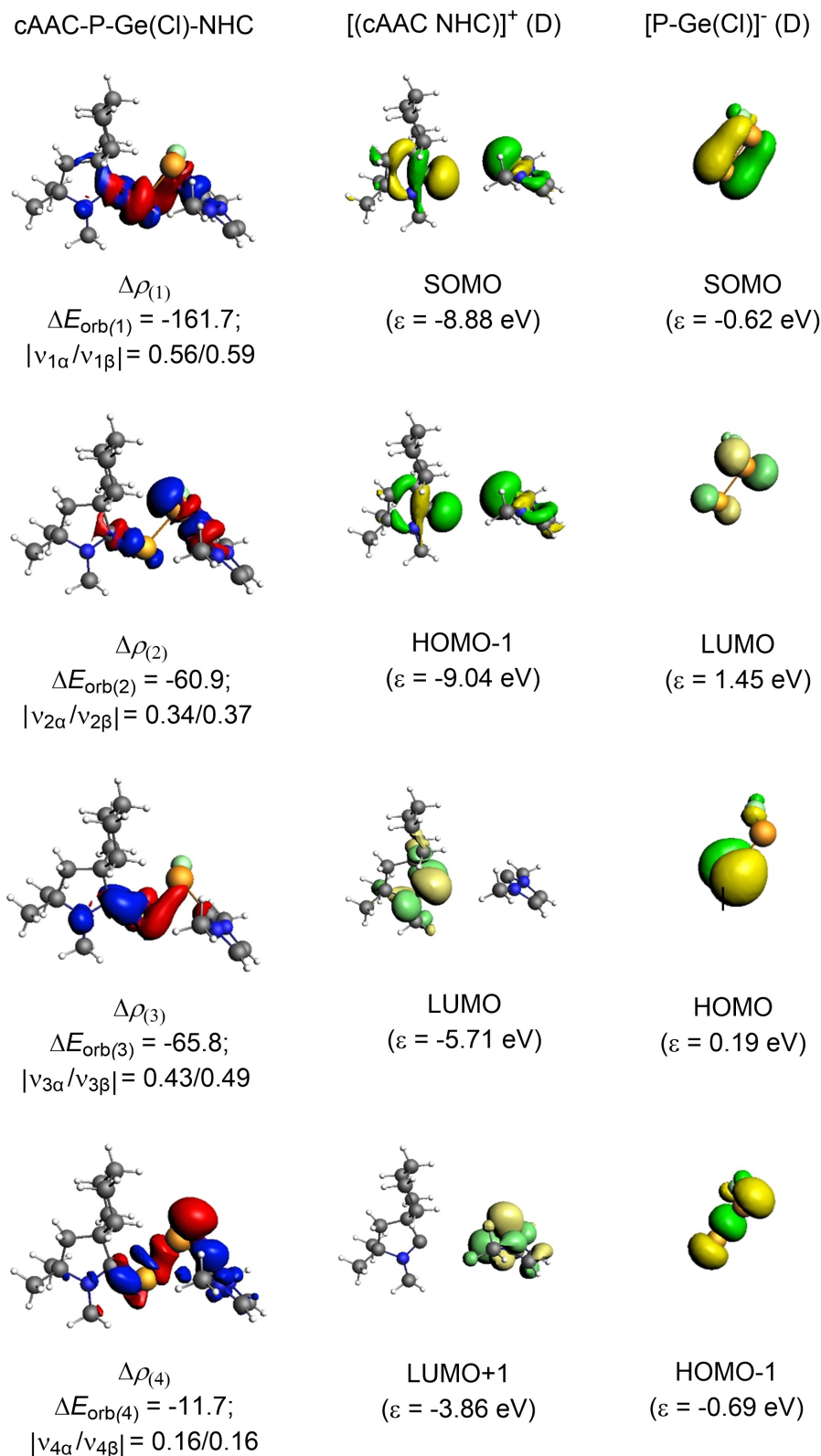

Figure 6. The shape of the deformation densities $\triangle\rho_{(1)-(4)}$ that correspond to $\triangle E_{orb(1)-(4)}$, and the associated MOs of cAAC-PGe(Cl)-cAAC (**3′**) and the fragments orbitals of [(cAAC) (NHC)] and [PGeCl] in the doublet state (D) at the BP86-D3(BJ)/TZ2P level. Isosurface values are 0.002 au for $\triangle\rho_{(1-3)}$ and 0.0005 au for $\triangle\rho_{(4)}$. The eigenvalues $|\nu_n|$ give the size of the charge migration in e. The direction of the charge flow of the deformation densities is red→blue.

Chem. Eur. J. **2022**, e202201242 (7 of 9)

© 2022 Wiley-VCH GmbH

Chemistry–A European Journal

Research Article
doi.org/10.1002/chem.202201242

Chemistry Europe
European Chemical
Societies Publishing

Table 1 summarizes the EDA-NOCV results from which it is evident that the central PGeCl unit in **3a′** prefers to be anionic (PGeCl)$^-$ and the ligand-pair [(cAAC^{Me})(NHC^{Me})] prefers to be cationic [(cAAC^{Me})(NHC^{Me})]$^+$ in their doublet states due to the electron deficient nature of the central PGeCl unit and the electron rich nature of the ligand pair (the best bonding scenario; Scheme 3). The contribution due to the electrostatic interaction energy between (cAAC NHC)$^+$ and PGeCl fragments is signifiantly higher (55.5%) that of orbital interaction energy ($\Delta E_{orb} = 45.2\%$). The stabilization due to the favorable dispersion energy (3.2%) is small. The total orbital interaction energy (ΔE_{orb}) can be further divided into four pairwise contributions ($\Delta E_{orb(1)}$–$\Delta E_{orb(4)}$) (Figure 6), where four different types of bonding interactions have been observed.

The $\Delta E_{orb(1)}$ represents an electron-sharing C$_{cAAC/NHC}$-PGe σ bond via the interaction of SOMO of (cAAC NHC)$^+$ having σ-symmetry with π-type SOMO of (PGeCl)$^-$ in doublet states. It contributes nearly 50% of the total orbital interaction energy (ΔE_{orb}). The $\Delta E_{orb(2)}$ shows the formation of one σ-dative C$_{NHC/cAAC}$→PGe bond due to the overlap of HOMO-1 of (cAAC NHC)$^+$ with π*-orbital of P=Ge bond contributing only 18.5% to ΔE_{orb}. The formation of a C$_{cAAC}$=P π-bond has been in the deformation densities of $\Delta E_{orb(3)}$ contributing 20% to ΔE_{orb}. The $\Delta E_{orb(3)}$ is slightly higher than $\Delta E_{orb(2)}$. $\Delta E_{orb(3)}$ involves the overlap of lone pair of electrons on P-atom of PGeCl with π*$_{C-N}$-orbital of cAAC. The $\Delta E_{orb(1,3)}$ show the loss of double bond character of P-GeCl bond in their deformation densities (charge flow red→blue). $\Delta E_{orb(4)}$ represents the weak π-back donations from P and Ge atoms of PGeCl fragment to the π*-orbitals on cAAC/NHC. $\Delta E_{orb(4)}$ is six times smaller in magnitude than $\Delta E_{orb(2)}/\Delta E_{orb(3)}$ (Table 1). The magnitude of C$_{cAAC/NHC}$-PGe bond is significantly higher than other interactions due to the covalent electron-sharing nature of the bond (see Supporting Information for detailed EDA-NOCV analyses). EDA-NOCV analyses of the P—Ge bond reveals that it is an electron-sharing σ-bond. It contributes 81.8% of the $\triangle E_{orb}$. The stabilization due to the favourable dispersion energy is found to be 3.2%. The best bonding scenario of compound **3′** has been depicted in Scheme 3.

Conclusion

In conclusion, we have demonstrated the first efficient synthetic route for the elusive, neutral, monomeric hetero-bileptic ligand-stabilized singlet phosphinidiene-chlorogermylenes (**3a–3c**), and phosphinidiene-chlorosilylene (**6**) under the elimination of potassium chloride salt. **3**, **6** are new class of main group compounds containing low coordinate germanium/silicon and phosphorus atoms in their lower oxidation states. **3a–3c**, and **6** have been isolated in moderate yields and characterized by X-ray single-crystal diffraction, NMR spectroscopy amd mass spectrometry. The stability, electron densities distributions and the chemical bonding of the model compound **3′** has been studied by quantum chemical calculations, such as, DFT, NBO, QTAIM and EDA-NOCV analyses. The HOMO, HOMO-1, and HOMO-2 of **3′** are lone pair of electrons on Ge/P-atoms, C$_{cAAC}$=P π bond, P=Ge π-bonds, respectively. EDA-NOCV calculations

of **3′** showed that the central unit PGeCl prefers to be anionic (PGeCl)$^-$ and the ligand-pair [(cAAC^{Me})(NHC^{Me})] prefers to be cationic [(cAAC^{Me})(NHC^{Me})]$^+$ in their doublet states to give rise to the best bonding scenario due to the electron deficient nature of the central PGeCl unit and the electron rich nature of the ligand pair. There are electron-sharing C$_{cAAC/NHC}$–PGe σ bond, contributing −161.7 kcal/mol, one coordinate C$_{NHC/cAAC}$→PGe σ bond contributing −60.9 kcal/mol, and dative C$_{cAAC}$←P π bond contributing −65.8 kcal/mol between these two charged fragments. The fourth minor bonding interaction is due to charge flow from lone pair of electrons on Ge and P—Ge σ-bond to the cAAC ligand contributing −11.7 kcal/mol as weak π backdonation. Interestingly, the C$_{cAAC}$←P π backdonation is stronger than the C$_{NHC/cAAC}$→PGe σ donation. The magnitude of C$_{cAAC/NHC}$–PGe bond is significantly higher than other interactions due to the covalent electron-sharing nature of the bond. This is a new addition to the low coordinate Ge–P chemistry utilizing the bonding diversities of two different carbene ligands.

Experimental Section

Synthesis of compound 3a: A THF solution of NHC:→GeCl$_2$ (**2**, 269 mg, 0.5 mmol, 1 equiv.) cooled to −78 °C (acetone/liquid nitrogen bath) was slowly added through a cannula to the Schlenk flask containing a THF solution of Cy-cAAC=PK (**1a**, 200 mg, 0.5 mmol, 1 equiv.) at −78 °C with constant stirring and maintaining the same reaction temperature for 15 min. Afterwards, the temperature of the reaction mixture was slowly raised to room temperature and stirred for 2 h, resulting in a color change from brownish-red to orange-red. The reaction mixture was then filtered, and the filtrate was concentrated under vacuum up to complete dryness, resulting in a reddish-brown crystalline solid, which was further extracted with anhydrous hexane (15–20 mL), filtered and the filtrate was concentrated under vacuum to 1–2 mL and kept at −40 °C to obtain the orange-red rod-shaped single crystals (suitable for X-ray single-crystal diffraction) of **3a** (170 mg, 40% yield) after 3–4 days. **^{1}H NMR** (400 MHz, C$_6$D$_6$, 298 K) δ: 7.31 (d, $J = 7.4$ Hz, 3H, −ArH), 7.18 (d, $J = 7.8$ Hz, 6H, −ArH), 6.50 (s, 2H, −CH), 2.96–2.84 (m, $J = 6.8$ Hz, 6H, −CH(CH$_3$)$_2$), 1.60 (s, 3H, −CH_3), 1.55 (d, $J = 6.7$ Hz, 2H, −CH_2), 1.52 (d, $J = 6.8$ Hz, 16H, −CH(CH$_3$)$_2$), 1.45 (d, $J = 6.8$ Hz, 2H, − (cyclohexyl)), 1.40 (d, $J = 6.7$ Hz, 3H, − (cyclohexyl)), 1.33–1.23 (m, 4H, − (cyclohexyl)), 1.12 (dd, $J = 15.7$, 7.7 Hz, 24H, −CH(CH$_3$)$_2$) ppm; **^{13}C NMR** (101 MHz, C$_6$D$_6$, 298 K) δ: 212.9 (d, $J_{C-P} = 84.8$ Hz) (C$_{carbene}$), 175.0, 146.1, 145.8, 137.9, 134.7, 131.2, 130.4, 129.3, 125.7, 124.5, 124.3, 124.0, 67.3, 51.0, 29.3, 29.1, 29.0, 25.9, 25.8, 25.7, 23.3, 23.1, 21.4 ppm; **^{31}P NMR** (162 MHz, C$_6$D$_6$, 298 K) δ: 87.8 ppm; **HRMS** (ESI): m/z calculated for C$_{50}$H$_{71}$ClGeN$_3$P as [M+NH$_4$]$^+$ 871.4624; found: 871.4490 [M+NH$_4$]$^+$. **MP**: 198–200 °C.

Deposition Number(s) 2167245 (for **3a**), 2167246 (for **3b**), 2167248 (for **3c**), and 2180182 (for **6**) contain(s) 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.

Chem. Eur. J. **2022**, e202201242 (8 of 9)

© 2022 Wiley-VCH GmbH

## 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.
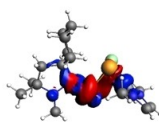
[1] R. Graf, *Org. Synth.* **1966**, *46*, 23.

[2] a) J. E. Huheey, E. A. Keiter, R. L. Keiter, *Inorganic Chemistry: Principles of Structure and Reactivity*. 4th Ed. Pearson Education Asia, **1999**. Chapter 2, Page 10–45; b) C. J. Miller, U. Chadha, J. R. Ulibarri-Sanchez, D. A. Dickie, R. A. Kemp, *Polyhedron* **2016**, *114*, 351–359; c) Y. Xiong, S. Yao, T. Szilvási, E. Ballestero-Martínez, H. Grützmacher, M. Driess, *Angew. Chem. Int. Ed.* **2017**, *56*, 4333–4336; *Angew. Chem.* **2017**, *129*, 4397–4400; d) S. Almstätter, M. Balázs, M. Bodensteinera, M. Scheer, *Chem. Commun.* **2011**, *47*, 9998–10000; e) C. N. Smit, F. M. Lock, F. Bickelhaupt, *Tetrahedron Lett.* **1984**, *25*, 3011; f) H. R. G. Bender, E. Niecke, M. Nieger, *J. Am. Chem. Soc.* **1993**, *115*, 3314–3315; g) https://en.wikipedia.org/wiki/Phosphasilene; h) V. Nesterov, N. Breit, S. Inoue, *Chem. Eur. J.* **2017**, *23*, 12014–12039.

[3] P. Jutzi, *Angew. Chem. Int. Ed. Engl.* **1975**, *14*, 232–245.

[4] a) V. Lattanzi, S. Thorwirth, D. T. Halfen, L. A. Mück, L. M. Ziurys, P. Thaddeus, J. Gauss, M. C. McCarthy, *Angew. Chem. Int. Ed.* **2010**, *49*, 5661–5664; *Angew. Chem.* **2010**, *122*, 5795–5798; b) D. Geiß, M. I. Arz, M. Straßmann, G. Schnakenburg, A. C. Filippou, *Angew. Chem.* **2015**, *127*, 2777–2782; *Angew. Chem. Int. Ed.* **2015**, *54*, 2739–2744.

[5] a) C.-H. Lai, M.-D. Su, S.-Y. Chu, *Inorg. Chem.* **2002**, *41*, 1320–1322; b) Y.-H. Hu, M.-D. Su, *Phys. Lett.* **2003**, *378*, 289–298; c) C.-H. Chen, M.-D. Su, *Eur. J. Inorg. Chem.* **2008**, *2008*, 1241–1247; d) D. Devarajan, G. Frenking, *Chem. Asian J.* **2012**, *7*, 1296–1311; and see Supporting Information for the optimized geometry of [PGeCl] molecule in singlet and triplet states.

[6] a) A. S. Ionkin, W. J. Marshall, *Organometallics* **2003**, *22*, 4136–4144; b) R. Pietschnig, A. Orthaber, *Phosphorus Sulfur Silicon Relat. Elem.* **2011**, *186*, 1361–1363; c) B. P. Johnson, S. Almstätter, F. Dielmann, M. Bodensteiner, M. Scheer, *Z. Anorg. Allg. Chem.* **2010**, *636*, 1275–1285; d) S. Inoue, W. Wang, C. Prasang, M. Asay, E. Irran, M. Driess, *J. Am. Chem. Soc.* **2011**, *133*, 2868–2871; e) A. Hinz, J. M. Goicoechea, *Chem. Eur. J.* **2018**, *24*, 7358–7363; f) S. Kundu, B. Li, J. Kretsch, R. Herbst-Irmer, D. M. Andrada, G. Frenking, D. Stalke, H. W. Roesky, *Angew. Chem. Int. Ed.* **2017**, *56*, 4219–4223; *Angew. Chem.* **2017**, *129*, 4283–4287.

[7] a) P. P. Power, *Nature* **2010**, *463*, 171–177; b) T. Chu, G. I. Nikonov, *Chem. Rev.* **2018**, *118*, 3608–3680; c) T. J. Hadlington, M. Driess, C. Jones, *Chem. Soc. Rev.* **2018**, *47*, 4176–4197; d) C. Weetman, S. Inoue, *ChemCatChem* **2018**, *10*, 4213–4228; e) V. Y. Lee, A. Sekiguchi, Organometallic Compounds of Low-Coordinate Si, Ge, Sn and Pb: From Phantom Species to Stable Compounds, John Wiley & Sons, Ltd: Chichester, **2010**.

[8] a) S. Yao, Y. Xiong, T. Szilvási, H. Grützmacher, M. Driess, *Angew. Chem. Int. Ed.* **2016**, *55*, 4781–4785; *Angew. Chem.* **2016**, *128*, 4859–4863; b) Y. Wu, L. Liu, J. Su, J. Zhu, Z. Ji, Y. Zhao, *Organometallics* **2016**, *35*, 1593–1596.

[9] A. J. Arduengo III, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361–363.

[10] V. Lavallo, Y. Canac, C. Präsang, B. Donnadieu, G. Bertrand, *Angew. Chem. Int. Ed.* **2005**, *44*, 5705–5709; *Angew. Chem.* **2005**, *117*, 5851–5855.

[11] a) Y. Wang, Y. Xie, P. Wei, R. B. King, H. F. Schaefer, P. v. R. Schleyer, G. H. Robinson, *Science* **2008**, *321*, 1069–1071; b) E. Rivard, *Chem. Soc. Rev.* **2016**, *45*, 989–1003; c) D. Franz, T. Szilvási, E. Irran, S. Inoue, *Nat. Commun.* **2015**, *6*, 10037–10042; d) B. Blom, G. Tan, S. Enthaler, S. Inoue, J. D. Epping, M. Driess, *J. Am. Chem. Soc.* **2013**, *135*, 18108–18120; e) S. J. Bonyhady, D. Collis, G. Frenking, N. Holzmann, C. Jones, A. Stasch, *Nat. Chem.* **2010**, *2*, 865–869; f) A. Rit, R. Tirfoin, S. Aldridge, *Angew. Chem. Int. Ed.* **2016**, *55*, 378–382; *Angew. Chem.* **2016**, *128*, 386–390; g) H. Braunschweig, R. D. Dewhurst, K. Hammond, J. Mies, K. Radacki, A. Vargas, *Science* **2012**, *336*, 1420–1422; h) C. D. Martin, M. Soleilhavoup, G. Bertrand, *Chem. Sci.* **2013**, *4*, 3020–3030.

[12] M. M. Siddiqui, S. K. Sarkar, S. Sinhababu, P. N. Ruth, R. Herbst-Irmer, D. Stalke, M. Ghosh, M. Fu, L. Zhao, D. Casanova, G. Frenking, B. Schwederski, W. Kaim, H. W. Roesky, *J. Am. Chem. Soc.* **2019**, *141*, 5, 1908–1912.

[13] a) E. Rivard, A. D. Sutton, J. C. Fettinger, P. P. Power, *Inorg. Chim. Acta* **2007**, *360*, 1278–1286; b) A. H. Cowley, D. M. Giolando, R. A. Jones, C. M. Nunn, J. M. Power, *Polyhedron* **1988**, *7*, 1909–1910; c) S. C. Goel, M. Y. Chiang, D. J. Rauscher, W. E. Buhro, *J. Am. Chem. Soc.* **1993**, *115*, 160–169; d) M. Westerhausen, M. M. Enzelberger, W. Schwarz, *J. Organomet. Chem.* **1995**, *491*, 83–90; e) K. Izod, J. Stewart, E. R. Clark, W. Clegg, R. W. Harrington, *Inorg. Chem.* **2010**, *49*, 4698–4707; f) M. J. Yoshifuji, *J. Organomet. Chem.* **2000**, *611*, 210–216.

[14] Y. Xiong, S. Yao, T. Szilvási, E. Ballestero-Martínez, H. Grützmacher, M. Driess, *Angew. Chem. Int. Ed.* **2017**, *56*, 4333–4336; *Angew. Chem.* **2017**, *129*, 4397–4400.

[15] Y. Xiong, S. Yao, G. Tan, S. Inoue, M. Driess, *J. Am. Chem. Soc.* **2013**, *135*, 5004–5007.

[16] M. Balmer, Y. J. Franzke, F. Weigend, C. Hänisch, *Chem. Eur. J.* **2020**, *26*, 192–197.

[17] D. H. Harris, M. F. Lappert, *J. Chem. Soc. Chem. Commun.* **1974**, 895–896.

[18] S. M. N. V. T. Gorantla, M. Francis, S. Roy, K. C. Mondal, *RSC Adv.* **2021**, *11*, 6586–6603.

[19] A. Kulkarni, S. Arumugam, M. Francis, P. G. Reddy, E. Nag, S. M. N. V. T. Gorantla, K. C. Mondal, S. Roy, *Chem. Eur. J.* **2021**, *27*, 200–207.

[20] S. Roy, P. Stollberg, R. Herbst-Irmer, D. Stalke, D. M. Andrada, G. Frenking, H. W. Roesky, *J. Am. Chem. Soc.* **2015**, *137*, 150–153.

[21] V. Lavallo, Y. Canac, C. Präsang, B. Donnadieu, G. Bertrand, *Angew. Chem. Int. Ed.* **2005**, *44*, 5705–5709; *Angew. Chem.* **2005**, *117*, 5851–5855.

[22] a) K. Izod, P. Evans, P. G. Waddell, M. R. Probert, *Inorg. Chem.* **2016**, *55*, 10510–10522; b) K. Izod, D. G. Rayner, S. M. El-Hamruni, R. W. Harringtonand, U. Baisch, *Angew. Chem. Int. Ed.* **2014**, *53*, 3636–3640; *Angew. Chem.* **2014**, *126*, 3710–3714.

[23] S. Pal, R. Dasgupta, S. Khan, *Organometallics* **2016**, *35*, 3635–3640.

[24] K. C. Thiemer, S. M. I. Al-Rafia, M. J. Farguson, R. McDonald, E. Rivard, *Chem. Commun.* **2009**, 7119–7121.

[25] A. P. Singh, H. W. Roesky, E. Carl, D. Stalke, J.-P. Demers, A. Lamge, *J. Am. Chem. Soc.* **2012**, *134*, 4998–5003.

[26] O. Back, G. Kuchenbeiser, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2009**, *121*, 5638–5641; *Angew. Chem. Int. Ed.* **2009**, 48, 5530–5533.

[27] Y. Z. Wang, Y. M. Xie, P. R. Wei, R. B. King, H. F. Schaefer, P. von R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2008**, *130*, 14970–14971.

[28] O. Back, B. Donnadieu, P. Parameswaran, G. Frenking, G. Bertrand, *Nat. Chem.* **2010**, *2*, 369–373.

[29] a) R. F. W. Bader, *Chem. Rev.* **1991**, *91*, 893–928; b) R. F. W. Bader, *Atoms in Molecules: A Quantum Theory*; USA: Oxford University Press, **1994**; c) R. F. W. Bader, *Acc. Chem. Res.* **1985**, *18*, 9–15; d) C. F. Matta, R. J. Boyd, *The Quantum Theory of Atoms in Molecules*; WILEY-VCH, **2007**.

[30] D. M. Andrada, G. Frenking, *Angew. Chem. Int. Ed.* **2015**, *54*, 12319–12324; *Angew. Chem.* **2015**, *127*, 12494–12500.
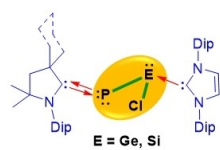
Hetero-bileptic Neutral Phosphinidene-Chlorotetrylenes

ΔE_{orb} = -161.7 kcal/mol

Elusive hetero-bileptic carbenes-stabilized singlet phosphinidene-chlorosilylene, and chlorogermylenes with majorly contributing covalent electron-sharing σ bonds are isolated and structurally characterized in the solid state.

E. Nag, M. Francis, S. Battuluri, B. B. Sinu, Dr. S. Roy*

1 – 10

Isolation of Elusive Phosphinidene-Chlorotetrylenes: The Heavier Cyanogen Chloride Analogues