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Synthesis and reactivity of N-heterocyclic carbene (NHC)-supported heavier nitrile ylides†

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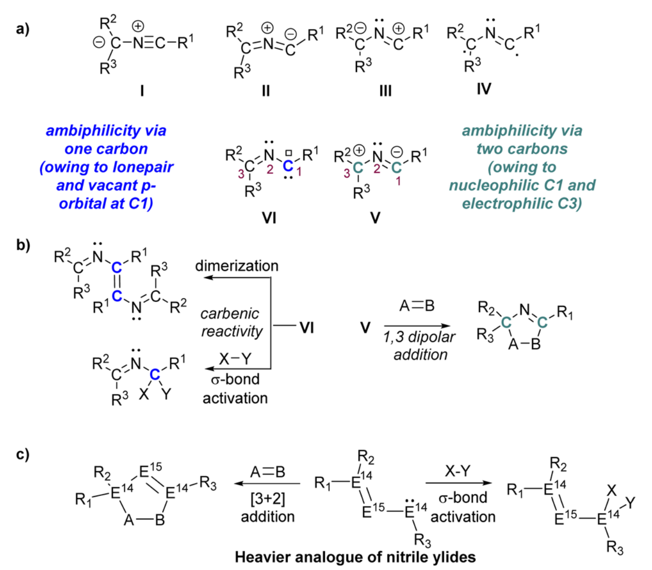
The synthesis and isolation of stable heavier analogues of nitrile ylide as N-heterocyclic carbene (NHC) adducts of phosphasilenyl-tetrylene [(NHC)(^{Ter}Ar)Si(H)PE^{14}(^{Ter}Ar)] (E^{14} = Ge **1**, Sn **2**; ^{Ter}Ar = 2,6-Mes$_2$C$_6$H$_3$, NHC = IMe$_4$) are reported. The delocalized Si–P–E^{14} π-conjugation was examined experimentally and computationally. Interestingly, the germanium derivative **1** exhibits a 1,3-dipolar nature, leading to an unprecedented [3 + 2] cycloaddition with benzaldehyde, resulting in unique heterocycles containing four heteroatoms from group 14, 15, and 16. Further exploiting the nucleophilicity of germanium, activation of the P–P bond of P$_4$ was achieved, leading to a [(NHC)(phosphasilenyl germapolyphide)] complex. Moreover, the [3 + 2] cycloaddition and the σ-bond activation by **1** resemble the characteristics of the classic nitrile ylide.

Introduction

1,3-Dipolar cycloadditions with nitrile ylides, a central theme in Huisgen's chemistry, offer a versatile approach for heteroatom incorporation into five-membered rings.[1–3] Nitrile ylides, with a C–N–C framework and delocalized π-electrons, exhibit diverse structures from bent to linear.[1–4] These highly reactive species, generated *in situ*, engage in cycloadditions with dienophiles, yielding valuable N-heterocycles for applications in materials science and natural product synthesis.[2,5] The electronic configurations of nitrile ylides reveal a rich diversity, categorized into six forms (**I–VI**, Scheme 1a), each imparting distinct reactivity.[6–10] Noteworthy, among these are nitrile ylides possessing allyl-zwitterionic (**V**) and carbenic character (**VI**), exhibiting dual ambiphilicity reminiscent of the 'imino carbene' concept.[11,12] This unique characteristic allows these species to engage in both 1,3-dipolar additions and carbene-type reactivity, including [3 + 2] cycloaddition, σ-bond activation, or dimerization *via* the carbene carbon (Scheme 1b).[10–12] However, the isolation of the elusive free carbenic nitrile ylide (type **VI**, Scheme 1a) remains a formidable task, with only one structurally characterized nitrile ylide known, possessing a propargylic structure.[13]

In recent years, significant progress has been made in exploring heavier main group compounds, particularly those with multiple bonds between group 14–15 elements and their derivatives.[14–33] This advancement is attributed to their unique synthetic potential and growing applications, ranging from small molecule activation to catalysis. While the chemistry of phosphasilenes (R$_2$Si=PR) is well-established within group 14–15 multiple bonded compounds,[14] those featuring multiple bonds between heavier group-14 elements (E^{14}, where E^{14} = Ge–Sn) and phosphorus remain relatively scarce.[16–18,22,24,30–33] The



Scheme 1 (a) Resonance structures of nitrile ylides, (b) reactivity of nitrile ylides, (c) reactivity of heavier analogues of nitrile ylides.

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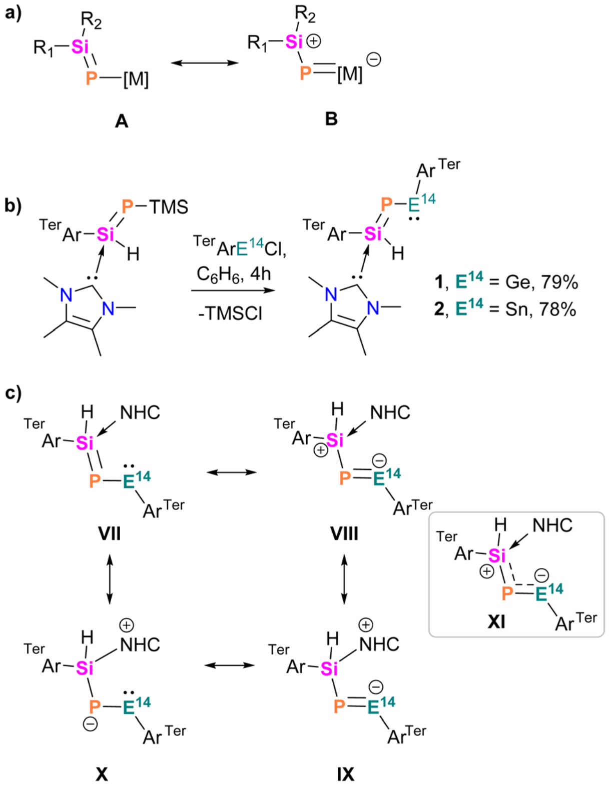
inherent polarity of the $\mathrm{E}^{14}{=}\mathrm{P}$ bond often results in intriguing 1,2-dipolar behaviour, leading to cycloadditions or addition onto the $\mathrm{E}^{14}{=}\mathrm{P}$ bonds. Notably, among E^{14}–P multiple bonded compounds, the homo or hetero-allenic heavier analogues of nitrile ylides ($\mathrm{R_2E^{14}E^{15}E^{14}R}$, E^{14} = Si–Pb, E^{15} = P, Scheme 1c) remains elusive, despite the known constitutional isomers of "heavy heteroallenes" ($\mathrm{R_2E^{14}{=}E^{14}{=}E^{15}R}$) that behave as 1,3-dipoles.[34–37] The persistent elusiveness of these compounds underscores the intricate challenges associated with their synthesis, highlighting uncharted territories within the expansive field of heavy main group chemistry.[38,39]

In this study, we introduce N-heterocyclic carbene (NHC)-coordinated bent nitrile ylides **1** and **2**, offering preliminary insights into the structural, bonding, and reactive characteristics of these intriguing heavier nitrile ylide analogues. Compound **1**, demonstrating both 1,3-dipolar addition and classical carbene reactivity, emerges as a compelling analogue reminiscent of type **VI** and type **V** nitrile ylides, respectively. The inorganic 'Huisgen'-type 1,3-dipolar additions of **1** towards the dienophile (PhCHO) resulted in the formation of an elusive cyclic five-membered phosphagermene (**3**), featuring the four heteroatoms Si, P, Ge, and O, including three heavier main group elements. Meanwhile, the activation of $\mathrm{P_4}$ by **1** led to the formation of the NHC-phosphasilenyl germapolyphide (**4**).

Results and discussion

The hypothesis that P-metallo-phosphasilenes ($\mathrm{R_2Si{=}P[M]}$, M = metal fragment) could exhibit 1,3-dipolar behaviour was grounded in the contribution of the zwitterionic **B** form to the electronic ground state (Scheme 2a).[40,41] Achieving the **B** form requires a coordinated effort involving electronic push on silicon and pull through the metal centre (M). This coordination is facilitated by a metal with an energetically accessible p-orbital associated with a ligand providing a 'pull' effect, such as aryl.[16] Therefore, we envisioned that the introduction of an electron-donating NHC-stabilized bulky (aryl)phosphasilene to the tetrylene centre *via* trimethylsilyl chloride (TMSCl) elimination could lead to the heavier nitrile ylides [(NHC)($\mathrm{R_2Si{=}P{-}E^{14}{-}R}$)], where the coordination of the NHC to silicon not only provides thermodynamic stabilization but also pushes the electron density from the Si=P moiety to the vacant p-orbital of the tetrylene centre.[14,42] Using this incentive, we treated aryl tetrylene chloride [$\mathrm{^{Ter}ArE^{14}Cl}$, E^{14} = Ge, Sn][43] with one equivalent of [(NHC)($\mathrm{^{Ter}Ar}$)Si(H)PTMS][44] at room temperature (Scheme 2b). This reaction resulted in the elimination of TMSCl and the selective formation of stable NHC-phosphasilenyl-tetrylene compounds **1** and **2**. Both compounds were isolated in good yields as red and orange crystals, exhibiting solubility in polar solvents while displaying limited solubility in nonpolar organic solvents such as benzene or toluene. Analysis of their ^{31}P NMR spectra in $\mathrm{C_6D_6}$ revealed signals relatively downfield at 150.7 ppm (**1**; calc. 165.3 ppm) and 94.5 ppm (**2**; calc. 141.1 ppm; $^1J_{(^{119}\mathrm{Sn},\mathrm{P})}$ = 1554 Hz) compared to the starting material [(NHC)($\mathrm{^{Ter}Ar}$)Si(H)PTMS] ($\delta(^{31}\mathrm{P})$ = −323 ppm; calc. −341.6 ppm).[44] These values fell within the range reported for phosphagermenes ($\mathrm{R_2Ge{=}PR}$, 87–416 ppm)[21,24–26,30,32] and phosphastannenes ($\mathrm{R_2Sn{=}PR}$, −25.1–204 ppm)[17,20,30] The ^{119}Sn NMR spectrum of **2** displayed a doublet at 1691 ppm ($^1J_{(^{119}\mathrm{Sn},\mathrm{P})}$ = 1554 Hz), falling within the range reported for bis(aryl)stannylenes (980–2323 ppm) and significantly downfield-shifted compared to phosphastannenes signals (499–658 ppm), indicating pronounced tetrylene character.[16–18] The $^1J_{(^{119}\mathrm{Sn},\mathrm{P})}$ coupling constant, positioned between typical values for Sn–P single (*ca.* 1000 Hz) and double bonds (2208–2295 Hz),[30] suggested the multiple bond character of the Sn–P bond. The ^{29}Si NMR spectra of **1** and **2** displayed distinct signals at −25.5 (calc. −26.5 ppm) and −22.7 ppm (calc. −23.9 ppm), respectively. The Si–P coupling constants for **1** (137 Hz) and **2** (142 Hz) fell within the range observed for NHC-coordinated phosphasilenes [(NHC)($\mathrm{R_2Si{=}PR}$)], $^1J_{(^{29}\mathrm{Si},\mathrm{P})}$ = 120–157 Hz).[14]



Scheme 2 (a) Resonance structures of P-metallo-phosphasilenes, (b) synthesis of NHC-phosphasilenyl-tetrylene complexes **1** and **2**, (c) possible resonance structures of **1** and **2**.

Single crystal X-ray diffraction (SC-XRD) analysis provided detailed insights into the structural features of compounds **1** and **2** (Fig. 1). In both compounds, the heavier metal centres (Ge and Sn) are di-coordinated and bound by a phosphasilene moiety [(NHC)($\mathrm{^{Ter}Ar}$)Si(H)P] and an *m*-terphenyl group ($\mathrm{^{Ter}Ar}$). The bond angles around the group 14 metals are (∢P1–E^{14}–C1: 102.6°(5) at Ge, and 95.8°(8) at Sn), larger than monomeric tetrylene-phosphinidenes $\mathrm{^{Ter}ArE^{14}P(IDipp)}$ (E^{14} = Ge, Sn; 89.5° at Ge, 86.6° at Sn)[16] and germylidenylpnictinidenes (93.0° at Ge) but within the range of acyclic bis(aryl)- and bis(phosphido)-tetrylenes.[18–20,45] The E^{14}–P bond distances in **1** (Ge1–P1: 2.236(6) Å) and **2** (Sn1–P1: 2.451(2) Å) are shorter than typical Ge–P and Sn–P single bonds and those in (aryl)(phosphido)-

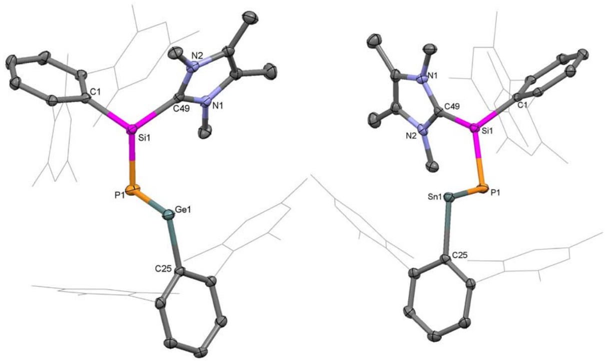


Fig. 1 Molecular structures of compound **1** (left) and **2** (right) in the solid state. Ellipsoids are set at the 50% probability level; hydrogen atoms are omitted for clarity.

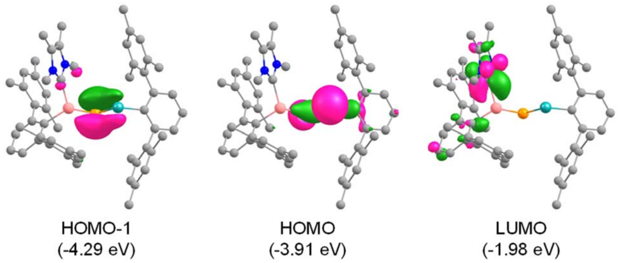


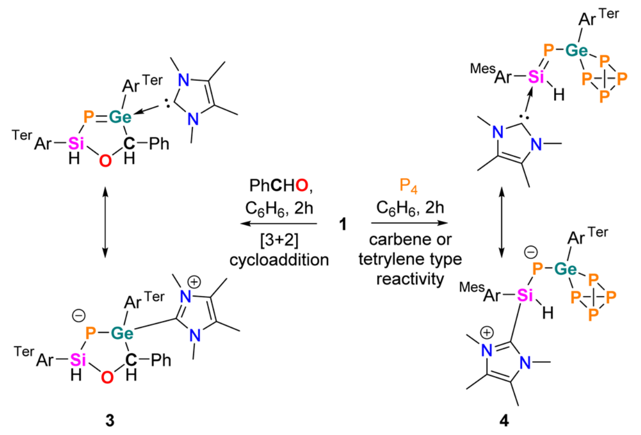
Fig. 2 Selected molecular orbitals of **1** (isosurface = 0.05 a.u.). Hydrogen atoms are omitted for clarity.

tetrylenes ($(^{Tipp}Ar)[(Me_3Si)_2P]E^{14}$ (Ge–P: 2.291 Å, Sn–P: 2.527 Å; $^{Tipp}Ar = 2,4\text{-}(2,4,6\text{-}{}^iPr_3C_6H_2)_2C_6H_3$),[46] cyclic phospha(germylene) (Ge–P: 2.247 Å),[25] and digerma-2,4-diphosphacyclobutadiene (avg. Ge–P: 2.26 Å).[32,47] The Ge1–P1 and Sn1–P1 bond distances in **1** and **2** are comparable to those in bis(phosphido) tetrylenes $[Dipp_2P]_2E^{14}$ (Ge–P: 2.234 Å, Sn–P: 2.447 Å),[19,20] $^{Ter}ArE^{14}P(IDipp)$ (Ge–P: 2.236 Å, Sn–P: 2.456 Å), germylidenylpnictinidenes (Ge–P: 2.242 Å),[18] and cyclic phosphagermene (Ge–P: 2.22 Å),[21] but longer than those in acyclic-phosphagermenes (2.138–2.174 Å)[22,24,31] and phosphastannenes (2.342 Å).[17] The Si1–P1 bond lengths in **1** (2.201(6) Å) and **2** (2.191(2) Å) are shorter than Si–P single bonds (average 2.26 Å) and slightly longer than NHC-stabilized arylphosphasilene (2.15–2.16 Å).[14,48,49] Overall, this suggests effective π-delocalization across the Si–P–E^{14} motif due to the donation from the NHC to Si (push effect) and the π-electron acceptance of the vacant p-orbital of the divalent germanium or tin atoms (pull effect).

Theoretical calculations confirmed the electronic ground states of **1** and **2** to be singlet with singlet–triplet energy gaps (ΔE^{S-T}) of 32.4 and 35.1 kcal mol^{-1}, respectively. Inspection of the molecular orbitals reveal that the HOMOs in **1** and **2** represent E^{14}–P σ-orbitals, while the π(E^{14}–P) symmetry with a major contribution from the more electronegative phosphorus is found in the HOMO−1 (Fig. 2 and S27†). The LUMOs possess vacant p_π-orbitals on the carbene carbons. The Wiberg bond indices (WBI) indicate partial double bond character for Si–P (1.118/1.170) and E^{14}–P (1.338/1.146) in **1**/**2**. Natural bond orbital (NBO) analysis locates lone pairs of electrons each on P (1.940/1.938 e) and E^{14} (1.946/1.967 e) centres in **1**/**2**. The bent geometries of the compounds are attributed to the participation of almost pure p-orbitals of phosphorus in the formation of Si–P and E^{14}–P bonds (Table S2†).[50] The positive Laplacian [$\nabla^2\rho(r)$] values at (3, −1) bond critical points of the Si–C^{NHC} bonds (+0.158/+0.155 in **1**/**2**), as suggested by quantum theory of atoms in molecules (QTAIM) calculations, indicate its donor–acceptor nature (Table S3†). In addition, the negative Laplacian values of the Si–P bonds (−0.136/−0.124) indicate true covalent interactions,[51] whereas the E^{14}–P bonds (−0.019/+0.042) exhibit highly polarized covalent nature. Therefore, both compounds can be better represented by the resonance form **XI.** Furthermore, comparison of the formation energies of **1** (−16.7 kcal mol^{-1}) and **2** (−10.9 kcal mol^{-1}) with their carbon (−56.6 kcal mol^{-1}) and silicon (−17.0 kcal mol^{-1}) analogues indicate that the lighter congeners might also be considered as viable targets for syntheses (Fig. S28†).

The electronic features of **1** and **2** differ significantly from the *P*-plumbyleniophosphasilene [$^tBu_3Si(R)Si{=}P\text{–}PbL$, L = β-diketiminate, R = $2,4,6\text{-}{}^iPr_3C_6H_2$],[52] where the π-delocalization across Si–P–Pb is perturbed due to the N-donation of *N*,*N*-substituted β-diketiminato (NacNac) to the vacant p-orbital of Pb and the poor $(Pb)p_\pi$–$(P)p_\pi$ interaction, leading to a preference for the **A** type of electronic structure in the ground state (Scheme 2a). In contrast, a facile π-delocalization observed across the Si–P–E^{14} motif in **1** and **2**, led to the electronic form **B.**

The reactivity of P-metallo-phosphasilenes remains unexplored. To investigate the 1,3-dipolar nature of **1** and **2**, the compounds were treated with one equivalent amount of dipolarophile (such as PhCHO, Scheme 3), resulted in the formation of oxaphosphasilagermole **3** in the case of **1**. The reaction led to an immediate colour change from orange to yellow, and the subsequent analysis by multinuclear NMR confirmed the quantitative conversion of **1** to **3**. The ^{31}P NMR of **3** displayed a distinct signal at −279 ppm, shifted upfield compared to **1**. The ^{29}Si NMR of **3** showed a downfield shift compared to **1**, and the Si–P coupling constant indicated a single bond between Si



Scheme 3 Synthesis of compounds **3** and **4** and their possible zwitterionic structures.

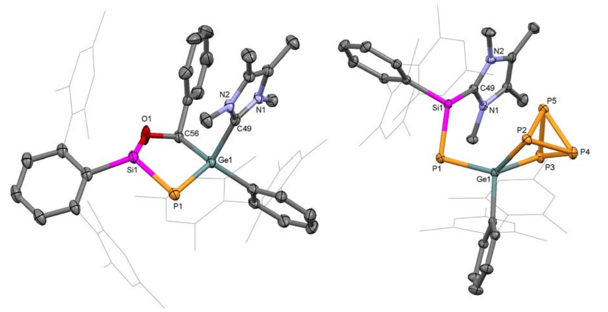


Fig. 3 Molecular structures of compounds **3** (left) and **4** (right) in the solid state. Ellipsoids are set at the 50% probability level; hydrogen atoms are omitted for clarity.

and P. SC-XRD analysis of **3** revealed a nonplanar five-membered ring, representing the first molecular snapshot of true heterocycles containing four heteroatoms of group 14, 15, and 16, with a low-valent phosphorus centre (Fig. 3). The Ge1–P1 bond length in **3** (2.248(1) Å) was shorter than the average Ge–P single bonds, indicating its partial multiple bond character. Therefore, compound **3** stands as a unique example of a base-stabilized cyclic five-membered phosphagermene. This finding is noteworthy, particularly in the context of 1,3-dipolar additions involving main group ylides with heavier elements, which are barely observed.[34–36,53–55]

The HOMO−1 and HOMO in **3** possess lone pair orbitals located on phosphorus, whereas the LUMO shows the vacant p_π-orbital on the carbene carbon (Fig. S29†). The partial double bond character in the Ge–P bond with calculated WBI of 1.140 in **3** gets significantly reduced compared to **1**. Moreover, the formation of **3** demonstrates the nucleophilicity of germanium and the electrophilicity of the silicon centre in **1**, like the 1,3-dipolar nature of nitrile ylides. Additionally, in **3**, the migration of NHC from silicon to the germanium centre suggests a donor–acceptor type interaction between Si and NHC in **1**. Notably, the reactivity of **1** with PhCHO markedly differs from the known reactivity of carbonyl compounds ($R_2C{=}O$) with E=P multiple bonded complexes or with terylenes (R_2E, E = Si–Pb). For example, reactivity of phosphasilene [$R_2Si{=}PSi^iPr_3$, R = 2,4,6-$^iPr_3(C_6H_2)$], phosphagermene, and ^{Ter}ArE^{14}P(IDipp) with carbonyl led to the [2 + 2] cycloaddition product,[16,56,57] whereas the reactivity of a silylene with carbonyl led to the [1 + 2] cycloaddition product[58] or forms the silacarbonyl ylide.[59,60] The reactivity of **1** with PhCHO could resemble the intramolecular vicinal frustrated P/B Lewis pair (FLP) [*e.g.* $(C_6F_5)_2P$–CHEt–$B(C_6F_5)_2$]-mediated activation of PhCHO, where, in the case of **1**, the germanium centre acts as a Lewis base and silicon behaves as a Lewis acid centre.[61,62]

Mechanistic investigations using a truncated model with the bulkier *m*-terphenyl group replaced with 2,6-dimethylphenyl,[63,64] suggest that the [2 + 2] cycloaddition of PhCHO into the Ge–P bond in **1M** demands an energy barrier of 8.2 kcal mol^{-1} (Fig. 4). Similarly, the [1 + 2] cycloaddition of PhCHO at the Ge centre requires an energy barrier of 9.3 kcal mol^{-1}. Instead, the [3 + 2] cycloaddition of PhCHO needs to surmount a remarkably lower barrier of 5.3 kcal mol^{-1}, resulting in slightly more stable **INT-4** with a noticeably longer Si–C^{NHC} bond (2.236 Å). The subsequent de-coordination of carbene from the Si centre *via* the transition state **TS-5** leads to **INT-5**. Finally, a barrierless re-coordination of NHC to the Ge centre in **INT-5** furnishes **3M**. Importantly, substantial stabilization of **3M** compared to [2 + 2] and [1 + 2] cycloaddition

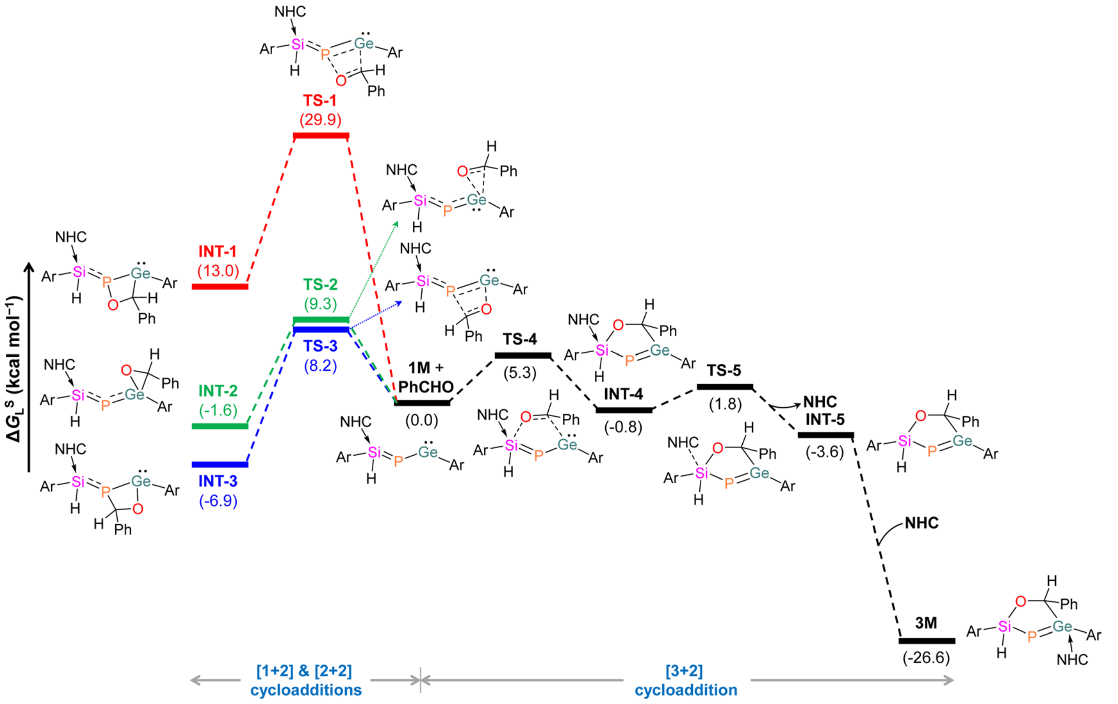


Fig. 4 Energy profile for the formation of **3M**. Ar = 2,6-dimethylphenyl; NHC = 1,3,4,5-tetramethylimidazol-2-ylidene.

intermediates indicates that the reaction is thermodynamically governed.

Thermally induced reversible addition of carbonyl across the E^{14}–P bond is known. Therefore, compound **3** was heated at elevated temperature (80 °C) under vacuum to verify reversibility. However, no evidence of reformation of **1** or elimination of PhCHO from **3** was observed, as confirmed by ^{1}H and ^{31}P NMR. In contrast, no reaction was observed between **2** and PhCHO, possibly due to the low nucleophilicity of tin. Reactivity of **1** and **2** with ketones such as acetone, benzophenone, *etc.*, was also tested, but no reaction was observed. This is possibly attributed to steric hindrance of the bulky aryl group attached to the group 14 metal centre. Further experimental studies revealed the inertness of **1** and **2** towards small molecules such as H_2, CO, HCCPh, H_2CCH_2, HBpin, and $PhSiH_3$ despite appreciably lower HOMO–LUMO energy gaps (ΔE^{H-L}: 1.93/2.04 eV in **1**/**2**).

Interestingly, the reaction of P_4 with **1** afforded selective insertion of Ge into the P–P bond, leading to germanium polyphosphide **4**. The ^{31}P NMR spectrum revealed resonances for five distinct ^{31}P nuclei (X, X′, A, A′ and Y) at $\delta = 197.7$ (m, P_X), 186.4 (m, $P_{X'}$), −125.9 (m, P_Y), −280.6 (m, P_A), −287.7 (m, $P_{A'}$). A similar type of P_4 activation was observed with seven-membered cyclic-benzamido-carbene leading to a carbene-P_4 adduct.[65] The isolation of **4** confirmed the carbenic nitrile ylide-like reactivity of **1**. Importantly, regioselective activation of P_4 by tetrylenes is rare.[66–68] Compound **4** is isostructural with reported $LSiP_4$ (L = β-diketiminate),[69] $(^{Mes}Ter)_2GeP_4$,[70] and $[^{Mes}TerSn(P_4)Si^{t}Bu_3]$ complexes.[71] In **4**, the Ge1–P1 bond (2.245(9) Å) is slightly longer than the Ge1–P1 bond in **1** but sufficiently shorter than the Ge1–P2 (2.372(9) Å) and Ge1–P3 (2.396(9) Å) single bonds (Fig. 3). Furthermore, the Si1–P1 (2.165(1) Å) bond in **4** is shorter than in **1** (Si–P: 2.20 Å) and lies in the range of NHC-stabilized arylphosphasilenes (2.15–2.16 Å). Thus, **4** represents the first example of an [(NHC)phosphasilenyl germapolyphide]. Moreover, P_4 activation by the Ge lone pair in **1M** results in **4M** with an energy barrier of 6.9 kcal mol^{-1}, indicating the strong germylene nature of **1** (Fig. S30†).

The reactivity of **1** with P_4 is contrary to silyl-phosphasilene-mediated P_4 activation. For example, $Trip_2Si{=}PR$, (R = $SiMe_2{}^{t}Bu$, $Si^{i}Pr_3$) was shown to activate P_4 *via* Si═P bond cleavage.[72] Moreover, the reactivity of **2** with P_4 led to a complicated mixtures of phosphorus-containing products. Notably, ^{Ter}Ar-EP(IDipp) (E = Ge, Sn) did not activate P_4.[16] Attempts to abstract NHC by treating **1** and **2** with Lewis acids (*e.g.*, BPh_3 and $B(C_6F_5)_3$) to generate donor-free phosphasilene-tetrylenes resulted in decomposed mixtures. This emphasizes the crucial role of NHC in stabilizing **1** and **2**. Additionally, photolysis of (**1**, **2**, and **4**) and proton scavenging from **1** and **2** with the trityl cation $[Ph_3C][B(C_6F_5)_4]$ led to inconclusive mixtures.

Conclusions

In conclusion, the study has demonstrated the synthesis, electronic structure, and reactivity of NHC-phosphasilenyl-stabilized germylene **1** and stannylene **2**. These compounds contain a heteroleptic delocalized π-bonding motif (Si–P–E^{14}, E^{14} = Ge, Sn) and provide access to the zwitterionic or carbenic form of the heavier nitrile-ylide analogues, as demonstrated for the germanium derivative. The synthesis of the ‘true heterocycle’[73] **3** from **1** represents the first example of the ‘inorganic Huisgen-type [3 + 2] cycloaddition’ reported for the group 14–15 multiple bonded complexes. Further coordination chemistry and catalytic applications of these intriguing compounds are currently under investigation.

Author contributions

D. S. carried out the synthetic and reaction studies, S. D. carried out the computational analyses, F. H. conducted the crystallographic studies. D. S., S. D., D. K. and S. I. wrote the manuscript. D. K. and S. I. managed the project.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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