

Limitations of Steric Bulk: Towards Phospha-germynes and Phospha-stannynes

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Abstract: The use of bulky aryl(silyl)amides (R) as substituents for the stabilisation of phospha-germynes and phospha-stannynes (R–Ge≡P and R–Sn≡P, respectively) is described. Such species can be transiently generated by photolysis of the phosphaketene precursors (RE(PCO); E = Ge, Sn). Utilisation of bulky amides R¹ and R² (R¹ = Ar^{**}NSi(O^tBu)₃, where Ar^{**} = 2,6-bis[bis(4-*tert*-butylphenyl)methyl]-4-methylphenyl; R² = Ar^{***}NSi(Pr)₃, where Ar^{***} = 2,6-bis[bis(3,5-di-*tert*-butylphenyl)methyl]-4-methylphenyl) facilitates the formation of diphosphene-type dimers, [(RGe)P]₂ and [(RSn)P]₂. In an effort to circumvent dimerisation, the bulkier R³ substituent (R³ = Ar^{***}NSi(4-*tert*-butylphenyl)₃) was employed in an analogous series of experiments. This affords cyclic germylenes and stannylene due to insertion of the terminal phosphide into Si–C bonds of the R³ substituent, which in case of the stannylene could act as a trap for another R³–Sn≡P moiety. All attempts to isolate terminal phosphide species were unsuccessful due to the reactivity of such compounds towards the organic periphery of the bulky amides, highlighting the limitations of highly sterically demanding functionalities.

The notion that main group elements of the third period or higher are reluctant to form multiple bonds is known as the double bond rule.^[1] The high reactivity of compounds containing such multiple bonds has historically been tamed by making use of sterically demanding substituents, which kinetically stabilise these species by shielding their reactive bonds (thus limiting their propensity to oligomerise or react with other molecular substrates/solvent).^[2]

For example, bulky alkyl and aryl substituents have been used for the isolation heavy alkene analogues.^[3–5] In these compounds steric bulk is provided by two monodentate substituents on each of the heavier atoms. By contrast, heavy azobenzene (PhN=NPh) analogues require only one monodentate substituent on the main group elements, and consequently, the individual bulk of such substituents needs to be greater, e.g. 2,4,6-tris-*tert*-butylphenyl group.^[6] Bulky silyl and terphenyl ligands have also been used for the synthesis of dipnictenes,^[7–12] and heavy alkyne analogues of the group 14 elements (which also feature a single substituent on each of the two heavy atoms).^[13–22]

Despite these advances, there are still examples of species that cannot be isolated with known ligand supports. One such family of compounds is heavy nitrile analogues such as phospha-germynes and phospha-stannynes (R–Ge≡P and R–Sn≡P, respectively). The major limitation in accessing such

species is that all of the steric protection must be offered by a single monodentate substituent and, to date, no ligands capable of providing such shielding are known.

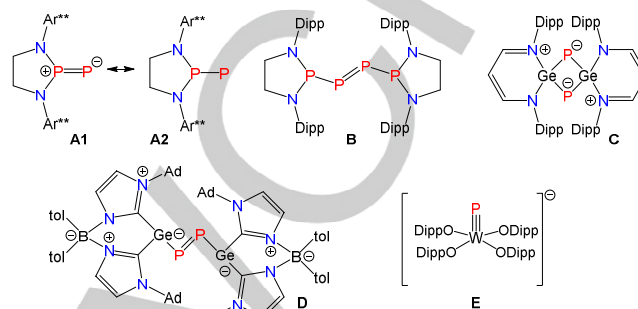


Figure 1. Selected terminal phosphides/phosphinidenes and dimerization products of such compounds. Dipp = 2,6-diisopropylphenyl; Ad = adamantyl; tol = *para*-tolyl.

Terminal phosphides and phosphinidenes have become accessible over the last two decades. While transition metal pnictides have been known since Schrock and Cummins described the first terminal phosphides in 1995,^[23–26] related examples for main group systems are still rare. Bertrand recently demonstrated that ligand bulk can indeed lead to the stabilisation of a terminal phosphorus atom bonded to a main group element centre in the form of a phosphino-phosphinidene (Figure 1; A).^[27–29] The utilisation of a less bulky substituent set resulted in the formation of the phosphanyl-diphosphene B. In related studies, Driess and co-workers succeeded in the isolation of two isomers of a Ge₂P₂ species which are stabilised by bidentate substituents. The less bulky substituent allowed the isolation of a Ge₂P₂ heterocycle (C), while with enhanced bulk a diphosphene-type chain isomer (D) could be obtained.^[30–32] All of the aforementioned species were generated by photolysis of phosphaketenes which lose carbon monoxide acting as a source of a monoanionic phosphide (P[−]). This strategy has recently been shown to be a general route to terminal nitrides, phosphides and arsenides by Cummins and co-workers who were able to isolate anionic tungsten complexes such as E.^[33]

In order to generate stable neutral terminal phosphides of the main group elements (nitrile analogues), the particular challenge is to develop a monodentate substituent sufficiently bulky to prevent the oligomerisation or dimerisation of REP (E = Ge, Sn) fragments. With this in mind, we decided to further develop the class of aryl(silyl)amides to obtain monomeric phospha-germynes and phospha-stannynes, as this class of substituents has been successfully employed by the Jones group for the isolation of low coordinate compounds.^[34–36] In order to stabilise heavy nitrile analogues, three requirements were identified for the functionalities associated with the group 14 element. The substituents need to be: 1) monodentate, 2) monoanionic, and 3) sufficiently bulky to shield two atoms in the binding pocket. To survey the properties of such ligands, an initial computational study was carried out. A family of

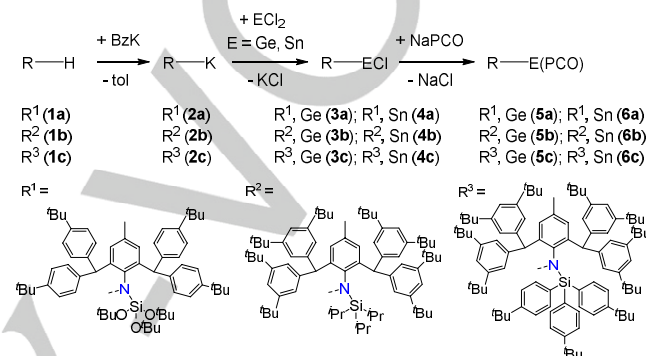
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chlorostannylenes were used as model systems, as they are feasible starting materials for the envisaged phosphastannynes (see Scheme 1).

Four different substituents were tested in these studies. Power's bulkiest terphenyl substituent, ^{Trip}Ter, and Jones' extremely bulky amide, R*, (Ar*N(SiMe₃), Ar* = 2,6-bis(diphenyl)methyl-4-methylphenyl) were taken as starting points.^[2,37] However, in both ^{Trip}TerSnCl and R*SnCl the SnCl moiety is still rather exposed, so more significant long-range bulk is required. This can be achieved by attaching *tert*-butyl groups to the aryl backbone. Jones has previously demonstrated the high tunability of his bulky amide systems both modification of the silyl moiety (SiMe₃, SiⁱPr₃, SiPh₃, Si(O^tBu)₃) and the aryl functionality in systems such as N(Ar[†]){Si(O^tBu)₃}, Ar[†] = 2,6-bis(diphenyl)methyl-4-*isopropyl*phenyl).^[38] This prompted us to calculate three additional target substituents: R¹ (Ar**NSi(O^tBu)₃; Ar** = 2,6-bis[bis(4-*tert*-butylphenyl)methyl]-4-methylphenyl), R² (Ar***NSi(ⁱPr)₃; Ar*** = 2,6-bis[bis(3,5-*di-tert*-butylphenyl)methyl]-4-methylphenyl), and R³ (Ar***NSi(4-*tert*-butylphenyl)₃). These are pictured in Scheme 1. To evaluate the steric bulk of these supporting ligands, the % buried volume can be taken into account (Table 1).^[39,40] If we consider spheres of a 3.5 Å radius around the central tin atom we see that R* and R¹ differ only slightly. However with a larger spherical radius (6.0 Å) the development of long-range bulk becomes obvious. The calculations show that R³ is considerably bulkier than all the other substituents. In order to prevent dimerization of the larger RSnP moieties, the formation of a P=P bond of approximately 2.1 Å needs to be prevented, however the phosphorus atom already is 2.6 Å from the tin centre, consequently the conventional radius of 3.5 Å is insufficient to probe the extent of steric bulk needed. Despite their widespread use, buried volumes provide no information on the directionality of steric

bulk. Steric maps could give this information, but due to the orientation of the N–Sn bond in the target compounds, they mainly reflect the steric properties of the aryl group.^[41] For the same reason, conventional cone angles of the N–Sn axis are not very useful in this context, as for R1 360° is approached and exceeded for R2 and R3. However, the solid angle Ω as proposed by Guzei and Wendt (ECA) was found to be a useful parameter.^[42] Among the studied systems equivalent cone angles of 192° (^{Trip}Ter) for the bulkiest terphenyl, 199° for Jones' amide (R*), 224° for R1, 258° for R2 and 264° for R3 were determined, which indicates that the features of the aryl group dominate this parameter.

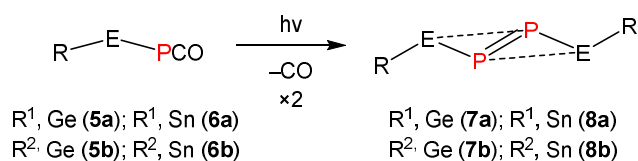


Scheme 1. General phosphaketene synthesis for RE(PCO) (R = R¹, R², R³; E = Ge, Sn). Bz = benzyl.

Our initial series of experiments targeted R¹ substituted species. The secondary amine R¹H (**1a**) was deprotonated by benzyl potassium in toluene (Scheme 1).

Table 1. Development of substituents. Space-filling models and steric properties of ^{Trip}TerSnCl, R*SnCl, R¹SnCl, R²SnCl and R³SnCl.

	^{Trip} TerSnCl	R*SnCl	R ¹ SnCl	R ² SnCl	R ³ SnCl
space-filling model					
V _{bur} 3.5 (6.0) Å	48.9 (48.6)	62.4 (48.7)	62.1 (62.8)	77.7 (72.2)	77.5 (73.9)
ECA [°]	192.46	199.36	224.15	258.33	263.56
steric map 3.5 Å					
steric map 6.0 Å					



Scheme 2. Photolysis of bulky germylenyl- and stannylenyl-phosphaketenes stabilised with R¹ or R² substituents.

Subsequent addition of GeCl₂-dioxane or SnCl₂ afforded the chlorogermylene and chlorostannylene (**3a** and **4a**), respectively, which were isolated as colourless solids. Metathesis reactions with [Na(dioxane)_x]PCO^[43,44] in toluene yielded the germylenyl- or stannylenyl-phosphaketenes (**5a** and **5b**), respectively, as pale yellow solids. The NMR spectroscopic properties show the characteristic features for phosphaketenes (**5a**, R¹Ge(PCO): $\delta(^{31}\text{P})$ -229.8 ppm; **6a**, R¹Sn(PCO): $\delta(^{31}\text{P})$ -263.3 ppm ($^1J_{\text{P-Sn}}$ = 838 Hz), $\delta(^{119}\text{Sn})$: +547 ppm). The ν_{as} vibrations of the phosphaketene moiety were observed at 1901 (**5a**, R¹Ge(PCO)) and 1880 cm⁻¹ (**6a**, R¹Sn(PCO)), respectively.

For both the **5a** and **6a** systems, photolysis (Scheme 2) affords products with ³¹P NMR resonances that are characteristic of diphosphenes (**7a**: $\delta(^{31}\text{P})$ +757.4; **8a**: $\delta(^{31}\text{P})$ +824.8, $\delta(^{119}\text{Sn})$ +235 ppm) and compare well with previously reported compounds (Driess' **D** +903.5,^[31] Wiberg's [(^tBu)₃SiP]₂ +818.6,^[45] and Yoshifujii's P₂Mes*₂ +492.4 ppm^[6,46]). The formation of dimeric [(R¹Ge)P]₂ and [(R¹Sn)P]₂ species is also supported by ¹H DOSY NMR spectroscopy. However, repeated attempts of crystallisation of these products failed. The stronger downfield shift of the ³¹P NMR resonance compared to the aryl-substituted diphosphene can be attributed to a better π -acceptor properties of the stannylene in analogy to the rationale for the downfield shift ¹³C NMR resonances of carbene complexes.^[47] These diphosphene species are the high-bulk isomers of cyclic-type diphosphenes [(RE)₂(μ -P)₂]. To obtain structural data, R² was employed as a surrogate for R¹. This substituent features a bulkier aryl group (Ar^{***}) and a less bulky silyl group (Si(ⁱPr)₃). While the synthetic procedures are analogous to the ones employed for R¹, compounds bearing R² are highly soluble in aliphatic solvents such as hexane. The ³¹P NMR resonances of **5b** and **6b** were found at -204.0 and -241.3 ($^1J_{\text{P-Sn}}$ = 860 Hz) ppm, respectively, which are slightly more downfield-shifted compared to the related R¹ species. The structures of the phosphaketenes feature Ge-P (2.369(1) Å) and Sn-P single bonds (2.597(2) Å) with acute C-P-Ge (83.5(2)°) and C-P-Sn 89.4(3)° angles (Figure 2).

Photolysis of **5b** and **6b** leads to the formation of products with characteristic downfield-shifted ³¹P NMR resonances at +745.7 (**7b**) and +797.8 (**8b**), albeit the reaction is only selective in case of the tin compound. For **8b**, single crystal diffraction experiments confirmed the presence of a diphosphene-type structure with a typically short P-P distance of 2.053(2) Å, that also features a short Sn-P bond of 2.647(1) Å, a longer secondary contact to the remote P atom of 2.854(1) Å and a Sn-P-P' angle of 73.54(4)° (Figure 2). It is noteworthy that in a related benzene solvate, the Sn-P and P-P bond lengths are comparable (2.664(1), 2.064(2) Å), but there is variation in the

length of the remote contact (2.760(1) Å) and consequently, the Sn-P-P angle (70.13(3)°), which indicates flexibility of the P₂ unit between the tin centres (Sn...Sn former 5.11, latter structure 5.02 Å). This type of diphosphene is structurally related to Mindiola's [(^{Dipp}PNacnac)(DippO)TiP]₂ compound (Ti-P 2.4200(15), 2.5961(15) Å, Ti-P-P 69.52(5)°).^[48]

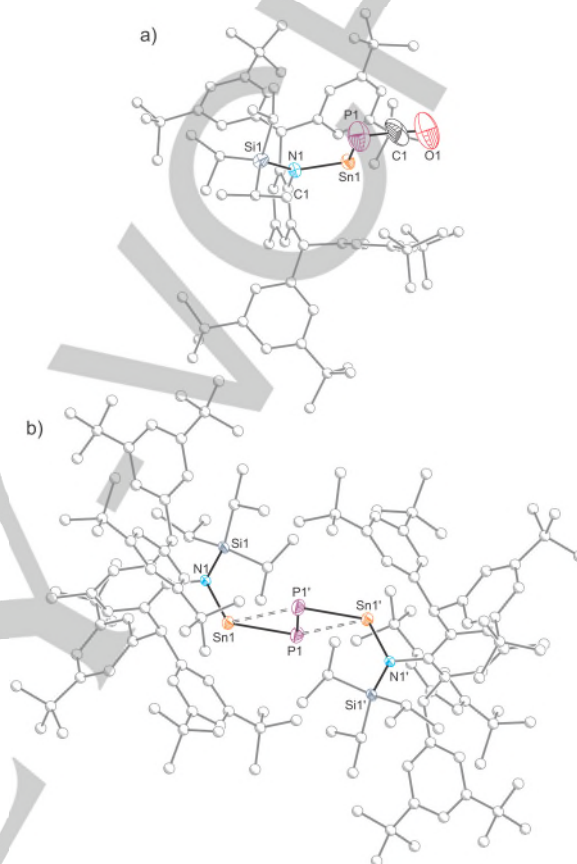
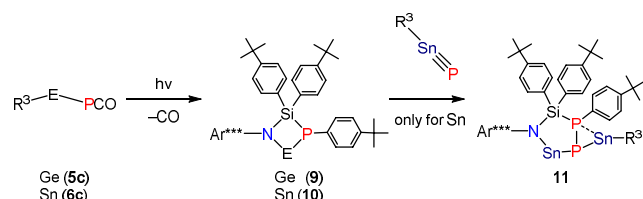


Figure 2. Molecular structures of a) **6b** and b) **8b**. Anisotropic displacement ellipsoids set at 50% probability. Hydrogen atoms have been omitted for clarity. All carbon atoms (with the exception of C1 for **6b**) are pictured as spheres of arbitrary radius. Symmetry operation $\bar{1}$: 1-x, 2-y, 1-z.

Despite the significant steric bulk of R¹ and R², dimerization of the transient heavier nitrile analogues could not be avoided. Consequently, the R³ substituent was employed in an analogous series of experiments, as it possesses greater long-range bulk. The synthetic procedure for the R³ systems is analogous to the above described for R¹ and R² species, and like R² compounds, the R³ species are readily soluble in alkane solvents. The phosphaketenes could be obtained in good yields. The R³E(PCO) species (Ge (**5c**); Sn (**6c**)) show characteristic upfield shifted ³¹P NMR resonances indicative of the formation of a phosphaketene compound. There are two possible isomers of such phosphaketene systems, (*cis*- and *trans*- relative to the Sn-N bond), however only for the germanium species is the interconversion of *cis* and *trans* is slow enough to observe both (**5c**: $\delta(^{31}\text{P})$ -208 ($\nu_{1/2}$ = 985 Hz), -216 ($\nu_{1/2}$ = 665 Hz); **6c**: $\delta(^{31}\text{P})$ -242.7 ($^1J_{\text{P-Sn}}$ = 850 Hz), $\delta(^{119}\text{Sn})$ +650 ppm). The ν_{as} vibration was observed at 1918 cm⁻¹ for **5c** and 1894 cm⁻¹ for **6c**.

Single-crystal structure elucidation revealed that the *cis*- and *trans*- isomers of **5c** co-crystallised, while only *cis*-**6c** was found (see SI). The molecular structures show the expected bent geometry at Ge and Sn. The phosphaketenes have N–E–P angles greater than 90° (**5c**: 98.96(7)°; **6c**: 96.68(5)°), while the E–P–C angles are acute (**5c**: 85.9(2)°; **6c**: 84.5(2)°) and the PCO moieties are close to linear (**5c**: 178.4(5)°; **6c**: 177.6(3)°). The bond lengths fall well within the expected values for phosphaketenes (**5c**: P–C 1.654(5), C–O 1.148(6) Å; **6c**: P–C 1.647(4), C–O 1.159(4)) and the E–P are slightly longer than the sum of covalent radii (Ge–P: 2.365(2), Σr_{cov} 2.32 Å; Sn–P: 2.628(1), Σr_{cov} 2.51).



Scheme 3. Photolysis of **5c** and **6c**.

A series of photolysis experiments targeted the generation of phosphastannyne and phosphagermyne species using **5c** and **6c** as precursors (Scheme 3). Exposure of **5c** to UV radiation at ambient temperature cleanly affords a single species (**9**), which is characterised by three distinctive NMR spectroscopic properties. The ^{29}Si NMR resonance shifts from –20.8 to –1.7 ppm and is split into a doublet due to coupling to ^{31}P ($^1J_{\text{Si-P}} = 23$ Hz). The broad ^{31}P NMR resonances of the phosphaketene **5c** at –208 and –216 ppm disappeared and instead, a new resonance was found at –62.0 ppm which was observed as a triplet attributed to the coupling to two equivalent protons ($^3J_{\text{P-H}} = 6$ Hz). This allows the conclusion that the phosphorus atom had inserted into one of the Si–C bonds. The formation of the four-membered heterocyclic germylene was confirmed by single-crystal X-ray diffraction experiments (Figure 3).

In the analogous experiment with **6c** the related four-membered heterocycle (**10**) could be observed at –61.9 ppm (t , $^3J_{\text{P-H}} = 7$ Hz, $^1J_{\text{P-Sn}} = 970$ Hz) in the ^{31}P NMR spectrum. The corresponding ^{119}Sn NMR resonance was found at +993 ppm. However, in this case, this product is only a minor species, while the major product is characterised by an AB spin system in the ^{31}P NMR spectrum at –20.0 and –130.1 ppm ($^1J_{\text{P-P}} = 264$ Hz). The product, **11** (Figure 3), could be isolated and single crystals were obtained. The structure features an $\text{R}^3\text{-Sn}\equiv\text{P}$ moiety that has formally inserted into the Sn–P bond of the four-membered heterocyclic stannylene, thereby the decomposition product provided a trap for the targeted phosphastannyne. The molecular structure shows a short Sn1–P1 (2.573(1) Å) bond within the five-membered heterocycle and two longer Sn–P bonds (2.672(1), 2.803(1) Å) within the three-membered cycle. The P–P distance of 2.169(1) Å corresponds well with the expected value for a single bond ($\Sigma r_{\text{cov}} = 2.22$ Å).^[49]

As the targeted phosphagermyne and phosphastannyne are not stable at ambient conditions, the photolysis experiments were carried out at –78 °C (Scheme 4). In both cases, the major product is a new species that is characterised by a singlet in the

$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at –29.3 (E = Ge (**12**): d, $^1J_{\text{P-H}} = 205$ Hz) and –41.4 (E = Sn (**13**): dd, $^1J_{\text{P-H}} = 191$, $^3J_{\text{P-H}} = 5$ Hz, $J_{\text{P-Sn}} = 860$ Hz) and, respectively.

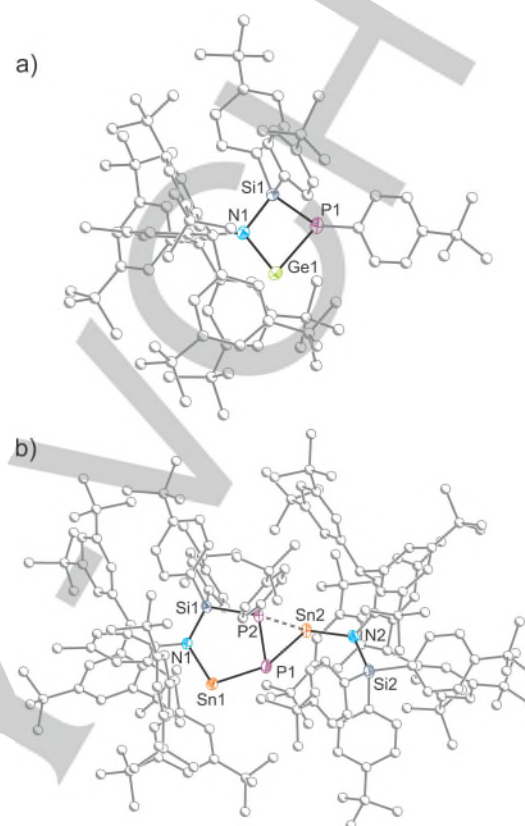
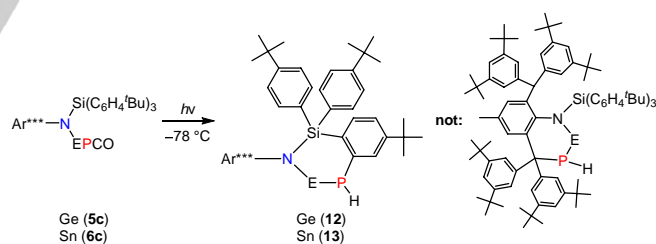


Figure 3. Molecular structures of a) **9** and b) **11**. Anisotropic displacement ellipsoids set at 50% probability. Hydrogen atoms have been omitted for clarity. All carbon atoms are pictured as spheres of arbitrary radius.



Scheme 4. Low temperature photolysis of **5c** and **6c**.

However, as revealed by the proton coupling, it is obvious that the observed species are not the targeted $\text{R-E}\equiv\text{P}$ compounds. This could be due to the insertion of the P atom into either one of the *ortho*-C–H bonds of the silyl group or into the C–H bond of the methine functionality both of which give rise to a six-membered heterocycle. ^1H – ^{31}P HMBC NMR experiments unequivocally revealed a second weak coupling to a proton (<3 Hz for **12**, 5 Hz for **13**), which indicates the attack at the silyl group and not the methine moiety. The formation of the aryl-C–H insertion product is also thermodynamically favoured, as for the methine C–H activation product the substituent has to undergo substantial deformation for the phosphorus atom to reach the

methine carbon, which is reflected in the relative stability of both isomers, as the former is favoured by 133 kJ mol⁻¹ (PBE1PBE/6-31G(d,p), fully relativistic ECP for Sn).

The sterically shielding amido substituents R¹ and R² enable the stabilisation of diphosphene-type dimers of phosphagermynes and phosphastannynes. We demonstrated that the bulk of aryl(silyl)amido substituent can be enhanced to a point where the dimerisation can be prevented with R³, but we also reached a limit to the utilisation of steric bulk. The phosphagermyne and phosphastannynne then generated are not stable enough to be isolated and different decomposition products could be obtained, with insertion of the terminal phosphorus atom into either Si–C or C–H bonds. While the steric properties of the amido substituent are desirable, the next challenge is now to maintain bulk while making the substituent more robust.

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Keywords: bulky amides • nitrile analogues • phosphorus • germanium • tin

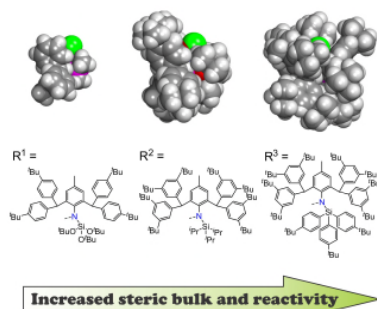
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Layout 1:

COMMUNICATION

Three new sterically encumbering amido substituents were developed and explored for their ability to stabilise $\text{Sn}\equiv\text{P}$ and $\text{Ge}\equiv\text{P}$ triple bonds.



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Limitations of Steric Bulk: Towards
Phospha-germynes and Phospha-
stannynes