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Intramolecular dearomative 1,4-addition of silyl and germyl radicals to a phenyl moiety†

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Herein, we present that the radicals [Ph$_3$PC(Me)EMes$_2$]$^\bullet$ (2^{Si} and 2^{Ge}) can be generated from the α-silylated and α-germylated phosphorus ylides Ph$_3$PC(Me)E(Cl)Mes$_2$ (1^{Si} and 1^{Ge}) through one-electron reduction with Jones' dimer (^{Mes}NacNacMg)$_2$ in benzene. Although isolation of the free radicals was not possible, the products of the intramolecular addition of the radicals to a phenyl substituent of the phosphorus moiety, followed by subsequent reaction with 2^{Si} or 2^{Ge} to the isolated species 3^{Si} and 3^{Ge}, respectively, were observed. This transformation witnesses a dearomative 1,4-addition of tetryl radical species to the phenyl scaffold in a stereoselective *anti*-fashion.

Radical species exhibit unique electronic properties and reactivities owing to their unpaired electrons, rendering them the focus of intense interest for decades. The Ph$_3$C$^\bullet$ radical (Gomberg radical) is probably the best-studied radical of group 14. It was long thought that, in solution, this species is in equilibrium with its symmetrical dimer, *i.e.* hexaphenylethane.[1] Further studies showed that this symmetrical dimer is only formed in the case of the heavier analogues of group 14,[2] whereas the Ph$_3$C$^\bullet$ radical actually attacks one phenyl ring of another Ph$_3$C$^\bullet$ molecule in *para* position resulting in an unexpected dearomatized regioisomeric σ-dimer (Scheme 1).[3]

The heavier Gomberg-type radicals (Mes$_3$E$^\bullet$) of silicon, germanium and tin bearing bulky mesityl substituents (Mes) were reported by Lappert and co-workers.[4] The authors described dimerization reactions or reactions with the solvent once the radicals were generated. The germyl radical showed the longest half-life time ($t_{1/2} > 24$ h at 0 °C) because the dimerization reaction is suppressed by steric hindrance compared to

the much larger tin atom ($t_{1/2} = 20$ s at 0 °C), and the reaction with the solvent is much slower than for the silicon ($t_{1/2} = ca.$ 20 s at 0 °C) analogue. The decomposition products were later described as a mixture of Si–H group-containing compounds, polymeric material and other products.[5]

The decay of such radicals was studied in detail by Ingold and co-workers. They found a similar reaction known for the Gomberg radical, where the Ph$_3$Si$^\bullet$ radical adds to a phenyl moiety of another molecule of Ph$_3$SiH in the *para* position.[6] This reactivity has been described before for the smaller alkyl-substituted radicals such as Me$_3$Si$^\bullet$ and Et$_3$Si$^\bullet$, which readily react with benzene.[7] Pears and co-workers studied the addition of Me$_3$Si$^\bullet$ and Me$_3$Ge$^\bullet$ radicals to benzene in detail. Irradiation of (Me$_3$Si)$_2$Hg in benzene gave the homolytic aromatic substitution products such as phenyltrimethylsilane (20%), 2,5-cyclohexadienyltrimethylsilane (12%) and hexamethyldisilane (27%), along with silylated biphenyls, phenylcyclohexadienes and bis(cyclohexadienyls). For the similar reaction involving (Me$_3$Ge)$_2$Hg, they obtained Me$_6$Ge$_2$ (98%), PhGeMe$_3$ (1%) and 2,5-cyclohexadienyltrimethylgermane (traces). This was ascribed to the significantly weaker Ge–C bond, whose formation is less favourable compared to the that of the dimer (Me$_3$Ge)$_2$ (Scheme 2a).[8] The chemistry of silyl and germyl radical species and their reactivity have been summarized in numerous review articles over the past decades.[9]

Considering the addition to multiple bonds or aromatic systems, germyl radicals are comparatively less reactive than their silicon counterparts. In some cases, however, such transformations were proven as powerful synthetic tools like the recent intramolecular addition of Ge radicals to an alkyne function reported by Durandetti and co-workers.[10]
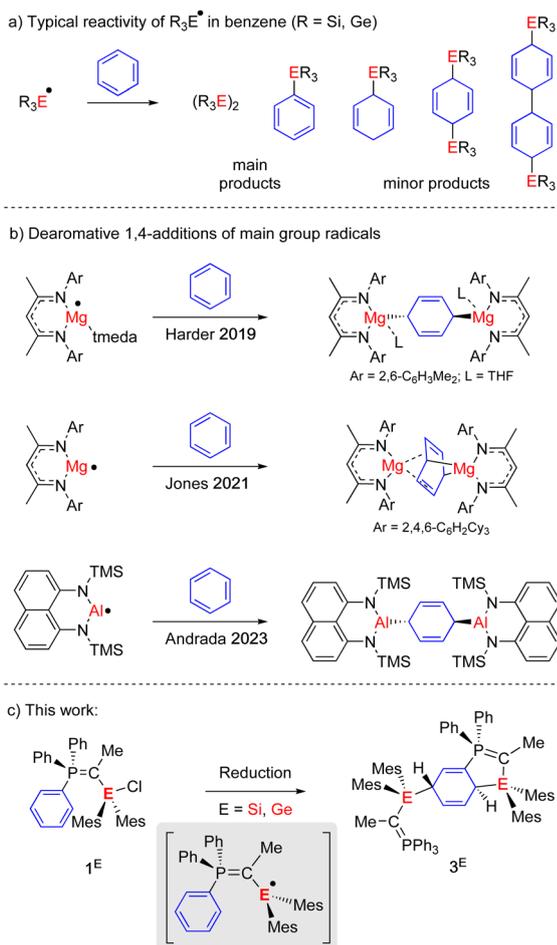
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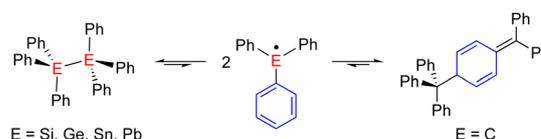
Scheme 1 Equilibrium of Gomberg-type radicals in solution.

a) Typical reactivity of R$_3$E$^\bullet$ in benzene (R = Si, Ge)

b) Dearomative 1,4-additions of main group radicals

c) This work:

**Scheme 2** (a) Typical reactivity of R$_3$E$^\bullet$ (E = Si, Ge) with benzene. (b) Recent reports of the dearomative 1,4-additions of main group element radicals to benzene. (c) Dearomative 1,4-addition of phosphorous ylide stabilized silyl and germyl radicals to a phenyl moiety reported in this work.

Dearomative 1,4-additions of radicals to benzene moieties resembling Birch-type reactivity are considered as promising tools for arene transformations.[9c] Reports from Harder,[11] Jones,[12] or Andrada[13] showcase this reaction mode for magnesium and aluminum compounds under reductive or photolytic conditions, clearly indicating the corresponding radicals to be the crucial intermediates (Scheme 2b). The Birch-type addition of silicon and germanium compounds to benzene scaffolds was by now achieved by cycloaddition strategies like the [4 + 3] cycloaddition reported by Wesemann[14] or the [2 + 2] cycloaddition reported by Cummins.[15] In our understanding, the dearomative 1,4-addition to phenyl rings is hard to accomplish with germyl radicals due to their low reactivity compared to group 2 or 13 and the relatively low Ge–C bond energies.

Herein, we present the observation of an intramolecular addition of phosphorus ylide-stabilized silyl and germyl radicals to a phenyl moiety at the ylidic P atom, followed by recombination of the formed phenyl radical with another group 14-centered radical (Scheme 2c).

We recently showed that α-silylated and α-germylated phosphorus ylides of the general formula Ph$_3$PC(R^1)E(Cl)R$^2_2$ (**1^E** with E = Si, Ge) constitute valuable precursors for accessing the cationic species [Ph$_3$PC(R^1)ER$^2_2$]$^+$.[16] We also became interested in whether the phosphorus ylides are capable of stabilizing group 14 radical species by the interaction of the P–C bond with the open-shell Si or Ge atoms. Studies indicated that for the mesityl-substituted derivatives Ph$_3$PC(Me)E(Cl)Mes$_2$ (**1^{Si}** and **1^{Ge}**), the radicals [Ph$_3$PC(Me)EMes$_2$]$^\bullet$ (**2^{Si}** and **2^{Ge}**) can be generated through reduction with Jones' dimer (^{Mes}NacNacMg)$_2$ in benzene, which leads to full conversion of the starting materials within several minutes (Scheme 3).[17] To our surprise, we were not able to isolate the free radicals. Although signals were detected during *in situ* cw-EPR spectroscopic studies, their intensity was very low, despite the high concentration of the samples. The lack of observable hyperfine couplings prevented a detailed EPR spectroscopic characterization. Although the appearance of EPR active species indicated radical pathways, initialised by one-electron reduction with Jones' reagent, the main product of the reaction seemed to be of diamagnetic nature.[18] *In situ* NMR spectroscopic studies showed a clean conversion of both starting materials (**1^{Ge}** and **1^{Si}**) into one new species (ESI, Fig. S10 and 11†). In the case of germanium, we were able to crystallize the Birch-type adduct **3^{Ge}** from hexanes (Fig. 1; space group $P\bar{1}$). It appears reasonable to assume that **3^{Ge}** is formed through the intramolecular attack of the initially formed germanium-centred radical **2^{Ge}** at one phenyl moiety of the Ph$_3$P fragment generating a five-membered ring bearing a radical in the aryl moiety. Afterwards, the phenyl-based radical recombines with another molecule **2^{Ge}** leading to the formation of **3^{Ge}**.

The P1–C1 bond in **3^{Ge}** (1.672(3) Å) is 10 pm shorter than the P2–C9 bond (1.682(3) Å), which is as long as the P1–C1 bond (1.683(3) Å) in **1^{Ge}** indicating the preservation of the ylidic function.[16] The bond lengths in the bridging six-membered ring (see caption of Fig. 1) clearly show the cyclohexadienyl character of the former aromatic moiety. The distances
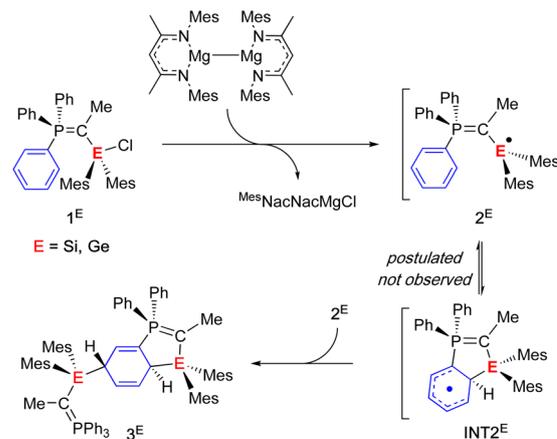
Scheme 3 Reduction of **1^E** with [^{Mes}NacNacMg]$_2$ in benzene at room temperature.
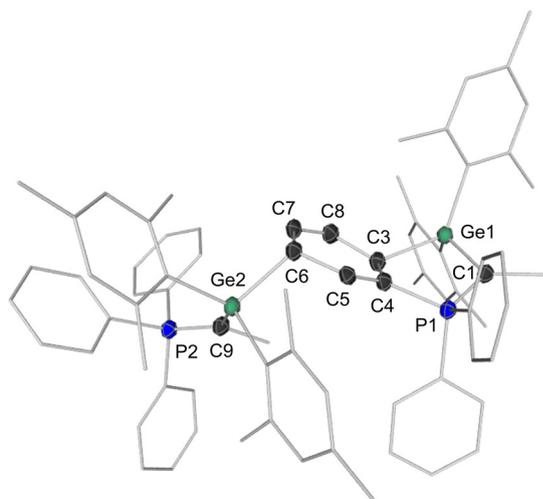
Fig. 1 Molecular structure of 3^{Ge}; ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): P1–C1 = 1.672(3), P2–C9 = 1.682(3), Ge1–C1 = 1.914(3), Ge1–C3 = 2.037(3), Ge2–C6 = 2.090(3), Ge2–C9 = 1.901(3), C3–C4 = 1.504(4), C3–C8 = 1.490(4), C5–C6 = 1.497(4), C6–C7 = 1.494(4), C4–C5 = 1.337(4), C7–C8 = 1.329(4); C1–Ge1–C3 = 95.49(12), P1–C1–Ge1 = 111.03(15), C9–Ge2–C6 = 103.71(12), P2–C9–Ge2 = 131.10(18), C3–C6–Ge1 = 125.2, C3–C6–Ge2 = 140.7.

between the bridging cyclohexyl ring and the germanium atoms are quite similar (Ge1–C3 = 2.037(3) Å; Ge2–C6 = 2.090(3) Å). The angles P1–C1–Ge1 = 111.03(15)° and P2–C9–Ge2 = 131.10(18)° differ by 20° from each other (*cf.* P1–C1–Ge1 = 126.85(11) for 1^{Ge}).[16]

The $^{31}P\{^1H\}$ NMR spectra of 3^{Si} and 3^{Ge} show two signals at δ_{31P} = 18.3 and 20.3 ppm (3^{Si}) and 18.1 and 18.5 ppm (3^{Ge}), respectively, which support the formation and stability of the unsymmetrical dimeric structures in solution. For 3^{Si}, two doublets with chemical shifts of δ_{29Si} = −11.8 and −34.7 ppm and $^2J_{PSi}$ coupling constants of 41.7 and 31.9 Hz were detected in the ^{29}Si NMR spectrum. In the ^1H NMR spectra, two distinct sets of signals for the mesityl and methyl moieties of 3^{Si} were detected. A set of multiplets for the cyclohexyl protons of the bridging ring is found at δ_{1H} = 8.14, 7.38, 7.08 and 6.95 ppm for 3^{Si}. The most characteristic signal at 8.14 ppm presents the *ortho* proton at the C5 atom. This is in good accordance with our previously reported *ortho*-substituted phosphorus ylides.[19] Similar spectra were obtained for 3^{Ge}, but the mesityl groups give four sets of signals, which could be due to a hindered rotation.

The fact that such reactivity with aromatic substrates was not reported so far for germyl and silyl radicals naturally raised the question on a conceivable equilibrium between dimeric (closed shell) and monomeric (radical) species. We therefore investigated solutions of 3^{Si} and 3^{Ge} in toluene-d_8 by variable temperature (VT) NMR experiments (293–363 K). However, both compounds showed no change in the ^1H NMR spectra at elevated temperatures (ESI, Fig. S8 and 9†), despite thermal activation of some hindered rotations along the steri-

cally crowded scaffolds, especially for the mesityl moieties. This suggested that within the probed temperature range, the dimerization of the radicals 2^E and $INT2^E$ (Scheme 3) is not reversible enough to form energetically unfavored monomer species in NMR-detectable amounts. Additionally, we challenged this question by more sensitive EPR spectroscopy, as especially 2^{Ge} was expected to show significant hyperfine coupling to germanium due to large calculated spin density on the Ge atom (ESI, Fig. S12 and 13†). However, both compounds 3^E are EPR-silent up to 80 °C, confirming the NMR observations discussed above that the dimerization of the radicals 2^E and $INT2^E$ is strongly exergonic.

To support these experimental findings, we computed the reaction pathway of the formation of 3^{Si} and 3^{Ge} at the PCM-M06-2X/def2-TZVPP//M06-2X/def2-SVP level. As can be seen from Fig. 2, the germanium-centred radical 2^{Ge} evolves into the radical intermediate $INT2^{Ge}$ in an endergonic transformation (ΔG = 8.7 kcal mol^{-1}) through the transition state **TS-Ge**, which is associated with the intramolecular addition of the radical to the adjacent phenyl group attached to the phosphorous. The computed barrier for this process is rather low ($\Delta G^{\ddagger}$ = 10.8 kcal mol^{-1}), which is mainly due to the close proximity of the reactive phenyl group to the Ge radical as a consequence of the occurrence of a stabilizing π–π interaction with one of the mesityl groups. This is confirmed by the relatively short distance between the centroids of both aryl groups
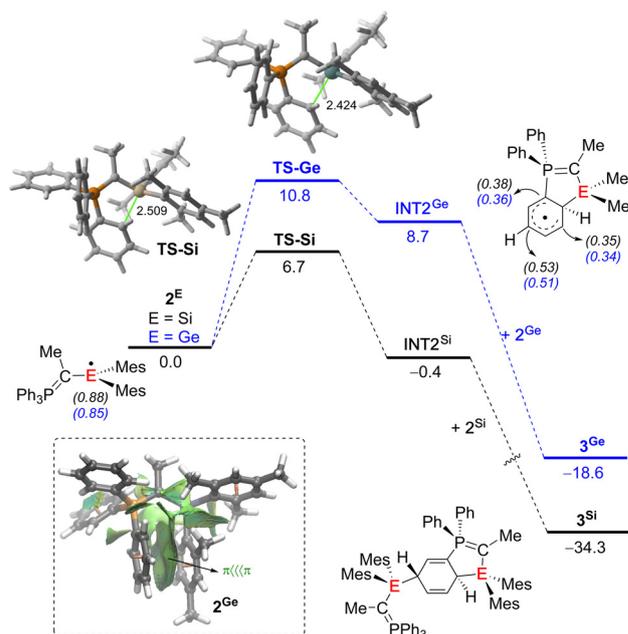

Fig. 2 Calculated reaction pathway to the formation of 3^{Si} and 3^{Ge}. Relative free energies (ΔG, at 298 K) and bond lengths are given in kcal mol^{-1} and angstroms, respectively. Values within parentheses indicate the computed spin-densities. Inset: contour plots of the reduced density gradient isosurfaces (density cutoff of 0.03 a.u.) for compound 2^{Ge}. The green surfaces indicate attractive non-covalent interactions All data have been computed at the PCM-M06-2X/def2-TZVPP//M06-2X-/def2-SVP level.

(3.56 Å) and by the NCIPLOT method, which clearly shows the existence of such π–π interaction (see inset in Fig. 2). In sharp contrast, the analogous intermolecular reaction involving benzene (solvent) proceeds with a much higher barrier of 29.0 kcal mol^{-1} indicating that this alternative reaction is not competitive. Indeed, the NMR spectroscopic studies of the reduction reaction showed also no reaction between the intermediary formed radicals 2^{Si} and 2^{Ge} with the solvent benzene-d_6. Subsequent recombination with another molecule 2^{Ge} in a barrierless process leads to the highly exergonic formation of 3^{Ge}. The analogous process involving 2^{Si} is favoured from both kinetic ($\Delta G^{\ddagger}$ = 6.7 kcal mol^{-1}) and thermodynamic (ΔG = −34.3 kcal mol^{-1}) points of view, which is not surprising considering the higher stability of the Si–C bond compared to the Ge–C bond.

Conclusively, we observed the dearomative 1,4-additions of the phosphorus ylide-stabilized silicon (2^{Si}) and germanium (2^{Ge}) radicals to phenyl moieties resembling Birch-type reactivity. The radicals [Ph$_3$PC(Me)EMes$_2$]$^{\bullet}$ were generated from α-silylated and -germylated phosphorus ylides Ph$_3$PC(Me)E(Cl)Mes$_2$ through one-electron reduction with Jones' dimer (^{Mes}NacNacMg)$_2$ in benzene. We observed the reaction because the radicals are (1) sterically shielded, (2) stabilized within the ylide π-system and (3) the barrier for intramolecular attack is low due to activation of the ring by the PPh$_3$ fragment and the close proximity of the reactive centres.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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