ABSTRACT: The preparation of triethylphosphine adducts of cyclic disilylated or digermylated germylenes was achieved by reaction of 1,4-dipotassio-1,1,4,4-tetrakis(trimethylsilyl)tetramethyltetrasilane with GeBr₂·(dioxane) and PEt₃. Phosphine abstraction with B(C₆F₅)₃ allowed formation of the base-free germylenes, which undergo 1,2-trimethylsilyl shifts to the germylene atom to form the respective silagermene or digermene, which further dimerize in [2 + 2] cycloadditions to tricyclic compounds. The reasons responsible for the germylenes’ completely different reactivities in comparison to the previously studied analogous stannylenes and plumbylenes were elucidated in a theoretical study.

1. INTRODUCTION

Over the last few years the advent of stable N-heterocyclic carbenes (NHCs) has revolutionized several branches of chemistry.¹⁻³ However, even before the first stable carbenes were reported already examples of stable germylenes, stannylenes, and plumbylenes were known.⁴ Having a close relationship to NHCs, most of these compounds derive their stability from the π-donation of attached nitrogen substituents, while compounds with more electropositive substituents were found to be much more reactive and thus more difficult to prepare and isolate. Seminal work by Klinkhammer and colleagues has nevertheless shown that stable examples of silylated stannylenes and plumbylenes can be obtained in a straightforward way.⁵⁻⁷ More recently Escudie, Castel and coworkers have reported that silylated and germylated stannylenes can be stabilized using coordinating NHCs.⁸ The same strategy was shown to stabilize also the silylated chlorogermylene (Me₃Si)₃SiGeCl.⁸ Previous attempts by Stalke and Heine⁹ and by Klinkhammer¹⁰ showed that the reaction of [tris(trimethylsilyl)silyl]lithium with GeBr₂ did not give bis[tris(trimethylsilyl)silyl]germanium as a stable compound but its isomer hexakis(trimethylsilyl)disilagermirane as the product of a rearrangement reaction. Using (Me₃Si)₃GeLi as the nucleophile, Mallela et al. reported similar chemistry leading to hexakis(trimethylsilyl)germirane.¹¹

Recently, we have reported on the synthesis of examples of cyclic disilylated stannylenes¹² and plumbylenes.¹³ The difference between the aforementioned work by Klinkhammer⁵ and our attempt was that we utilized a 1,4-tetrakis(trimethylsilyl)-tetramethyltetrasilanylene¹₄,¹⁵ unit, which can be considered as a linked variation of two tris(trimethylsilyl)silyl groups. While we initially expected these compounds to exhibit a chemical behavior similar to that of the acyclic analogues, it turned out that the cyclic nature renders the tetrylene atom more accessible so that dimerization becomes a more facile process.¹₂,¹³

With the elements Pb, Sn, and Ge exhibiting decreasing stability of the divalent state in this order, the respective disilylated tetrylenes reflect this by showing different mechanisms of stabilization. While bis[tris(trimethylsilyl)silyl]-lead⁵ was found to be monomeric even in the solid state, for the cyclic plumbylene a dimerization in the crystal was observed (Figure 1). The higher congener bis[tris(trimethylsilyl)silyl]tin was found to be monomeric in solution and dimeric in the solid state,⁶ while for the cyclic stannylene dimerization to a distannene in solution and the solid state was observed (Figure 1).
The synthesis of adducts of a disilylated germylene in the current study, together with the findings of Stalke, Klinkhammer, and Mallela, show that the decreased stability of disilylated germynes leads to a different mechanism of stabilization in comparison to analogous stannylene12 and plumbylenes.13 These results are consistent with older work by Klinkhammer and a very recent account by Lai, Li, and coworkers.17

2. RESULTS AND DISCUSSION

Synthesis. Reaction of 1,4-dipotassiumsalane14,15 or the respective 1,4-digermanium analogue 1a with GeBr₂(dioxane) and PEt₃ (Scheme 1) led to the clean formation of the germylene-PEt₃ adducts 2 and 2a. With these precursors in hand, it was possible to release the free germynes 3 and 3a by abstracting the phosphane with the strong Lewis acid B(C₆F₅)₃ (Scheme 1). As expected, germynes 3 and 3a are not stable but undergo a facile dimerization process. The interesting result is, however, that the dimerization process is not related to that observed for the analogous stannylene.12 The latter was found to dimerize to a distannene (Figure 1), whereas germynes 3 and 3a dimerize to the tricyclic compounds 5 and 5a (Scheme 1).

For the stannylene dimerization process the first step was found to be the formation of an exocyclic distannene, which then rearranges to its endocyclic isomer.12 In contrast to this, the first step of the germylene dimerization is a 1,2-trimethysilyl shift from the α-position to the germanium atom. The thus formed silagermene (4) or digermene (4a) undergoes a [2 + 2] cycloaddition to form 5 and 5a. The first step of this reaction sequence is likely analogous to what happened in the reactions described by Stalke, Klinkhammer, and Mallela.15 However, the acyclic examples can react by another 1,2-trimethysilyl shift to give an isomeric silylene, which eventually inserts into the Si–Si bond, thus forming a three-membered ring. While the cyclic silagermene 4 and digermene 4a could also undergo an additional 1,2-trimethysilyl shift, final insertion of the thus formed silylene or germylene into a Si–Si or Si–Ge bond is not likely, due to the cyclic nature of the molecule. Lacking opportunities for further intramolecular stabilization, 4 and 4a therefore react in an intermolecular [2 + 2] cycloaddition.

Reactions of 2 and 2a with 2,3,4,5-tetramethylimidazol-2-ylidene (NHCMe) proceeded smoothly to exchange PEt₃ against the carbene ligand and afforded the carbene-stabilized germynes 6 and 6a (Scheme 1).

NMR Spectroscopy. The NMR spectra of 2 and 2a do not exhibit very unusual chemical shifts. As the tricoordinated germanium atoms have configurational stability, the respective 1H, 13C, and 29Si spectra display different symmetry (vide infra). The 31P resonances at 14.8 ppm for 2 and 15.0 ppm for 2a are almost identical. They are interesting in comparison with the analogous stannylene and plumbylene PEt₃ adducts, for which resonances at −1.0 and −60 ppm, respectively, were observed.12,13 29Si resonances for the trimethylsilyl groups were found at −7.9 ppm for 2 and −2.0 and −4.1 ppm for 2a, which corresponds to a typical chemical shift difference between SiMe₃ and GeMe₃ groups attached to either Si or Ge. In addition, the SiMe₂ shifts of −22.7 ppm for 2 and −16.9 ppm for 2a and the resonance of the quaternary Si atom of 2 at −127.1 ppm are perfectly reasonable and do not differ much from the analogous compound with a dimethylgermylene unit in the ring.19 The 29Si NMR spectra of 6 and 6a are fairly similar to those of 2 and 2a, with all resonances shifted slightly to lower field. The 13C NMR shifts of the carbene carbon atoms of 6 and 6a were found at 174.0 and 175.6 ppm, which in comparison to the signal for the free carbene (213.7 ppm)21 also indicates the substantial Lewis acidity of the germynes 3 and 3a.

When PE₃ was abstracted from 2 at low temperature, direct NMR spectroscopic observation of silagermene 4 was possible. Especially the sp³-hybridized silicon atom with a chemical shift of δ 149.6 ppm is quite diagnostic for the detection of this molecule. This resonance is very close to that observed for the related stannylene (8BuMe₂Si)₂Ge→Si(SiBuMe₂)₂ (δ 144.0 ppm).22 In addition, 29Si NMR chemical shift calculations at the MP2/GIAO level predict for the silagermene...
The results of our computations suggest that the 1,2 silyl shift which transforms the germylene 3 into the silagermene 4 is slightly exergonic ($\Delta G^{298\circ} = -11$ kJ mol$^{-1}$) and is connected with a barrier of $\Delta G^{298\circ} = 69$ kJ mol$^{-1}$ (Figure 3). Although the isomeric hausene 7 is also close in energy ($G^{298\circ} = -3$ kJ mol$^{-1}$), it is separated from the silagermene 4 by a prohibitively high barrier. The results of our experimental study of the germylene–phosphane complex 2 and its transition state, 2(TS), for inversion. (M06-2X/def2tztzv (Ge), 6-311+G(dp) (P), 6-31G(d) (Si, C, H); hydrogen atoms omitted for clarity; color code Ge (red), Si (gray), P (orange), C (black)).

Figure 2. Tube representation of the germylene–phosphane complex 2 and its transition state, 2(TS), for inversion. (M06-2X/def2tztzv (Ge), 6-311+G(dp) (P), 6-31G(d) (Si, C, H); hydrogen atoms omitted for clarity; color code Ge (red), Si (gray), P (orange), C (black)).
mol silyl shift proceeds with a slightly smaller barrier (formation from silagermene 4 conditions. Similarly, silylene 8 energy differs by merely 6 kJ mol$^{-1}$ (calculated for the forward reaction 4 → 7) which practically excludes its formation from silagermene 4 under the applied reaction conditions. Similarly, silylene 8 is markedly destabilized in comparison to other investigated isomers ($G_{298}^{\text{rel}}(8) = 66$ kJ mol$^{-1}$), most probably due to the occurrence of sterically unfavorable vicinal 1,1,2,2-tetrakis(trimethylsilyl) substitution in this compound. This result suggests that silylene 8 is not of further relevance for the discussion.

From a thermodynamic point of view, the dimerization of germylene 3 to give digermene 10 and finally, after skeletal rearrangement,$^{12}$ the endocyclic digermene 11 (Figure 3) is practically thermoneutral in comparison to the formation of the silagermene 4. In contrast, the head-to-tail (HTD) and in particular the head-to-head (HHD, Figure 3) dimerizations of silagermene 4 to the tricyclic compounds 5 (HHD) and 9 (HTD) are strongly exergonic. These computational results suggest that, in agreement with the experimental results, the transient germylene 3 is converted under thermodynamic control preferentially to the head-to-head dimer 5. The large difference in Gibbs free energies between the HHD isomer 5 and the HTD isomer 9 of $\Delta G^{298}(5/9) = 84$ kJ mol$^{-1}$ is a result of the greater steric congestion in the HTD 9, as for smaller model systems this marked energy difference is not reflected by the results of the calculations. For example, the calculations for the two different cyclic dimers of H$_2$Si=Ge(H)SiH$_3$ predict an energy difference of merely 6 kJ mol$^{-1}$ in favor of the head-to-head dimer.

Quite similar results were obtained for the transformation of the germanium-substituted germylene 3a. In this case the 1,2-silyl shift proceeds with a slightly smaller barrier ($\Delta G^{298} = 52$ kJ mol$^{-1}$) to give the more stable digermene 4a ($G_{298}^{\text{rel}}(4a) = -13$ kJ mol$^{-1}$). Again the dimerization to give the head-to-head dimer 5a is favored over the formation of the corresponding head-to-tail dimer 9a ($\Delta G^{298}(5a/9a) = 83$ kJ mol$^{-1}$).

**X-ray Crystallography.** Crystal structure analysis provided molecular structures of compounds 2, 2a, 5, 5a, 6, and 6a in the solid state (Table S1, Supporting Information). As expected, compound pairs 2 and 2a, 5 and 5a, and 6 and 6a display isotypic behavior. The structures of 2 (Figure S-1, Supporting Information) and 2a (Figure 4) feature the five-membered ring in an envelope conformation with one of the E(SiMe$_3$)$_2$ units out of plane. The base ligands coordinate in an approximately orthogonal way to the plane which is spanned by the divalent tetrel atom and its two neighboring atoms of 2, 2a, 6, and 6a. For the NHC adducts 6 (Figure S-3, Supporting Information) and 6a (Figure 5) the angle between the EGe(II)E plane and the base–Ge bond base is more acute (6, 104.9°; 6a, 104.2°) in comparison to the PET$_3$ adducts (2, 113.6°). For 6 and 6a thus almost planar five-membered rings were observed. The tricyclic compounds 5 (Figure S-2, Supporting Information) and 5a (Figure 6) are interesting in that sense that they are highly branched. The fact that the [2 + 2] cycloaddition of the respective silgermene or digermene occurs in a head-to-head fashion leads to a dimer with a Ge–Ge bond with maximum branched atoms in the α-positions. The steric...
bulk of this arrangement leads to a very long Ge–Ge bond of 2.575(1) Å for 5a. The direct influence of steric can be estimated when this bonds is compared to the other Ge–Ge bond of the four-membered ring of 5a, which are with 2.4832(9) and 2.4617(9) Å much shorter. Related structures containing digermane units with silyl or germyl substituents feature Ge–Ge bond lengths ranging from 2.457 to 2.491 Å.

3. CONCLUSION

Although the chemistry of germynes has received much attention in recent times, most of the studied compounds are either N-heterocyclic compounds or at least carry π-donating substituents such as amino or alkoxy groups. Tetrylenes with more electropositive substituents are much more reactive, and substituents such as amino or alkoxy groups. Tetrylenes with 

*Organometallics* 2013, 32, 3404-3410

either Schlenk techniques or a glove box. All solvents were dried using a column-based solvent purification system.\textsuperscript{27} GeBr\textsubscript{2} (dioxane),\textsuperscript{38} 1,3,4,5-tetramethylimidazol-2-ylidene,\textsuperscript{39} 1,4,6,15 and 1a\textsuperscript{30} were prepared according to literature procedures. Potassium tert-butanoate was purchased from Merck. All other chemicals were obtained from different suppliers and used without further purification.

\textsuperscript{3400}°C (75.4 MHz),\textsuperscript{31}P (124.4 MHz), and\textsuperscript{29}Si NMR spectra (59.3 MHz) were recorded on a Varian INOVA 300 spectrometer. If not noted otherwise, C\textsubscript{2}D\textsubscript{6} was used as the solvent for all samples. To compensate for the low isotopic abundance of\textsuperscript{29}Si, the INEPT pulse sequence\textsuperscript{30,31} was used for the amplification of the signal.

**X-ray Structure Determination.** For X-ray structure analyses the crystals were mounted onto the tip of glass fibers, and data collection was performed with a Bruker-AXS SMART APEX CCD diffractometer using graphite-monochromated Mo K\textsubscript{α} radiation (0.71073 Å). The data were reduced to F\textsuperscript{2}, and corrected for absorption effects with SAIN\textsuperscript{32} and SADAB\textsuperscript{3,33} respectively. The structures were solved by direct methods and refined by full-matrix least-squares methods (SHELXL97).\textsuperscript{35} If not noted otherwise, all non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in calculated positions to correspond to standard bond lengths and angles. All diagrams were drawn with 30% probability thermal ellipsoids, and all hydrogen atoms were omitted for clarity. Unfortunately the obtained crystal quality of some substances was poor. This fact is reflected by quite high R and low \( \theta \) values.

Crystallographic data (excluding structure factors) for the structures of compounds 2, 2a, 5, 5a, 6 and 6a reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC 866887 (2), 866886 (2a), 866885 (5), 866890 (5a), 866889 (6), and 866888 (6a). Copies of the data can be obtained free of charge at http://www.ccdc.cam.ac.uk/products/csd/request/.

**2-Germa-1,1,3,3,3-tetrakis(trimethylsilyl)-2,2,3,3-tetramethylcyclopentasilan-2-ylidene–Triethylphosphane Adduct (2)**

Compound 1 (freshly prepared from (Me\textsubscript{3}Si)\textsubscript{3}Si(SiMe\textsubscript{2})\textsubscript{2}Si(SiMe\textsubscript{3})\textsubscript{3}, 1.85 g, 3.03 mmol) and KO\textsubscript{Bu} (714 mg, 6.36 mmol) in 10 mL of DME dissolved in 40 mL of THF/DME (3/1) was slowly added to a mixture of GeBr\textsubscript{2} (dioxane) (1.07 g, 3.33 mmol) and Ph\textsubscript{3}P (393 mg, 3.33 mmol) in 20 mL of THF at \( -80^\circ \) C. The mixture turned orange, and a white precipitate was formed. The mixture was stirred for 12 h and slowly reached ambient temperature. The solvent was removed under reduced pressure, and the dark orange residue was extracted with pentane (4 × 10 mL). After concentration to 10 mL and storage at \( -20^\circ \) C yellow crystals of 2 (1.42 g, 71%) were obtained. Mp: 139–144 °C dec. \textsuperscript{1}H NMR (δ in ppm): 0.43 (s, 36H, SiMe\textsubscript{3}), 0.51 (s, 121H, SiMe\textsubscript{2}), 0.82 (m, 9H, CH\textsubscript{2}CH\textsubscript{2}), 1.61 (m, 6H, CH\textsubscript{2}P), \textsuperscript{13}C NMR (δ in ppm): -1.2 (s, SiMe\textsubscript{3}), 3.8 (broad, SiMe\textsubscript{2}), 8.3 (d, \( J_{\text{CP}} = 5.7 \) Hz, CH\textsubscript{2}CH\textsubscript{2}), 19.9 (d, \( J_{\text{CP}} = 19.7 \) Hz, CH\textsubscript{2}P), \textsuperscript{29}Si NMR (δ in ppm): -7.9 (broad, s, SiMe\textsubscript{3}), -22.7 (d, \( J_{\text{SP}} = 9.7 \) Hz, SiMe\textsubscript{2}), -127.1 (d, \( J_{\text{SP}} = 15.2 \) Hz, SiSiMe\textsubscript{3}). \textsuperscript{11}P NMR (δ in ppm): 14.8. Anal. Calc. for C\textsubscript{2}H\textsubscript{8}GePh\textsubscript{3}Si\textsubscript{18} (656.03): C: 40.28, H: 9.68. Found: C: 39.36, H: 9.48. UV absorption: \( \lambda_{\text{max}} \) 261 nm (shoulder) (\( \epsilon_{\text{1}} = 2.2 \times 10^{4} \) M\textsuperscript{-1} cm\textsuperscript{-1}), \( \lambda_{\text{max}} \) 361 nm (\( \epsilon_{\text{2}} = 3.7 \times 10^{4} \) M\textsuperscript{-1} cm\textsuperscript{-1}), \( \lambda_{\text{max}} \) 414 nm (\( \epsilon_{\text{3}} = 1.9 \times 10^{4} \) M\textsuperscript{-1} cm\textsuperscript{-1}).

**1,2,3-Trigerma-1,1,3,3,3-tetrakis(trimethylsilyl)-2,2,3,3-tetramethylcyclopentasilan-2-ylidene–Triethylphosphane Adduct (2a)**

The procedure for 2 was carried out using 1a (freshly prepared from (Me\textsubscript{3}Si)\textsubscript{3}Si(SiMe\textsubscript{2})\textsubscript{2}Si(SiMe\textsubscript{3})\textsubscript{3}, 1.40 g, 2.00 mmol), KO\textsubscript{Bu} (471 mg, 4.20 mmol), GeBr\textsubscript{2} (dioxane) (705 mg, 2.20 mmol), and Ph\textsubscript{3}P (307 mg, 2.60 mmol). Yellow crystalline 2a was isolated (710 mg, 48%). Mp: 149–153 °C dec. \textsuperscript{1}H NMR (δ in ppm): 0.42 (s, 18H, SiMe\textsubscript{3}), 0.51 (s, 18H, SiMe\textsubscript{2}), 0.53 (s, 6H, SiMe\textsubscript{3}), 0.54 (s, 6H, SiMe\textsubscript{2}), 0.85 (m, 9H, CH\textsubscript{2}CH\textsubscript{2}), 1.61 (m, 6H, CH\textsubscript{2}P), \textsuperscript{13}C NMR (δ in ppm): -0.5 (SiMe\textsubscript{3}), -0.1 (SiMe\textsubscript{2}), -8.7 (d, \( J_{\text{CP}} = 5.3 \) Hz, CH\textsubscript{2}CH\textsubscript{2}), 20.1 (d, \( J_{\text{CP}} = 18.9 \) Hz, CH\textsubscript{2}P), \textsuperscript{29}Si NMR (δ in ppm): -2.0 (d, \( J_{\text{SP}} = 13.6 \) Hz, SiMe\textsubscript{3}), -4.1 (d, \( J_{\text{SP}} = 7.9 \) Hz, SiMe\textsubscript{2}), -16.9 (d, \( J_{\text{SP}} = 7.8 \) Hz, SiMe\textsubscript{2}). \textsuperscript{11}P NMR (δ in ppm): 15.0. Anal. Calc. for C\textsubscript{2}H\textsubscript{8}GePh\textsubscript{3}Si\textsubscript{18} (745.14): C: 35.46; H: 8.36. UV absorption: \( \lambda_{\text{max}} \) 259 nm (shoulder) (\( \epsilon_{\text{1}} = 2.1 \times 10^{4} \) M\textsuperscript{-1} cm\textsuperscript{-1}).
1,2-Digerma-1,2,3,3,6,7,10,10-octakis(trimethylsilyl)octamethyltricyclo[5.3.0.016]decasilane (5). A solution of 2 (200 mg, 0.305 mmol) was dissolved in 5 mL of pentane and slowly added to a stirred solution of B(C6F5)3 (156 mg, 0.305 mmol) in 5 mL of pentane. The mixture turned orange during the addition, and a colorless precipitate was formed. After 2 h the mixture was hydrolyzed with dilute H2SO4 (0.5 M), the organic layer was separated, the aqueous phase was extracted with Et2O (3 x 30 mL), and the extract was dried over Na2SO4. The solvent was removed under reduced pressure, and the yellowish resin crystallized from hexane, giving colorless crystals (105 mg, 64%). Mp: 180–186 °C dec. 1H NMR (δ ppm): 0.37 (s, 18H, SiMe2), 0.41 (s, 18H, SiMe2), 0.42 (s, 18H, SiMe2), 0.50 (s, 6H, SiMe2), 0.57 (s, 6H, SiMe2), 0.58 (s, 18H, SiMe2), 0.62 (s, 6H, SiMe2), 0.74 (s, 6H, SiMe2). 13C NMR (δ ppm): 1.0 (SiMe2), 1.6 (SiMe2), 2.3 (SiMe2), 4.6 (SiMe2), 5.1 (SiMe2), 5.3 (SiMe2), 6.1 (SiMe), 7.3 (SiMe2). 29Si NMR (δ ppm): −1.5 (SiMe2), −6.7 (SiMe2), −6.9 (SiMe2), −8.7 (SiMe2), −17.2 (SiMe2), −25.1 (SiMe2), −69.7 (SiMe2), −94.1 (SiMe2). Anal. Calcd for C32H96Ge6Si13 (1253.97): C, 30.65; H, 8.05; Si, 39.50. Found: C, 30.6; H, 8.0; Si, 39.5.

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

Acknowledgments
Support of the study was provided by the Austrian Fonds zur Förderung der wissenschaftlichen Forschung (FWF) via projects P-22678 and P-25124 and by the Deutsche Forschungsgemeinschaft (DFG) via project Mu1440/8-1. The High End Computing Resource Oldenburg (HERO) at the CvO University is thanked for computing time.

References
(23) Computed at MP2/GIAO/6-311G(d,p) (Si, Ge) and 6-31G(d) levels (C, H) using a structure of $C_{2v}$ molecular symmetry, optimized at M06-2X/def2tzvp.
(26) All calculations were done at the M06-2X/def2tzvp (Ge) and 6-31G(d) (Si, C, H) levels of theory. This model chemistry was calibrated using smaller systems for energies against the results of higher level computations up to the CCSD level and, for structures, against the experimental solid-state structures; see the Supporting Information for details.
(27) All calculations were done using the G09 program, Version B.01, 2010.