

# Photolysis of Phosphaketenyltetrylenes with a Carbazolyl Substituent

Chenxin Li<sup>[a]</sup> and Alexander Hinz<sup>\*[a]</sup>

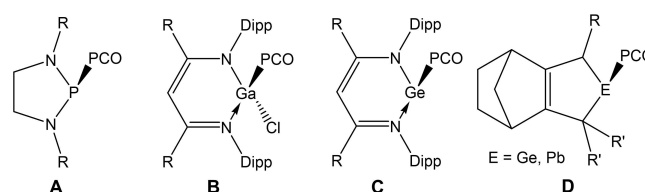
Phosphaketenes of divalent group 14 compounds can potentially serve as precursors for the synthesis of heavy multiple-bond systems. We have employed the <sup>dtbp</sup>Cbz substituent (<sup>dtbp</sup>Cbz = 1,8-bis(3,5-ditertbutylphenyl)-3,6-ditertbutylcarbazolyl) to prepare such phosphaketenyltetrylenes [(<sup>dtbp</sup>Cbz)EPCO] (E = Ge, Sn, Pb). While the phosphaketenyltetrylenes are stable at ambient conditions, they can be readily decarbonylated photo-

lytically. For the germylene and stannylene derivatives, dimeric diphosphene-type products [(<sup>dtbp</sup>Cbz)EP]<sub>2</sub> (E = Ge, Sn) were obtained. In contrast, photolysis of the phosphaketenytplumbylene, via isomerisation of the [(<sup>dtbp</sup>Cbz)PbP] intermediate to [(<sup>dtbp</sup>Cbz)PPb], afforded an unsymmetric and incompletely decarbonylated product [(<sup>dtbp</sup>Cbz)<sub>2</sub>Pb<sub>2</sub>P<sub>2</sub>CO] formally comprising a [(<sup>dtbp</sup>Cbz)PPb] and a [(<sup>dtbp</sup>Cbz)PbPCO] moiety.

## Introduction

Phosphaketenes have been recognised as versatile building blocks predominantly since work by Grützmacher<sup>[1,2]</sup> and Goicoechea<sup>[3]</sup> have made stable salts of the PCO<sup>-</sup> anion available on multigram scale.<sup>[4,5]</sup> A particular focus has been set on the generation of multiple bond species with main group elements of groups 13, 14 or 15. These attempts are commonly conducted by salt metathesis to generate phosphaketene compounds and subsequent decarbonylation, or by addition of Lewis acids or bases.

For instance, (phospholidino)phosphaketene (A, Scheme 1)<sup>[6]</sup> could be isomerized by strong nucleophiles such as NHCs to yield CPO species<sup>[7,8]</sup> and subsequent reduction afforded carbene-stabilized dicarbon diphosphide.<sup>[9]</sup> Goicoechea and co-workers found unexpected heterocycles, when an arsanylphosphaketene was treated with Lewis acids,<sup>[10]</sup> and Gilliard and co-workers found that with heavier homologues, Sb or Bi phosphaketenes, two NHCs could be coordinated to the PCO moiety with concomitant loss of the respective dipnictanes.<sup>[11]</sup> In another line of investigation, Bertrand and co-workers photolytically decarbonylated a phosphanyl phosphaketenes to give singlet a phosphinophosphinidene<sup>[12]</sup> which showed ambiphilic characteristics<sup>[13]</sup> and underwent ligand exchange reactions to replace CO by other moieties such as isonitriles,



Scheme 1. Selected known phosphaketene compounds.

carbenes, or Ga(I).<sup>[14,15]</sup> The phosphanyl phosphaketene was also used for the synthesis of various heterocycles.<sup>[16]</sup>

Phosphaketenes with group 13 substituents also attracted great interest. Goicoechea also studied boryl derivatives of PCO<sup>-</sup> and their isomerisation behaviour,<sup>[17]</sup> while Gilliard and coworkers utilised a borylphosphaketene as precursor for BP-doped phenanthryne. The group of Braunschweig studied adducts of the boraphosphaketene H<sub>2</sub>BPCO and their decarbonylation.<sup>[18]</sup> The heavier homologues, gallylphosphaketenes (B), were prepared by the groups of Grützmacher,<sup>[19]</sup> Goicoechea,<sup>[20]</sup> and Schulz and used as precursors for gallaphosphene synthesis.<sup>[21–23]</sup>

Among the group 14 derivatives, there are base-stabilised (i.e. tricoordinated tetrylenes) and base-free examples with dicoordinated tetrylenes. The tricoordinated species were investigated by the groups of Driess (C),<sup>[24,25]</sup> Kato (D),<sup>[26,27]</sup> Goicoechea,<sup>[28]</sup> Zhao,<sup>[29]</sup> and Aldridge,<sup>[30]</sup> and gave interesting products after decarbonylation. There is less precedence for base-free phosphaketenylyl tetrylenes. Goicoechea and Hinz reported on terphenyl- and aryl(silyl)amide-stabilised examples for Ge and Sn,<sup>[31,32]</sup> which demonstrated that steric bulk indeed allows control over the aggregation of decarbonylation products.

Recently, the Tan group prepared germlyenes with very bulky hydrindacene-based substituents which could serve as synthetic equivalents of [RGeP].<sup>[33]</sup>

We have previously introduced group 14 compounds with the bulky carbazolyl substituent <sup>dtbp</sup>Cbz (<sup>dtbp</sup>Cbz = 1,8-bis(3,5-ditertbutylphenyl)-3,6-ditertbutylcarbazolyl) that stabilised pseudo-monocoordinated cationic derivatives.<sup>[34,35]</sup> In this con-

[a] C. Li, A. Hinz

Karlsruhe Institute of Technology (KIT),  
Institute of Inorganic Chemistry (AOC),  
Engesserstr. 15,  
76131 Karlsruhe (Germany)  
E-mail: alexander.hinz@kit.edu

Supporting information for this article is available on the WWW under <https://doi.org/10.1002/asia.202300698>

This manuscript is part of a special collection on 17th International Conference on the Coordination and Organometallic Chemistry of Germanium, Tin and Lead (ICCO-CGTL).

© 2023 The Authors. Chemistry - An Asian Journal published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

tribution we present phosphaketenyltetrylenes with that carbazolyl substituent and investigated their photolysis.

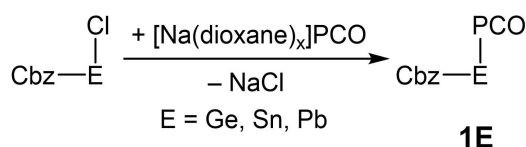
## Results and Discussion

The chlorotetrylenes [(<sup>dtbp</sup>Cbz)ECl] were prepared and treated with [Na(dioxane)<sub>x</sub>][PCO] in toluene (Scheme 2). As a readily accessible and more cost-efficient starting material instead of the chlorogermylene, also the bromogermylene [(<sup>dtbp</sup>Cbz)GeBr] can be employed. This can be prepared (see SI 2.1) from [(<sup>dtbp</sup>Cbz)K] and GeBr<sub>2</sub>(dioxane),<sup>[36]</sup> which in turn can be synthesised in high yield from GeBr<sub>4</sub> (accessible from the elements)<sup>[37]</sup> and tetramethyldisiloxane.

The metathesis reactions of halotetrylenes with PCO<sup>-</sup> salts proceeded smoothly and allowed the isolation of the phosphaketenyltetrylenes in good yields. The products could be obtained in crystalline form, but single crystals without co-crystallised solvent molecules were never allowed to establish a valid structural model. It should be noted, that a similar problem was already encountered with the chlorotetrylenes [(<sup>dtbp</sup>Cbz)ECl] (E=Sn, Pb), and the same unit cell was found for the corresponding phosphaketenes [(<sup>dtbp</sup>Cbz)EPCO] (**1Sn**, **1Pb**).

The phosphaketenylylgermylene **1Ge** could be crystallised with *n*-hexane in the asymmetric unit, which allowed the elucidation of the molecular structure (Figure 1).

The spectroscopic features of the tetrylenes **1E** reflect the presence of a phosphaketenylyl moiety with the characteristic



Scheme 2. Synthesis of phosphaketenylyltetrylenes [(<sup>dtbp</sup>Cbz)EPCO] (**1E**, E = Ge, Sn, Pb).

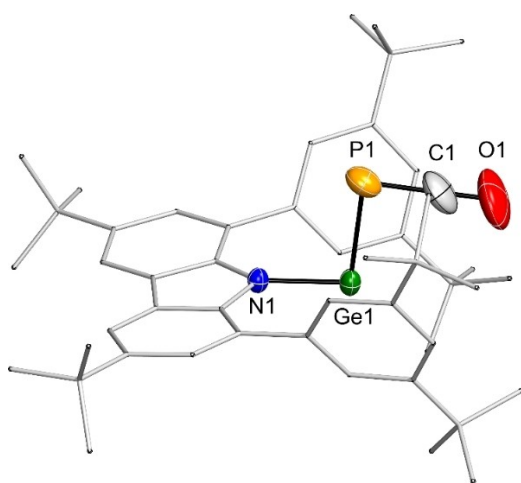
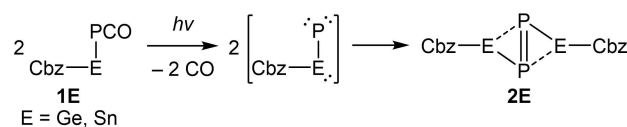


Figure 1. Molecular structure of [(<sup>dtbp</sup>Cbz)GePCO] (**1Ge**). Thermal ellipsoids with 50% probability. Selected bond lengths [Å] and angles [°]: Ge1–N1 1.9457(11), Ge1–P1 2.3875(5), P1–C1 1.641(3), O1–C1 1.153(3), N1–Ge1–P1 94.02(4), C1–P1–Ge1 86.37(9), O1–C1–P1 178.9(3).

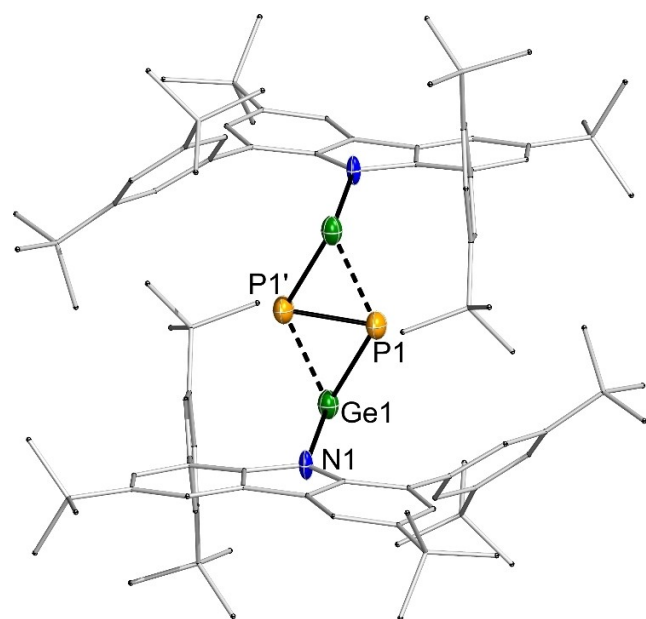
highfield-shifted <sup>31</sup>P NMR resonances (**1Ge** –234.3, **1Sn** –259.7, **1Pb** –241.0 ppm). For the stannylene **1Sn** and the plumbylene **1Pb**, satellite signals were observed with <sup>1</sup>J(<sup>31</sup>P–<sup>119</sup>Sn)=920 Hz and <sup>1</sup>J(<sup>31</sup>P–<sup>207</sup>Pb)=1110 Hz, respectively. The corresponding doublet in the <sup>119</sup>Sn NMR spectrum was recorded at +515.3 ppm while the <sup>207</sup>Pb NMR resonance could not be detected. The <sup>13</sup>C NMR resonances of the PCO moieties were observed as doublets due to coupling to the <sup>31</sup>P nucleus at 194.35 (<sup>1</sup>J(<sup>13</sup>C–<sup>31</sup>P)=103 Hz, **1Ge**), 190.91 (<sup>1</sup>J(<sup>13</sup>C–<sup>31</sup>P)=100 Hz, **1Sn**), and 189.14 ppm (<sup>1</sup>J(<sup>13</sup>C–<sup>31</sup>P)=105 Hz, **1Pb**), respectively. These coupling constants are considerably larger than observed for <sup>1</sup>J<sub>CP</sub> in phosphines (i.e. PMe<sub>3</sub> 10.9 Hz),<sup>[38]</sup> but agrees well with the <sup>1</sup>J<sub>CP</sub> observed in other P=C double bond species such as NHC-phosphinidene adducts<sup>[39,40]</sup> or other phosphaketenes (i.e. HPCO).<sup>[41]</sup> The <sup>31</sup>P NMR data show that in **1E**, the nucleus is less shielded than base-stabilised phosphaketenylyltetrylenes,<sup>[24,25,27,32]</sup> but more shielded than in dicoordinated arylsilylamido-stabilised phosphaketenylyl tetrylenes. In the IR spectrum, the ν(C=O) mode was detected at 1915, 1897, and 1882 cm<sup>-1</sup> for **1Ge**, **1Sn**, and **1Pb**. The UV/vis spectra of the three compounds differ only marginally as they show broad bands at 340 and 355 nm which extend further into the visible spectral region to cause the yellow or orange colour, respectively (see Figure S19).

The solutions of the phosphaketenylylgermylene and phosphaketenylylstannylene were irradiated with a medium-pressure Hg lamp to facilitate decarbonylation (Scheme 3). Indeed, clean reactions were observed by <sup>31</sup>P NMR spectroscopy, leading to new and broad <sup>31</sup>P NMR resonances at +696.4 ppm (ν<sub>1/2</sub>=60 Hz) for **2Ge** and +783.7 ppm (ν<sub>1/2</sub>=100 Hz) for **2Sn**. Already the pronounced downfield shift of the <sup>31</sup>P NMR signals indicated the formation of a diphosphene structural motif<sup>[17,25,42]</sup> which compare well to known bis(tetrylenyl)diphosphenes with a bulky aryl(silyl)amido substituent (+745.7 [(RGe)P]<sub>2</sub>, +797.8 ppm [(RSn)P]<sub>2</sub>).<sup>[32]</sup> However, the products tended to form microcrystalline precipitates out of these solutions within short time spans and could not be redissolved in large amounts, which hampered their solution-phase characterisation.

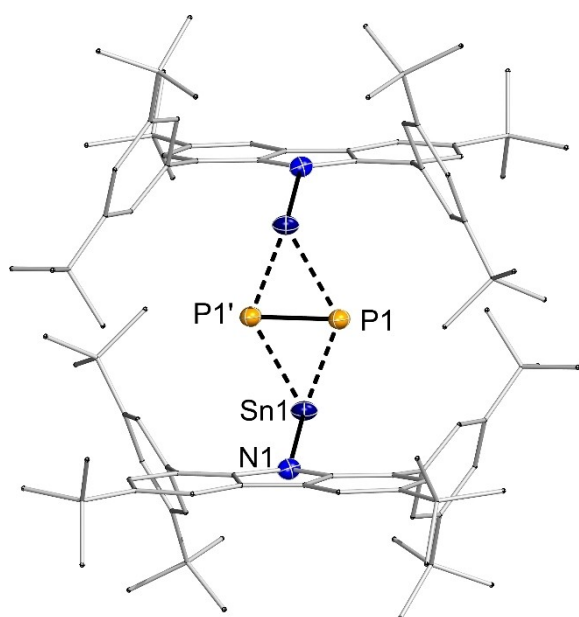
The structure of **2Ge** and **2Sn** was elucidated by single-crystal X-ray diffraction experiments (Figures 2 and 3). The key structural features comprise short P–P distances of 2.047(3) Å (**2Ge**) and 2.040(3) Å (**2Sn**), and only a small difference between the symmetry-independent Ge–P and Sn–P contacts, respectively (**2Ge**: Ge–P 2.488(2), Ge1–P1' 2.557(2); **2Sn** Sn1–P1 2.702(2), Sn1–P1' 2.710(2) Å). The differences in these distances are smaller than observed previously in bis(stannylenyl)diphosphenes, (2.647(1)/2.854(1) Å; 2.664(1)/2.760(1) Å),<sup>[32]</sup> which highlights the flexibility of the P<sub>2</sub> moiety coordinated by two tetrylenyl substituents and strongly ionic



Scheme 3. Photolysis of phosphaketenylyltetrylenes [(<sup>dtbp</sup>Cbz)EPCO] (**1E**, E = Ge, Sn) yielding diphosphenes **2E**.



**Figure 2.** Molecular structure of  $[(\text{dtbpcbz})\text{GeP}_2]_2$  (**2Ge**). Thermal ellipsoids with 50% probability. Selected bond lengths [Å] and angles [°]: Ge1–N1 1.952(5), Ge1–P1 2.4883(17), Ge1–P1' 2.5566(19), P1–P1' 2.047(3), P1–Ge1–P1' 47.86(6), P1'–P1–Ge1 67.82(8), P1–P1'–Ge1 64.32(9).



**Figure 3.** Molecular structure of  $[(\text{dtbpcbz})\text{SnP}_2]_2$  (**2Sn**). Thermal ellipsoids with 50% probability. Selected bond lengths [Å] and angles [°]: Sn1–N1 2.169(5), Sn1–P1 2.7018(18), Sn1–P1' 2.7100(18), P1–P1' 2.040(3), P1–Sn1–P1' 44.28(7), P1'–P1–Sn1 68.07(9), P1–P1'–Sn1 67.65(9).

interaction. The E–P–P'–E' dihedrals in **2Ge** and **2Sn** amount to  $180^\circ$ , as perfectly planar  $\text{E}_2\text{P}_2$  moieties are formed.

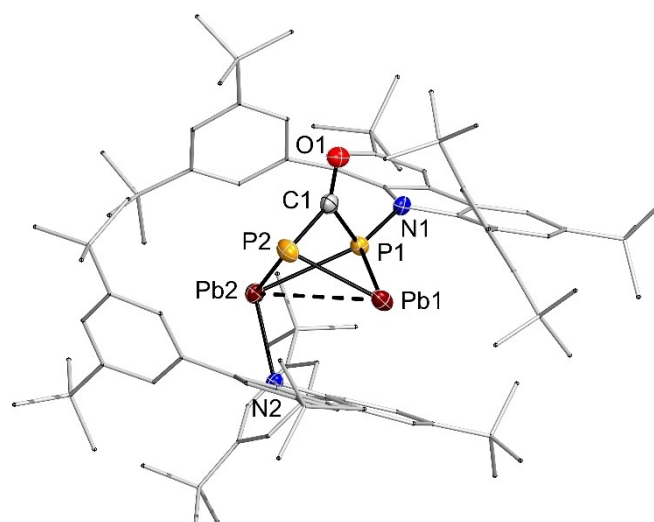
The NBO analysis<sup>[43]</sup> of both **2Ge** and **2Sn** showed two very similar E–P contacts in the respective molecules. The NBO charge on the  $[\text{P}_2]$  fragment was calculated as  $-0.42$  and  $-0.65$  e for **2Ge** and **2Sn**, respectively, not fully compensating the charge accumulated on a Ge (+0.82 e) or Sn (+1.00 e)

atom. The E–P Wiberg bond indices amount to 0.63 and 0.53 for **2Ge** and to 0.54 and 0.50 for **2Sn**. The NBO formalism indicates the bond with the higher WBI as covalent, while the other one can be described as dative interaction of a P lone pair into the empty E orbital by second order perturbation theory calculations (**2Ge**: 19 kcal/mol; **2Sn**: 14 kcal/mol). Similar donations were found for donation of the E–P bond into the vacant orbital of the not involved E atom (37; 33 kcal/mol), from a P lone pair to the antibonding E–P orbital (10; 10 kcal/mol), from the P–P  $\sigma$  bond (14; 8 kcal/mol) and from the P–P  $\pi$  bond (10; 7 kcal/mol). This reflects a highly dynamic situation where both E–P contacts are essentially equivalent, reminiscent of an ionic interaction between the  $[\text{Cbz}-\text{Ge}]^+$  and  $[\text{P}_2]^{2-}$  fragments.

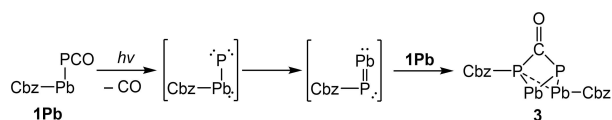
Surprisingly, the outcome of photolysis experiments with **1Pb** differed from the behaviour of its lighter congeners (Scheme 3). The  $^{31}\text{P}$  NMR spectrum of the reaction mixture showed two sets of doublets at 33.27 and 139.07 ppm with  $J_{\text{PP}}$  of 82.2 Hz. The signals still displayed broad  $^{207}\text{Pb}$  satellites. All  $^1\text{H}$  NMR resonances are broadened which indicates hindered molecular motion. Thus, not reductive elimination of  $\text{Pb}^0$  occurred as previously observed by Kato.<sup>[27]</sup>

The compound **3** also crystallised out of the reaction mixture and allowed the elucidation of its molecular structure (Figure 4). The central structural motif is a  $\text{Pb}_2\text{P}_2\text{CO}$  core, which has two  $\text{dtbpcbz}$  substituents bonded to one P and one Pb atom and thus can be envisaged as comprising a  $[(\text{dtbpcbz})\text{PPb}]$  and a  $[(\text{dtbpcbz})\text{PbPCO}]$  moiety. This indicates an isomerisation process of the intermediately generated  $[(\text{dtbpcbz})\text{PbP}]$  species to  $[(\text{dtbpcbz})\text{PPb}]$  (Scheme 4). The latter compound then attacks one further molecule of  $[(\text{dtbpcbz})\text{PbPCO}]$  (**1Pb**) to form **3**.

The bond metrics corroborate the presence of a weaker dative bond between P1 and Pb2 dative as it is the longest of the P–Pb distances (Pb2–P1 2.8918(11) Å vs. Pb1–P2 2.6744(14), Pb1–P1 2.7422(11), Pb2–P2 2.7018(13) Å). The



**Figure 4.** Molecular structure of  $[(\text{dtbpcbz})_2\text{Pb}_2\text{P}_2\text{CO}]$  (**3**). Thermal ellipsoids with 50% probability. Selected bond lengths [Å] and angles [°]: Pb1–Pb2 3.976(1), Pb1–P2 2.6744(14), Pb1–P1 2.7422(11), Pb2–N2 2.383(3), Pb2–P2 2.7018(13), Pb2–P1 2.8918(11), P1–N1 1.758(4), P1–C1 1.826(5), P2–C1 1.867(5), O1–C1 1.217(5), P2–Pb1–P1 65.16(4), P2–Pb2–P1 62.76(3).

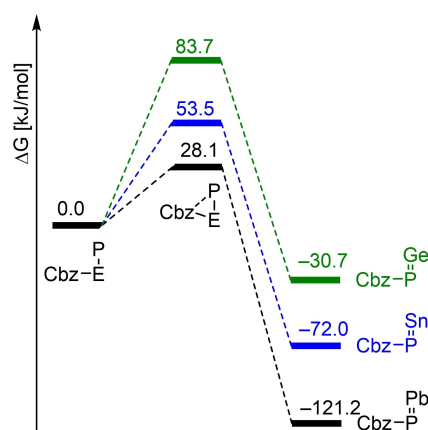


**Scheme 4.** Photolysis of phosphaketenylplumbylene  $[(^{dtbp}\text{Cbz})\text{PbPCO}]$  (**1Pb**) yielding diphosphenes **3**.

Pb–Pb distance amounts to 3.976(1) Å and thus precludes the presence of a Pb–Pb bond.

The P–C contacts are of similar length (P1–C1 1.826(5), P2–C1 1.867(5) Å). The  $\nu(\text{CO})$  vibration, observed as a shoulder at  $1599\text{ cm}^{-1}$  is superimposed with a band due to arene in-plane vibrations at  $1590\text{ cm}^{-1}$ . The assignment can be corroborated by DFT calculations, as the  $\nu(\text{CO})$  of **1Pb** was calculated at  $2027\text{ cm}^{-1}$  and observed at  $1882\text{ cm}^{-1}$ , yielding a scaling factor of 0.928. The unscaled calculated  $\nu(\text{CO})$  of **3** was calculated at  $1720\text{ cm}^{-1}$ , which leads to an expected scaled value of  $1596\text{ cm}^{-1}$ .

The unexpected isomerisation prompted us to computationally investigate this process (Gaussian16, PBE0-GD3BJ, Def2-SVP). For all three molecules  $[(^{dtbp}\text{Cbz})\text{EP}]$  the isomeric  $[(^{dtbp}\text{Cbz})\text{PE}]$  (E = Ge, Sn, Pb) is the more stable compound (Figure 5). The activation barrier required for the monomolecular rearrangement decreases along the sequence Ge > Sn > Pb from 83.7 kJ/mol to 53.5 and 28.1 kJ/mol, respectively. In the same manner, the energy gain upon isomerisation increases in the sequence Ge < Sn < Pb from –30.7 to –72.0 and –121.2 kJ/mol. Both trends highlight that for the heaviest congener, the initially formed  $[(^{dtbp}\text{Cbz})\text{EP}]$  is least thermodynamically favourable and most likely to rearrange which is in line with previous computational work by Su and co-workers.<sup>[44–46]</sup> Consequently, such isomerisation process was only observed for the photolysis of the Pb derivative  $[(^{dtbp}\text{Cbz})\text{PbPCO}]$ .



**Figure 5.** Calculated isomerisation pathways for  $[(^{dtbp}\text{Cbz})\text{EP}]$  (E = Ge, Sn, Pb).

## Conclusions

We have prepared three phosphaketenyl tetrylene bearing a bulky carbazoyl substituent. Their photolysis lead to the formation of diphosphene-type dimeric products for the germylene and stannylene case, respectively. This behaviour had been previously observed and underscores the high demand for sterically encumbering substituents to stabilise a hypothetical monomeric phosphagermyne or phosphastannyne. In contrast to this mode of dimerisation, in case of plumbylene photolysis a different outcome was observed. An unsymmetric and incompletely decarbonylated product comprising a  $[(^{dtbp}\text{Cbz})\text{PPb}]$  and a  $[(^{dtbp}\text{Cbz})\text{PbPCO}]$  subunit was obtained. This indicates that after photolysis, the initially formed  $[(^{dtbp}\text{Cbz})\text{PbP}]$  rapidly isomerises to  $[(^{dtbp}\text{Cbz})\text{PPb}]$ . This was observed for the first time and rationalised with the aid of DFT calculations.

## Supporting Information

The authors have cited additional references within the Supporting Information.<sup>[47–53]</sup>

## Acknowledgements

Financial support by the German Research Foundation (DFG) through the Emmy Noether Programme (HI 2063/1-1) and by the China Scholarship Council (CSC Fellowship for C.L.) is gratefully acknowledged. We thank Prof. Frank Breher and Prof. Peter Roesky for their continuous support. This work was carried out with the support of the Karlsruhe Nano Micro Facility (KNMF), a Helmholtz Research Infrastructure at Karlsruhe Institute of Technology (KIT). We acknowledge support by the state of Baden-Württemberg through bwHPC and DFG through grant no. INST 40/575-1 FUGG (JUSTUS 2 cluster). Open Access funding enabled and organized by Projekt DEAL.

## Conflict of Interests

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.

**Keywords:** tetrylenes · phosphaketene · photolysis · isomerization · diphosphene

- [1] F. F. Puschmann, D. Stein, D. Heift, C. Hendriksen, Z. A. Gal, H.-F. Grützmaier, H. Grützmaier, *Angew. Chem. Int. Ed.* **2011**, *50*, 8420–8423.  
[2] D. Heift, Z. Benkó, H. Grützmaier, *Dalton Trans.* **2014**, *43*, 831–840.

- [3] A. R. Jupp, J. M. Goicoechea, *Angew. Chem. Int. Ed.* **2013**, *52*, 10064–10067.
- [4] J. M. Goicoechea, H. Grützmacher, *Angew. Chem. Int. Ed.* **2018**, *57*, 16968–16994.
- [5] L. Weber, *Eur. J. Inorg. Chem.* **2018**, *2018*, 2175–2227.
- [6] Z. Li, X. Chen, M. Bergeler, M. Reiher, C. Su, H. Grützmacher, *Dalton Trans.* **2015**, *44*, 6431–6438.
- [7] Z. Li, X. Chen, Z. Benkő, L. Liu, D. A. Ruiz, J. L. Peltier, G. Bertrand, C.-Y. Su, H. Grützmacher, *Angew. Chem. Int. Ed.* **2016**, *55*, 6018–6022.
- [8] Z. Li, X. Chen, Y. Li, C.-Y. Su, H. Grützmacher, *Chem. Commun.* **2016**, *52*, 11343–11346.
- [9] Z. Li, X. Chen, D. M. Andrada, G. Frenking, Z. Benkő, Y. Li, J. R. Harmer, C.-Y. Su, H. Grützmacher, Z. Benkő, Y. Li, J. R. Harmer, C.-Y. Su, H. Grützmacher, *Angew. Chem. Int. Ed.* **2017**, *56*, 5744–5749.
- [10] M. Mehta, J. E. McGrady, J. M. Goicoechea, *Chem. Eur. J.* **2019**, *25*, 5445–5450.
- [11] J. E. Wallely, L. S. Warring, E. Kertész, G. Wang, D. A. Dickie, Z. Benkő, R. J. Gilliard, *Inorg. Chem.* **2021**, *60*, 4733–4743.
- [12] L. Liu, D. A. Ruiz, D. Munz, G. Bertrand, *Chem* **2016**, *1*, 147–153.
- [13] M. M. Hansmann, R. Jazzar, G. Bertrand, *J. Am. Chem. Soc.* **2016**, *138*, 8356–8359.
- [14] M. M. Hansmann, G. Bertrand, *J. Am. Chem. Soc.* **2016**, *138*, 15885–15888.
- [15] D. W. N. Wilson, J. Feld, J. M. Goicoechea, *Angew. Chem. Int. Ed.* **2020**, *59*, 20914–20918.
- [16] M. M. Hansmann, D. A. Ruiz, L. Liu, R. Jazzar, G. Bertrand, *Chem. Sci.* **2017**, *8*, 3720–3725.
- [17] D. W. N. Wilson, M. P. Franco, W. K. Myers, J. E. McGrady, J. M. Goicoechea, *Chem. Sci.* **2020**, *11*, 862–869.
- [18] S. Hagspiel, F. Fantuzzi, R. D. Dewhurst, A. Gärtner, F. Lindl, A. Lamprecht, H. Braunschweig, *Angew. Chem. Int. Ed.* **2021**, *60*, 13666–13670.
- [19] Y. Mei, J. E. Borger, D. J. Wu, H. Grützmacher, *Dalton Trans.* **2019**, *48*, 4370–4374.
- [20] D. W. N. Wilson, W. K. Myers, J. M. Goicoechea, *Dalton Trans.* **2020**, *49*, 15249–15255.
- [21] M. K. Sharma, C. Wölper, G. Haberhauer, S. Schulz, *Angew. Chem. Int. Ed.* **2021**, *60*, 6784–6790.
- [22] M. K. Sharma, C. Wölper, G. Haberhauer, S. Schulz, *Angew. Chem. Int. Ed.* **2021**, *60*, 21784–21788.
- [23] M. K. Sharma, P. Dhawan, C. Helling, C. Wölper, S. Schulz, *Chem. A Eur. J.* **2022**, *28*, e202200444.
- [24] S. Yao, Y. Xiong, T. Szilvási, H. Grützmacher, M. Driess, *Angew. Chem. Int. Ed.* **2016**, *55*, 4781–4785.
- [25] Y. Xiong, S. Yao, T. Szilvási, E. Ballester-Martínez, H. Grützmacher, M. Driess, *Angew. Chem. Int. Ed.* **2017**, *56*, 4333–4336.
- [26] N. Del Rio, A. Baceiredo, N. Saffon-Merceron, D. Hashizume, D. Lutters, T. Müller, T. Kato, *Angew. Chem. Int. Ed.* **2016**, *55*, 4753–4758.
- [27] V. Timofeeva, J. M. L. Baeza, R. Nougé, M. Syroeshkin, R. Segundo Rojas Guerrero, N. Saffon-Merceron, G. Altınbaş Özpınar, S. Rathjen, T. Müller, A. Baceiredo, T. Kato, *Chem. Eur. J.* **2022**, *28*, DOI 10.1002/chem.202201615.
- [28] S. Bestgen, M. Mehta, T. C. Johnstone, P. W. Roesky, J. M. Goicoechea, *Chem. Eur. J.* **2020**, *26*, 9024–9031.
- [29] Y. Wu, L. Liu, J. Su, J. Zhu, Z. Ji, Y. Zhao, *Organometallics* **2016**, *35*, 1593–1596.
- [30] D. C. H. Do, A. V. Protchenko, P. Vasko, J. Campos, E. L. Kolychev, S. Aldridge, *Z. Anorg. Allg. Chem.* **2018**, *644*, 1238–1242.
- [31] A. Hinz, J. M. Goicoechea, *Dalton Trans.* **2018**, *47*, 8879–8883.
- [32] A. Hinz, J. M. Goicoechea, *Chem. Eur. J.* **2018**, *24*, 7358–7363.
- [33] Y. He, C. Dai, D. Wang, J. Zhu, G. Tan, *J. Am. Chem. Soc.* **2022**, *144*, 5126–5135.
- [34] A. Hinz, *Chem. Eur. J.* **2019**, *25*, 3267–3271.
- [35] A. Hinz, *Angew. Chem. Int. Ed.* **2020**, *59*, 19065–19069.
- [36] N. A. Viktorov, T. K. Gar, I. S. Nikishina, V. M. Nosova, D. A. Ivashchenko, V. F. Mironov, *J. Gen. Chem. USSR (Engl. Transl.)* **1986**, *56*, 1359–1363.
- [37] J. Hlina, J. Baumgartner, C. Marschner, *Organometallics* **2010**, *29*, 5289–5295.
- [38] L. K. Krannich, R. K. Kanjolia, C. L. Watkins, *Magn. Reson. Chem.* **1987**, *25*, 320–324.
- [39] A. J. Arduengo, III, H. V. R. Dias, J. C. Calabrese, *Chem. Lett.* **1997**, *26*, 143–144.
- [40] O. Back, M. Henry-Ellinger, C. D. Martin, D. Martin, G. Bertrand, *Angew. Chem. Int. Ed.* **2013**, *52*, 2939–2943.
- [41] A. Hinz, R. Labbow, C. Rennick, A. Schulz, J. M. Goicoechea, *Angew. Chem. Int. Ed.* **2017**, *56*, 3911–3915.
- [42] L. Weber, *Chem. Rev.* **1992**, *92*, 1839–1906.
- [43] E. D. Glendening, C. R. Landis, F. Weinhold, *J. Comput. Chem.* **2013**, *34*, 1429–1437.
- [44] C. H. Lai, M.-D. Su, S.-Y. Chu, *Inorg. Chem.* **2002**, *41*, 1320–1322.
- [45] C. Lai, M. Su, S. Chu, *J. Phys. Chem. A* **2002**, *106*, 575–579.
- [46] Y.-H. Hu, M.-D. Su, *Chem. Phys. Lett.* **2003**, *378*, 289–298.
- [47] M. Westerhausen, *Inorg. Chem.* **1991**, *30*, 96–101.
- [48] M. R. Crimmin, A. G. M. Barrett, M. S. Hill, D. J. MacDougall, M. F. Mahon, P. A. Procopiou, *Chem. Eur. J.* **2008**, *14*, 11292–11295.
- [49] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176–2179.
- [50] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2015**, *71*, 3–8.
- [51] G. M. Sheldrick, *Acta Crystallogr. Sect. C* **2015**, *71*, 3–8.
- [52] C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Crystallogr.* **2011**, *44*, 1281–1284.
- [53] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. v. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. v. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Jr Montgomery, J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, *Gaussian 16, Revision B.01*, Gaussian Inc. Wallingford CT **2016**.

Manuscript received: August 9, 2023

Revised manuscript received: September 12, 2023

Accepted manuscript online: September 13, 2023

Version of record online: September 22, 2023