Photolysis of Phosphaketenyltetrylenes with a Carbazolyl Substituent

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Phosphaketenes of divalent group 14 compounds can potentially serve as precursors for the synthesis of heavy multiple-bond systems. We have employed the \(^{\text{E}}\text{Cbz}\) substituent \((^{\text{E}}\text{Cbz} = 1,8\text{-bis}(3,5\text{-diterbutylphenyl})-3,6\text{-diterbutylcarbazolyl})\) to prepare such phosphaketenyltetrylenes \((^{\text{E}}\text{Cbz})\text{EPcO} (E = Ge, Sn, Pb)\). While the phosphaketenyltetrylenes are stable at ambient conditions, they can be readily decarbonylated photolytically. For the germylene and stannylene derivatives, dimeric diphenophosphate-type products \((^{\text{E}}\text{Cbz})\text{EPPbP}\) were obtained. In contrast, photolysis of the phosphaketenyplumbylene, via isomerisation of the \((^{\text{E}}\text{Cbz})\text{PZPb}\) intermediate to \((^{\text{E}}\text{Cbz})\text{PZPbPb}\), afforded an unsymmetric and incompletely decarbonylated product \((^{\text{E}}\text{Cbz})\text{PbPbCO}\) formally comprising a \((^{\text{E}}\text{Cbz})\text{PbPbCO}\) moiety.

Introduction

Phosphaketenes have been recognised as versatile building blocks predominantly since work by Grützmacher[1,2] and Goicoechea[3] have made stable salts of the \(\text{PCO}^-\) anion available on multigram scale.\[^{[3,4]}\] 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, (phospholindino)phosphaketene (A, Scheme 1)\[^{[5]}\] could be isomerized by strong nucleophiles such as NHCs to yield CPO species\[^{[6]}\] and subsequent reduction afforded carbene-stabilized dicarbon diphosphides.\[^{[7]}\] Goicoechea and coworkers found unexpected heterocycles, when an arsanylphosphaketene was treated with Lewis acids,\[^{[8]}\] and Gilliard and coworkers 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.\[^{[9]}\] In another line of investigation, Bertrand and co-workers photolytically decarbonylated a phosphanyl phosphaketene to give singlet phosphinophosphinidene\[^{[10]}\] which showed amphiphilic characteristics\[^{[11]}\] and underwent ligand exchange reactions to replace CO by other moieties such as isonitriles, carbenes, or Ga\(^{[11,11]}\). The phosphanyl phosphaketene was also used for the synthesis of various heterocycles.\[^{[12]}\]

Phosphaketenes with group 13 substituents also attracted great interest. Goicoechea also studied boryl derivatives of \(\text{PCO}^-\) and their isomerisation behaviour,\[^{[13]}\] while Gilliard and coworkers utilised a borylphosphaketene as precursor for BP-doped phenanthrene. The group of Braunšchweig studied adducts of the borophosphaketene \(\text{H}_2\text{BPCO}\) and their decarbonylation.\[^{[14]}\] The heavier homologues, gallylphosphaketenes (B), were prepared by the groups of Grützmacher,\[^{[15]}\] Goicoechea,\[^{[16]}\] and Schulz and used as precursors for gallaphosphene synthesis.\[^{[21-23]}\]

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

Recently, the Tan group prepared germynes with very bulky hydridacene-based substituents which could serve as synthetic equivalents of \([\text{RGeP}]\).\[^{[33]}\]

We have previously introduced group 14 compounds with the bulky carbazolyl substituent \(^{\text{E}}\text{Cbz}\) \((^{\text{E}}\text{Cbz} = 1,8\text{-bis}(3,5\text{-diterbutylphenyl})-3,6\text{-diterbutylcarbazolyl})\) that stabilised pseudo-monocoordinated cationic derivatives.\[^{[34,35]}\] In this con-

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Results and Discussion

The chlorotetrylenes \([\text{[\text{dioxane}]C\text{Bz}]}\text{ECI}\) were prepared and treated with \([\text{Na(dioxane)}]_2\text{PCO}\) in toluene (Scheme 2). As a readily accessible and more cost-efficient starting material instead of the chlorogermylene, also the bromogermylene \([\text{[\text{dioxane}]C\text{Bz}]}\text{GeBr}\) can be employed. This can be prepared (see SI 2.1) from \([\text{[\text{dioxane}]}\text{KB}\) and \(\text{GeBr}_3\text{dioxane})\), which in turn can be synthesised in high yield from \(\text{GeBr}_3\) (accessible from the elements)\(^{37}\) and tetramethylsiloxane.

The metathesis reactions of halotetrylenes with \(\text{PCO}^-\) 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 \(\text{[\text{dioxane}]C\text{Bz}]}\text{ECI}\) \((\text{E} = \text{Sn, Pb})\), and the same unit cell was found for the corresponding phosphaketenes \(\text{[\text{dioxane}]C\text{Bz}]}\text{EPCO}\) \((\text{E} = \text{Ge, Sn})\).

The phosphaketenylgermylene \(1\text{Ge}\) 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 \(1\text{E}\) reflect the presence of a phosphaketenyli moiety with the characteristic high-field-shifted \(^{31}\text{P}\) NMR resonances \((1\text{Ge} = 234.3, 1\text{Sn} = 259.7, 1\text{Pb} = 241.0 \text{ppm})\). For the stannylenes \(1\text{Sn}\) and the plumbene \(1\text{Pb}\), satellite signals were observed with \(\text{J}(1\text{Sn}) = 1100 \text{Hz}\) and \(\text{J}(1\text{Pb}) = 1110 \text{Hz}\), respectively. The corresponding doublet in the \(^{199}\text{Sn}\) NMR spectrum was recorded at \(+515.3 \text{ppm}\) while the \(^{207}\text{Pb}\) NMR resonance could not be detected. The \(^{113}\text{C}\) NMR resonances of the PCO moieties were observed as doublets due to coupling to the \(^{79}\text{Ge}\) nucleus at \(194.35 \text{ppm}\) \((\text{J}(1\text{Ge}) = 103 \text{Hz}, 1\text{Ge})\), \(190.91 \text{ppm}\) \((\text{J}(1\text{Ge}) = 100 \text{Hz}, 1\text{Sn})\), and \(189.14 \text{ppm}\) \((\text{J}(1\text{Ge}) = 105 \text{Hz}, 1\text{Pb})\), respectively. These coupling constants are considerably larger than observed for \(\text{J}_{\text{CP}}\) in phosphines \((\text{i.e. PMe}_3, 10.9 \text{Hz})\),\(^{38}\) but agrees well with the \(\text{J}_{\text{CP}}\) observed in other \(\text{P} = \text{C}\) double bond species such as \(\text{NHC-phosphinite adducts}\)^{39,40} or other phosphaketenes \((\text{i.e. HPCO})\).\(^{41}\) The \(^{31}\text{P}\) NMR data show that in \(1\text{E}\), the nucleus is less shielded than base-stabilised phosphaketenyltetrylenes,\(^{24,25,27,32}\) but more shielded than in dicoordinated arylylamido-stabilised phosphaketenyl tetrylenes. In the IR spectrum, the \(\nu(\text{C} = \text{P})\) for \(1\text{E}\) was observed at 1915, 1897, and 1882 \text{cm}^{-1}\) for \(1\text{Ge}, 1\text{Sn}, 1\text{Pb}\),\(^{15}\) respectively. Indeed, clean photolysis of \(1\text{Ge}\) led to the formation of a diphosphene structural motif\(^{16,17}\) which compare well to known bis(tetrylenyl)diphosphenes with a bulky aryl(silylamido)-stabilised phosphaketenyl tetrylenes. In the IR spectrum, the \(\nu(\text{C} = \text{P})\) for \(1\text{E}\) was observed at 1915, 1897, and 1882 \text{cm}^{-1}\) for \(1\text{Ge}, 1\text{Sn}, 1\text{Pb}\),\(^{15}\) respectively. 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 \(2\text{Ge}\) and \(2\text{Sn}\) was elucidated by single-crystal X-ray diffraction experiments (Figures 2 and 3). The key structural features comprise short \(\text{P} = \text{P}\) distances of 2.047(3) \text{Å} \((2\text{Ge})\) and 2.040(3) \text{Å} \((2\text{Sn})\), and only a small difference between the symmetry-independent \(\text{Ge} = \text{P}\) and \(\text{Sn} = \text{P}\) contacts, respectively \((2\text{Ge}: \text{Ge} = \text{P} = 2.488(2) \text{Å, } 1\text{Pb} = 2.557(2); 2\text{Sn}: \text{Sn} = \text{P} = 2.702(2) \text{Å, } 1\text{Pb} = 2.710(2) \text{Å})\). The differences in these distances are smaller than observed previously in bis(stannylenyl)diphosphenes, \((2.647(1)/2.854(1) \text{Å}; 2.664(1)/2.760(1) \text{Å})\),\(^{32}\) which highlights the flexibility of the \(\text{P} = \text{P}\) moiety coordinated by two tetrylenyl substituents and strongly ionic bonds between the phosphaketenyl moiety and the trisubstituted tetrylenyl substituents.
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–E orbital (10; 10 kcal/mol), from the P–P σ bond (14; 8 kcal/mol) and from the P–P π 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 [Cbz–Ge]⁺ and [P₂]²⁻ fragments.

Surprisingly, the outcome of photolysis experiments with 1Pb differed from the behaviour of its lighter congeners (Scheme 3). The ¹³P NMR spectrum of the reaction mixture showed two sets of doublets at 33.27 and 139.07 ppm with Jₚₚ of 82.2 Hz. The signals still displayed broad ²⁰⁷Pb satellites. All ¹H NMR resonances are broadened which indicates hindered molecular motion. Thus, not reductive elimination of Pb²⁺ occurred as previously observed by Kato.³⁹

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 Pb₂P₂CO core, which has two ²⁰⁶Czb substituents bonded to one P and one Pb atom and thus can be envisaged as comprising a [(²⁰⁶Czb)PbP] and a [(²⁰⁶Czb)PbPCO] moiety. This indicates an isomerisation process of the intermediately generated [(²⁰⁶Czb)PbP] species to [(²⁰⁶Czb)PbPCO] (Scheme 4). The latter compound then attacks one further molecule of [(²⁰⁶Czb)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 Pb-Pb distances (Pb₂–P₁ 2.8918(11) Å vs. Pb₁–P₁ 2.6744(14), Pb₁–P₁ 2.7422(11), Pb₂–P₂ 2.7018(13) Å). The

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**Figure 2.** Molecular structure of [(²⁰₆Czb)GeP]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’–Ge₁ 67.82(8), P₁–P₁’–Ge₁ 64.32(9).

**Figure 3.** Molecular structure of [(²⁰₆Czb)SnP]²⁻ (2Sn). Thermal ellipsoids with 50% probability. Selected bond lengths [Å] and angles [°]: Sn₁–N₁ 2.169(5), Sn₁–P₁ 2.7018(13), Sn₁–P₁’ 2.7100(18), P₁–P₁’ 2.040(3), P₁–Sn₁–P₁’ 44.28(7), P₁’–Sn₁ 68.07(9), P₁–P₁’–Sn₁ 67.65(9).

**Figure 4.** Molecular structure of [(²⁰₆Czb)Pb₂(PCO)₃] (3). Thermal ellipsoids with 50% probability. Selected bond lengths [Å] and angles [°]: Pb₁–P₁ 3.976(1), Pb₁–P₁ 2.6744(14), Pb₁–P₁ 2.7422(11), Pb₂–N₁ 2.383(3), Pb₂–P₂ 2.7018(13), Pb₂–P₂ 2.8918(11), P₁–N₁ 1.758(4), P₁–C₁ 1.826(5), P₂–C₂ 1.867(5), O₁–C₁ 1.217(5), P₂–P₁–Sn₁ 65.16(4), P₂–P₂–P₁ 62.76(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 ν(CO) vibration, observed as a shoulder at 1599 cm⁻¹ is superimposed with a band due to arene in-plane vibrations at 1590 cm⁻¹. The assignment can be corroborated by DFT calculations, as the ν(CO) of 1Pb was calculated at 2027 cm⁻¹ and observed at 1882 cm⁻¹, yielding a scaling factor of 0.928. The unscaled calculated ν(CO) of 3 was calculated at 1720 cm⁻¹, which leads to an expected scaled value of 1596 cm⁻¹.

The unexpected isomerisation prompted us to computationally investigate this process (Gaussian16, PBE0-GD3BJ, Def2-SVP). For all three molecules ([τ(Cbz)Pb(PCO)] the isomeric ([τ(Cbz)Pb(PE)]) 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 congeners, the initially formed [τ(Cbz)Pb(PCO)] is least thermodynamically favourable and most likely to rearrange which is in line with previous computational work by Su and co-workers. Consequently, such isomerisation process was only observed for the photolysis of the Pb derivative ([τ(Cbz)Pb(PCO)].

Conclusions

We have prepared three phosphaketenylenyltetrylenes bearing a bulky carbazolyl substituent. Their photolysis lead to the formation of diphoshene-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 phosphastanynyne. 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 [τ(Cbz)Pb(PCO)] and a [τ(Cbz)Pb(PCO)] subunit was obtained. This indicates that after photolysis, the initially formed [τ(Cbz)Pb(PCO)] rapidly isomerises to [τ(Cbz)Pb(PCO)]. 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.

Acknowledgements

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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.

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