Main-Group Chemistry

International Edition: DOI: 10.1002/anie.201701337
German Edition: DOI: 10.1002/ange.201701337

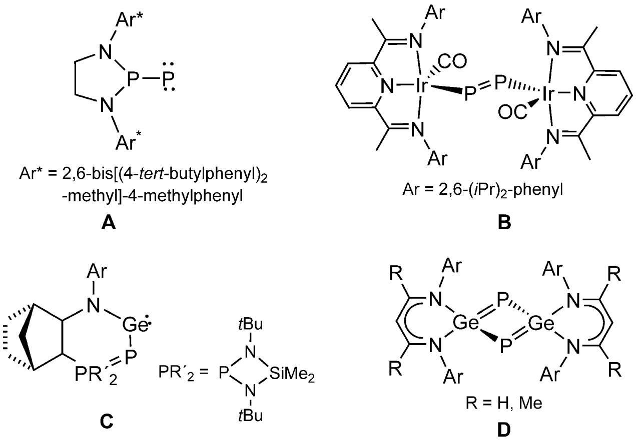
Unexpected Photodegradation of a Phosphaketenyl-Substituted Germyliumylidene Borate Complex

*Yun Xiong, Shenglai Yao, Tibor Szilvási, Ernesto Ballestero-Martínez, Hansjörg Grützmacher, and Matthias Driess**

In memory of Gerd Becker

Abstract: *The first zwitterionic borata-bis(NHC)-stabilized phosphaketenyl germyliumylidene [(L_2(O=C=P)Ge:] **2** (L_2 = (p-tolyl)$_2$B[1-(1-adamantyl)-3-yl-2-ylidene]$_2$) has been synthesized by salt-metathesis reaction of [L_2(Cl)Ge:] **1** with sodium phosphaethynolate [(dioxane)$_n$NaOCP]. Unexpectedly, its exposure to UV light affords, after reductive elimination of the entire PCO group, the unprecedented [L_2Ge-GeL_2] complex **3** in 54% yields bearing the Ge_2^{2+} ion with Ge in the oxidation state +1. In addition, the 1,3-digermylium-2,4-diphosphacyclobutadiene [L_2Ge(μ-P)$_2$GeL_2] **4** and bis(germyliumylidenyl)-substituted diphosphene [(L_2Ge-P=P-GeL_2)] **5** could also be obtained in moderate yields. The formation of **3–5** and their electronic structures have been elucidated with DFT calculations.*

The 2-phosphaethynolate anion, PCO$^-$, the phosphorus analogue of the cyanate ion, NCO$^-$, is an ambident ligand owing to its two resonance structures, 2-phosphaethynolate versus 2-phosphaketenide, P≡C-O$^-$↔$^-$P=C=O. However, the presence of unfavorable P–C multiple bonding causes a much higher reactivity of this species if compared with the cyanate anion which has impeded its characterization and isolation. In a landmark discovery, Becker et al. were able to synthesize P≡C–OLi as the first isolable and structurally characterized PCO species from the reaction of dimethyl carbonate with LiP(SiMe$_3$)$_2$ in 1992.[1a] Its reactivity towards oxidizing reagents was investigated by the same group.[1b,c] Following this seminal work, facile access to the more stable [(dioxane)$_n$NaOCP] salts,[2] developed by Grützmacher and coworkers, has enabled comprehensive reactivity studies on the PCO anion in recent years.[3–5] Because the PCO moiety readily undergoes elimination of CO under UV irradiation or thermolysis it led to the formation of a range of unexpected novel phosphorus compounds. Striking examples include the phosphanyl supported phosphinidene **A** (Scheme 1),[4a] the dimetalladiphosphene **B**,[4b] and the phosphoranylidenylgermylene **C**.[4c] Employing the β-diketiminate ligands L, we and others reported the formation of the 1,3-digerma-2,4-diphosphacyclobutadiene framework in **D**, through CO-release from the corresponding phosphaketenyl-substituted germylenes, [LGePCO], and head-to-tail dimerization of LGeP.[5]



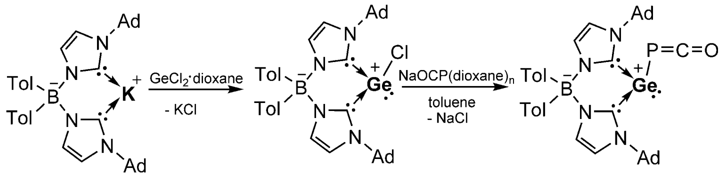
Scheme 1. Selected CO-release products **A–D** from the corresponding phosphaketenyl precursors.

Recently, N-heterocyclic carbenes (NHCs) have proven to serve as efficient donor ligands for the stabilization of many reactive species.[6] In this context, we successfully employed a bis-NHC borate ligand in the stabilization of the chlorogermyliumylidene [ClGe:]$^+$, hydrogermyliumylidene [HGe:]$^+$, and germanium dication Ge^{2+}.[7] Encouraged by these results we synthesized the new sterically encumbered bis-NHC-supported chlorogermyliumylidene borate [L_2GeCl] **1** (Scheme 2, L_2 = (p-tolyl)$_2$B[1-(1-adamantyl)-3-yl-2-ylidene]$_2$) aiming at generating the phosphaketenyl-substituted germyliumylidene borate [L_2Ge-PCO)] **2**. Herein, we report the synthesis and unusual reactivity of **2** which led to the isolation of the first [Ge^I–Ge^I]$^{2+}$ diborate complex **3**, [L_2Ge-GeL_2], as the main product. In addition, the zwitterionic 1,3-digermylium-2,4-diphosphacyclobutadiene diborate [L_2Ge(μ-P)$_2$GeL_2] **4** and the first bis(germyliumylidenyl)di-

---

[*] Dr. Y. Xiong, Dr. S. Yao, M. Sc. E. Ballestero-Martínez, Prof. Dr. M. Driess
Department of Chemistry: Metalorganics and Inorganic Materials
Technische Universität Berlin
Strasse des 17. Juni 135, Sekr. C2, 10623 Berlin (Germany)
E-mail: matthias.driess@tu-berlin.de
Dr. T. Szilvási
Department of Chemical & Biological Engineering
University of Wisconsin-Madison
1415 Engineering Drive, Madison, WI 53706 (USA)
Prof. Dr. H. Grützmacher
Department of Chemistry and Applied Biosciences, ETH Zürich
Vladimir-Prelog Weg 1, Hönggerberg, 8093 Zürich (Switzerland)

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under: http://dx.doi.org/10.1002/anie.201701337.



Ad = 1-adamantyl, Tol = *p*-tolyl **1** **2**

Scheme 2. Synthesis of the bis-NHC supported chlorogermyliumylidene borate **1** and the corresponding phosphaketenyl germyliumylidene borate **2**.

phosphene diborate complex [L$_2$Ge-P=P-GeL$_2$] **5** could also be obtained (Scheme 3).

The synthesis of the chlorogermyliumylidene borate **1** is straightforward, starting from the potassium salt [L$_2$K] and GeCl$_2$(dioxane) (Scheme 2). It can be isolated as an off-white powder in 90% yields and was fully characterized (see Supporting Information).

The equimolar reaction of **1** with [(dioxane)$_n$NaOCP] ($n =$ 2.5–2.8) in toluene affords the desired phosphaketenylgermyliumylidene borate [L$_2$Ge-PCO)] **2** in 67% yield as yellow crystals (Scheme 2). The ^{31}P-NMR spectrum of **2** shows a singlet at $\delta = -325.8$ ppm, which is shifted upfield by more than 20 ppm compared with those of the β-diketiminato ligand supported phosphaketenyl germylenes [LGePCO] ($\delta = -298.9$–-304.9 ppm).[5] The IR-spectrum of **2** exhibits an intense stretching vibration mode at $\nu = 1879$ cm^{-1} for the PCO group, which falls in the range of those values observed for related [LGePCO] compounds (1879–1895 cm^{-1}).[5]

The molecular structure of **2** has been established by an single-crystal X-ray diffraction analysis. It crystallizes in the monoclinic space group $P2_1/c$ (Figure 1). The Ge^{II} atom, coordinated by two carbene-carbon atoms and one phosphorus atom, adopts a trigonal pyramidal geometry. This implies that the vertex of the pyramid features a lone pair of electrons for the Ge^{II} center. The P-C-O angle is almost linear (176.7(2)°), and the Ge–P distance of 2.483(1) Å is comparable to those in related [LGePCO] compounds (2.476(1)–2.514(1) Å).[5] The P–C distance of 1.617(2) Å in **2** falls also in the range for those in [LGePCO] (1.609(4)–1.643(2) Å), while the C–O bond distance of 1.162(3) Å in **2** is slightly shorter than those in [LGePCO] (1.166(3)–1.170(3) Å).

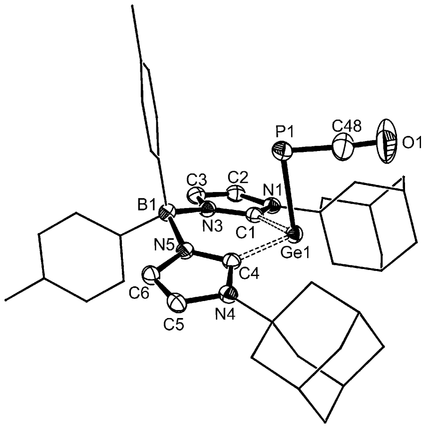
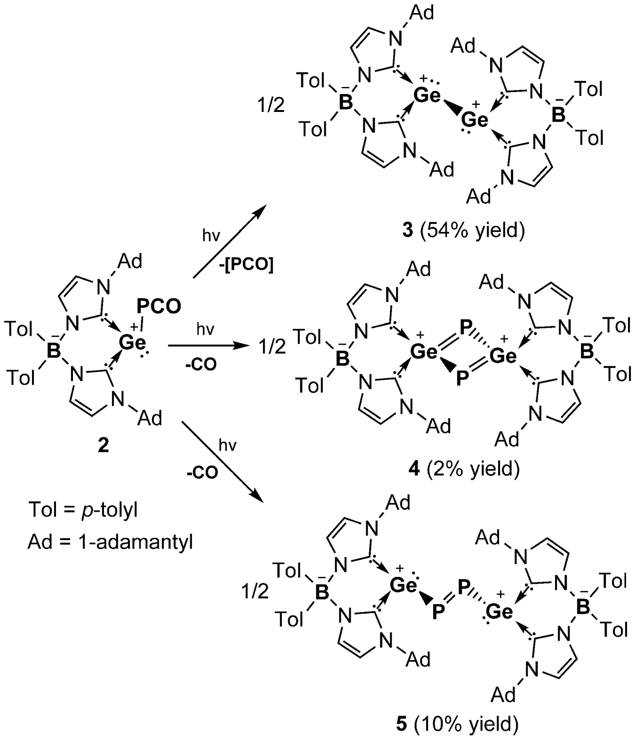


Figure 1. Molecular structure of **2**. Thermal ellipsoids are set at 50% probability. H atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Ge1–C1 2.044(2), Ge1–C4 2.047(2), Ge1–P1 2.483(1), P1–C48 1.617(2), O1–C48 1.162(3); C4-Ge1-C1 90.57(6), C4-Ge1-P1 90.59(4), C1-Ge1-P1 92.48(4), O1-C48-P1 176.7(2).

Compound **2** is not only air- and moisture-sensitive, but also sensitive towards daylight in solutions as indicated by the slow color change from yellow to orange-red. In line with that, UV/Vis measurements revealed an absorption maximum at 354 nm arising from the π–π* transition of the P=C bond in **2**, which shows a significant red-shift compared with those of [LGePCO] (320 and 325 nm).[5a] Irradiation of the yellowish toluene solutions of **2** in the UV/Vis region of $\lambda = 320$–400 nm for 2 h at room temperature afforded a dark-red solution. After work-up of this solution the bis(germyliumylidene) diborate [L$_2$Ge-GeL$_2$] **3** could be obtained as the main product in 54% yields in the form of an orange solid (Scheme 3). In addition, two more products could be isolated through fractional crystallization: 1) orange crystals of the 1,3-digermylium-2,4-diphosphacyclobutadiene diborate [L$_2$Ge(μ-P)$_2$GeL$_2$] **4** in 2% yield, and 2) deep red crystals of the bis(germyliumylidenyl)diphosphene diborate [L$_2$Ge-P=P-GeL$_2$] **5** in 10% yield.

The mechanisms are still unknown. However, the formation of **4** and **5** can be sketched by means of DFT calculations (for details see Supporting Information); they result from the two possible reactive intermediates L$_2$Ge≡P and L$_2$(Ge:)-P: after liberation of CO. Notably, the phosphinidene species L$_2$(Ge:)-P: is predicted to be favored over the phosphagermyne L$_2$Ge≡P: by 4.5 kcal mol^{-1}. Subsequent dimerization via head-to-tail and head-to-head fashion of the unsaturated Ge–P moiety in the phosphinidene affords **4** and **5**. As further UV-irradiation or prolonged heating of **4** and **5** did not lead to **3**,



Scheme 3. Formation of the bis(germyliumylidene) diborate **3**, 1,3-digermylium-2,4-diphosphacyclobutadiene diborate **4**, and bis(germyliumylidenyl)diphosphene diborate **5** after exposure of **2** to UV light.

compound **3** results from **2** through unprecedented photolytic reductive elimination of the entire PCO group and subsequent Ge^I–Ge^I bond formation. The fate of the PCO fragment is currently unknown but led to unidentified phosphorus-containing compounds in the reaction mixture (^{31}P-NMR).

Compound **3** has been fully characterized by ^{1}H- and ^{13}C-NMR spectroscopy, elemental analysis, and IR spectroscopy. The molecular structure of **3** determined by an X-ray diffraction analysis exhibits a [Ge^I-Ge^I]$^{2+}$ moiety supported by two bis-NHC borate ligands in the *trans* conformation (Figure 2). The average Ge–C distance of 2.058(3) Å in **3** is quite close to that in **2** (2.045(2) Å). Both Ge atoms in **3** are three-coordinated and each adopts a trigonal-pyramidal geometry, implying their germyliumylidene character. The Ge–Ge distance of 2.673(1) Å in **3** is longer than the Ge–Ge distance (2.569(5) Å) in the neutral digermylene {[PhC-(N*t*Bu)$_2$]Ge:}$_2$ by about 0.1 Å,[8a] presumably, a result of the steric congestion caused by the adamantyl groups and the electronic interaction between the two Ge atoms. In agreement with that, DFT calculations revealed a Ge–Ge distance of 2.701 Å (vs. 2.673(1) Å by X-ray) with Mayer Bond Order (MBO) of 0.58, indicating a weak Ge–Ge single bond. It should be mentioned here that two mono NHCs supported diatomic :Ge=Ge: species were described recently by Jones and co-workers.[6b] Recently, a cryptand-encapsulated germanium(II) dication was reported by Baines as the first structurally characterized Ge^{2+} dication supported by Lewis donors.[8b] The zwitterionic compound **3** represents the first example of a bis(germyliumylidene) complex bearing the Ge$_2$$^{2+}$ ion with Ge in the oxidation state +1.

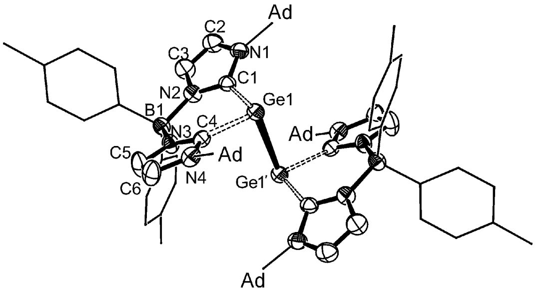


Figure 2. Molecular structure of **3**. Ad = 1-adamantyl. Thermal ellipsoids are set at 50% probability. H atoms are omitted for clarity. Symmetry transformations used to generate equivalent atoms with (′): $-x+1$, $-y+1$, $-z+1$. Selected interatomic distances [Å] and angles [°]: Ge1–C1 2.062(3), Ge1–C4 2.053(3), Ge1–Ge1′ 2.673(1); C1-Ge1-C4 89.65(11), C4-Ge1-Ge1′ 93.26(8), C1-Ge1-Ge1′ 96.74(8).

Compound **4** is sparingly soluble in organic solvents. Its ^{31}P NMR spectrum recorded in C$_6$D$_6$ exhibits a signal at $\delta =$ 28.4 ppm (vs. GIAO ^{31}P NMR: $\delta = 15$ ppm). This signal is significantly shifted upfield compared to that of **D** (Scheme 1, $\delta = 87.0$ ppm for R = H; $\delta = 131.9$ ppm for R = Me).[5] The molecular structure of **4** established by an X-ray single crystal diffraction analysis reveals a planar four-membered Ge$_2$P$_2$ ring supported by two anionic bis-NHC borate ligands (Figure 3). The two Ge atoms are thus each coordinated by two bis-NHC-carbene carbon and two P atoms and adopt a distorted tetrahedral coordination geometry. The average Ge–C distance of 2.047(2) Å is close to those in **2** (2.045(2) Å) and in **3** (2.058(3) Å), indicating a similar bonding situation between the bis-NHC and the Ge atoms in these complexes. In contrast, the Ge–P distances of 2.272(1) Å and 2.291(1) Å in **4** are significantly shorter than the Ge–P bond in **2** (2.483(1) Å). Consistently, the calculations show slight alteration in the bond length of Ge–P bonds (2.320 and 2.297 Å) and the MBO exhibits two distinct Ge–P bonds (1.01 and 1.12, respectively). This is obviously owing to the extensive σ- and π-electron resonance stabilization within the Ge$_2$P$_2$ ring and reminiscent of the bonding situation of **D** (Ge–P distances ranging from 2.255(1) to 2.272(1) Å).[5]

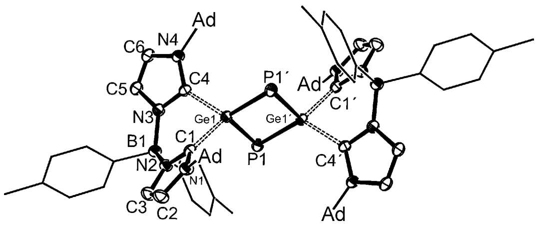


Figure 3. Molecular structure of **4**. Ad = 1-adamantyl. Thermal ellipsoids are set at 50% probability. For clarity, all H atoms and benzene molecules as co-crystalized solvent are omitted for clarity. Symmetry transformations used to generate equivalent atoms with (′): $-x+2$, $-y+2$, $-z+1$. Selected interatomic distances [Å] and angles [°]: Ge1–C1 2.045(2), Ge1–C4 2.049(2), Ge1–P1 2.291(1), Ge1–P1′ 2.272(1), Ge1–Ge1′ 2.867(1); C1-Ge1-C4 88.29(7), C1-Ge1-P1′ 120.70(6), C4-Ge1-P1′ 124.63(6), C1-Ge1-P1 110.98(5), C4-Ge1-P1 109.82(5), P1′-Ge1-P1 102.16(2), Ge1′-P1-Ge1 77.84(2).

Compound **5** is insoluble in common organic solvents and no solution NMR data could be obtained. The solid state ^{31}P NMR spectrum of the dark-red crystals of **5** exhibits a singlet at $\delta = 903.5$ ppm (vs. GIAO ^{31}P NMR: $\delta = 916$ ppm), which is strongly shifted downfield compared with those of other reported diphosphene species such as *t*Bu$_3$Si-P=P-Si*t*Bu$_3$ ($\delta = 818.6$ ppm),[9] **B** (Scheme 1, $\delta = 682$ ppm),[4b] a boryl-substituted diphosphene ($\delta = 605$ ppm),[10] and organo-substituted diphosphenes ($\delta = 440$–599 ppm).[11] The unusual downfield shift of **5** indicates a very strong electron-withdrawing property of the L$_2$Ge^{II} moiety.

The molecular structure of **5** has been determined by an single-crystal X-ray diffraction analysis. As shown in Figure 4, the centrosymmetric structure features a GePP′Ge′ moiety in a "Z" form with the Ge1-P1-P1′ angle of 95.43(4)°. Similar to that observed in **2**, each Ge atom in **5** is three coordinated and adopts a trigonal-pyramidal geometry. The average Ge–C distance of 2.059(2) Å and the Ge–P distance of 2.439(1) Å in **5** are comparable to the corresponding values in **2** (Ge–C 2.045(2) Å, Ge–P 2.483(1) Å). The P–P distance of 2.045(1) Å in **5** is close to those in a boryl-substituted diphosphene (2.066(2) Å)[10] and in **B** (2.021(1) Å),[4b] indicating P=P bond character and confirmed by DFT calculations which revealed a P–P bond of 2.048 Å with MBO of 1.87. Remarkably, although there have been many examples of diphosphenes reported in the literature since the first isolation of a stable derivative by Yoshifuji and co-workers in 1981,[12] most of the P=P species are supported by organic substituents[9–12] or coordinated by transition metals.[4b,13] Compound **5** represents the first example of a Ge-substituted diphosphene.

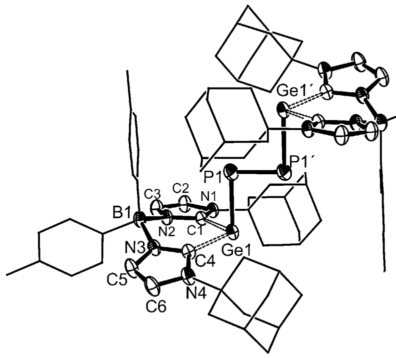


Figure 4. Molecular structure of **5**. Thermal ellipsoids are set at 50% probability. H atoms are omitted for clarity. Symmetry transformations used to generate equivalent atoms with (′): $-x+2$, $-y+1$, $-z+1$. Selected interatomic distances [Å] and angles [°]: Ge1–C1 2.063(2), Ge1–C4 2.054(2), Ge1–P1 2.439(1), P1–P1′ 2.045(1); C1-Ge1-C4 91.06(8), C4-Ge1-P1 96.01(6), C1-Ge1-P1 94.40(6), P1′-P1-Ge1 95.43(4).

In summary, we reported the synthesis and unusual reactivity of the phosphaketenyl-substituted germyliumylidene borate **2** which surprisingly led to the first $[\mathrm{Ge^{I}–Ge^{I}}]^{2+}$ complex **3** as the main product owing to the unexpected photolytic reductive elimination of the entire PCO group in **2**. Additionally, the 4π-electron resonance-stabilized 1,3-digermylium-2,4-diphosphacyclobutadiene derivative **4** and the first zwitterionic bis(germyliumylidenyl)diphosphene **5** could also be obtained as minor products through release of CO and subsequent dimerization of the initially formed elusive [L_2GeP] species.

Acknowledgements

We are grateful to the Deutsche Forschungsgemeinschaft (DR-226-17/3) for financial support. T.S. thanks for generous support by The New Széchenyi Plan TAMOP-4.2.2/B-10/1-2010-0009. E.B.-M. thanks MICITT-Costa Rica and Universidad de Costa Rica for a scholarship.

Conflict of interest

The authors declare no conflict of interest.

Keywords: germanium · main-group chemistry · phosphagermyne · phosphinidene · phosphorus

---

[1] a) G. Becker, W. Schwarz, N. Seidler, M. Westerhausen, *Z. Anorg. Allg. Chem.* **1992**, *612*, 72; b) G. Becker, G. Heckmann, K. Hübler, W. Schwarz, *Z. Anorg. Allg. Chem.* **1995**, *621*, 34; c) G. Becker, K. Hübler, M. Niemeyer, N. Seidler, B. Thinus, *Z. Anorg. Allg. Chem.* **1996**, *622*, 197.

[2] a) F. F. Puschmann, D. Stein, D. Heift, C. Hendriksen, Z. A. Gal, H.-F. Grützmacher, H. Grützmacher, *Angew. Chem. Int. Ed.* **2011**, *50*, 8420; *Angew. Chem.* **2011**, *123*, 8570; b) D. Heift, Z. Benkő, H. Grützmacher, *Dalton Trans.* **2014**, *43*, 831.

[3] a) S. Alidori, D. Heift, G. Santiso-Quinones, Z. Benkő, H. Grützmacher, M. Caporali, L. Gonsalvi, A. Rossin, M. Peruzzini, *Chem. Eur. J.* **2012**, *18*, 14805; b) D. Heift, Z. Benkő, H. Grützmacher, *Dalton Trans.* **2014**, *43*, 5920; c) D. Heift, Z. Benkő, H. Grützmacher, *Chem. Eur. J.* **2014**, *20*, 11326; d) Z. Li, X. Chen, M. Bergeler, M. Reiher, C. Su, H. Grützmacher, *Dalton Trans.* **2015**, *44*, 6431; e) 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; *Angew. Chem.* **2016**, *128*, 6122.

[4] a) L. Liu, D. A. Ruiz, D. Munz, G. Bertrand, *Chem* **2016**, *1*, 147; b) L. Liu, D. A. Ruiz, F. Dahcheh, G. Bertrand, R. Suter, A. M. Tondreau, H. Grützmacher, *Chem. Sci.* **2016**, *7*, 2335; c) N. Del Rio, A. Baceiredo, N. Saffon-Merceron, D. Hashizume, D. Lutters, T. Müller, T. Kato, *Angew. Chem. Int. Ed.* **2016**, *55*, 4753; *Angew. Chem.* **2016**, *128*, 4831; d) M. M. Hansmann, G. Bertrand, *J. Am. Chem. Soc.* **2016**, *138*, 15885; e) M. M. Hansmann, R. Jazzar, G. Bertrand, *J. Am. Chem. Soc.* **2016**, *138*, 8356; f) C. Camp, N. Settineri, J. Lefèvre, A. R. Jupp, J. M. Goicoechea, L. Maron, J. Arnold, *Chem. Sci.* **2015**, *6*, 6379; g) A. R. Jupp, M. B. Geeson, J. E. McGrady, J. M. Goicoechea, *Eur. J. Inorg. Chem.* **2015**, 639; h) T. P. Robinson, M. J. Cowley, D. Scheschkewitz, J. M. Goicoechea, *Angew. Chem. Int. Ed.* **2015**, *54*, 683; *Angew. Chem.* **2015**, *127*, 693.

[5] a) S. Yao, Y. Xiong, T. Szilvási, H. Grützmacher, M. Driess, *Angew. Chem. Int. Ed.* **2016**, *55*, 4781; *Angew. Chem.* **2016**, *128*, 4859; b) Y. Wu, L. Liu, J. Su, J. Zhu, Z. Ji, Y. Zhao, *Organometallics* **2016**, *35*, 1593.

[6] See for examples: a) Y. Wang, Y. Xie, P. Wie, R. B. King, H. F. Schaefer, P. v. R. Schleyer, G. H. Robinson, *Science* **2008**, *321*, 1069; b) A. Sidiropoulos, C. Jones, A. Stasch, S. Klein, G. Frenking, *Angew. Chem. Int. Ed.* **2009**, *48*, 9701; *Angew. Chem.* **2009**, *121*, 9881; c) K. C. Mondal, H. W. Roesky, M. C. Schwarzer, G. Frenking, B. Niepötter, H. Wolf, R. Herbst-Irmer, D. Stalke, *Angew. Chem. Int. Ed.* **2013**, *52*, 2963; *Angew. Chem.* **2013**, *125*, 3036; d) Y. Xiong, S. Yao, G. Tan, S. Inoue, M. Driess, *J. Am. Chem. Soc.* **2013**, *135*, 5004; e) Y. Xiong, S. Yao, S. Inoue, J. D. Epping, M. Driess, *Angew. Chem. Int. Ed.* **2013**, *52*, 7147; *Angew. Chem.* **2013**, *125*, 7287.

[7] a) Y. Xiong, T. Szilvási, S. Yao, G. Tan, M. Driess, *J. Am. Chem. Soc.* **2014**, *136*, 11300; b) Y. Xiong, S. Yao, T. Szilvási, M. Driess, *Eur. J. Inorg. Chem.* **2015**, 2377.

[8] a) S. Nagendran, S. Sen, H. W. Roesky, D. Koley, H. Grubmueller, A. Pal, G. Herbst-Irmer, *Organometallics* **2008**, *27*, 5459; b) P. A. Rupar, V. N. Staroverov, K. M. Baines, *Science* **2008**, *322*, 1360.

[9] N. Wiberg, A. Wörner, H.-W. Lerner, K. Karaghiosoff, *Z. Naturforsch. B* **2002**, *57*, 1027.

[10] S. Asami, M. Okamoto, K. Suzuki, M. Yamashita, *Angew. Chem. Int. Ed.* **2016**, *55*, 12827; *Angew. Chem.* **2016**, *128*, 13019.

[11] a) A. H. Cowley, J. E. Kilduff, T. H. Newman, M. Pakulski, *J. Am. Chem. Soc.* **1982**, *104*, 5820; b) P. Jutzi, U. Meyer, B. Krebs, M. Dartmann, *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 919; *Angew. Chem.* **1986**, *98*, 894; c) M. Scholz, H. W. Roesky, D. Stalke, K. Keller, F. T. Edelmann, *J. Organomet. Chem.* **1989**, *366*, 73.

[12] M. Yoshifuji, I. Shima, N. Inamoto, *J. Am. Chem. Soc.* **1981**, *103*, 4587.

[13] S. Yao, T. Szilvasi, N. Lindenmaier, Y. Xiong, S. Inoue, M. Adelhardt, J. Sutter, K. Meyer, M. Driess, *Chem. Commun.* **2015**, *51*, 6153, and references therein.

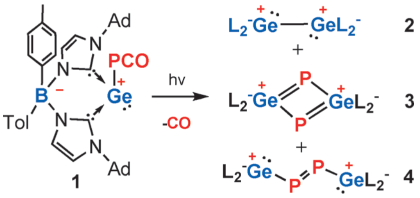
Manuscript received: February 7, 2017
Final Article published: ■■ ■■, ■■■■

Communications

Main-Group Chemistry

Y. Xiong, S. Yao, T. Szilvási,
E. Ballestero-Martínez, H. Grützmacher,
M. Driess* ______ ■■■■–■■■■

Unexpected Photodegradation of a Phosphaketenyl-Substituted Germyliumylidene Borate Complex



Three birds with one stone: UV irradiation of the PCO-functionalized germyliumylidene **1** supported by a bis-NHC borate ($\mathbf{L_2}^-$) affords the first digermyliumylidene dication complex **2** as the main product through reductive elimination of the PCO group in **1** and subsequent Ge^I–Ge^I bond formation. In addition, the unusual 1,3-digermylium-2,4-diphosphacyclobutadiene diborate **3** and the unprecedented bis(germyliumylidenyl)diphosphene diborate **4** are also isolated in low yields.