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N-nacnac stabilized tetrelenes: formation of an *N,P*-heterocyclic germylene via C—C bond insertion
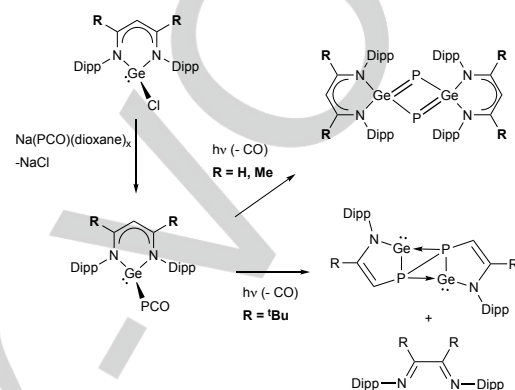
Dinh Cao Huan Do,[a] Andrey V. Protchenko,[a] Petra Vasko,[a] Jésus Campos,[a] Eugene Kolychev,[a] and Simon Aldridge*[a]

Dedicated to Werner Uhl on the occasion of his 65th birthday

Abstract: The use of an amino-functionalised β-diketiminate ("N-nacnac") ligand in low-valent germanium chemistry is reported, with a view to comparison with 'conventional' Nacnac- systems. Transmetallation of the N-nacnac ligand from lithium allows access to a versatile chlorogermylene system, and subsequent substituent exchange processes are used to generate related hydrido-, and phosphaketenyl-germylenes. The latter undergoes photolytically-induced cleavage of the P—CO bond to yield an unusual imine-coordinated *N,P*-heterocyclic germylene. On the basis of DFT calculations this transformation is proposed to occur via concerted attack by the electron-rich carbon-carbon bond of the N-nacnac backbone accompanying CO loss, rather than via the generation of a free phosphinidene.

As a class of well-established main group complexes, donor-supported chlorogermylenes, R(L)Ge^{II}Cl, are known to serve as convenient starting materials for a range of reactive molecular entities, in large part due to their simple/convenient synthesis,[1] and the versatility of the chloride group towards further chemical transformations.[1a-d,1i,2a-i] Stabilization of such sub-valent compounds is often achieved by the employment of sterically bulky and electron-rich ancillary ligands; these two requirements can be fulfilled by the use of the chelating mono-anionic β-diketiminate (or "Nacnac") ligand family, [HC{(R)C(R')N}$_2$]$^-$.[3a-c] Prominent examples of (Nacnac)Ge^{II}Cl systems acting as precursors to more exotic molecular species include (i) hydride-for-halide exchange, leading to a robust Ge^{II} hydride complex;[4a-c] (ii) one-electron reduction, affording a remarkable two-coordinate germanium-centred radical,[5] and most recently, (iii) salt metathesis with a source of the [PCO]$^-$ anion leading to Ge^{II} phosphaketenyl complexes, which are reported to undergo photolytic decarbonylation to give transient germa-phosphinidene species.[3c,6]
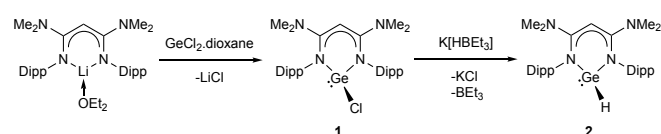
We were interested in the latter chemistry, not least because of its close relationship to the synthetic route used by the group of Bertrand to generate a "bottle-able" singlet phosphinidene.[7a,b] In addition, it has been demonstrated that the steric/electronic profile of the Nacnac-backbone substituents exert a strong influence on the reactivity profile of the putative germa-phosphinidene species generated on ejection of CO from Ge^{II}-PCO systems.[3c, 6] Having recently reported a series of novel

[a]   Mr. D. C. H. Do, Dr. A. V. Protchenko, Dr. P. Vasko, Dr. J. Campos, Dr. E. Kolychev, Prof. S. Aldridge
       Inorganic Chemistry Laboratory, University of Oxford
       South Parks Road, Oxford OX1 3QR
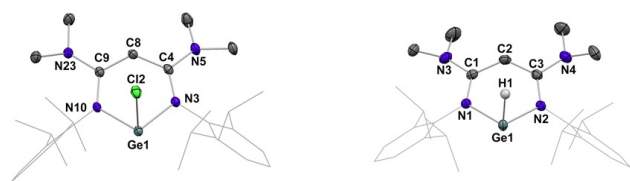   E-mail: Simon.Aldridge@chem.ox.ac.uk

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Scheme 1. Previously reported Nacnac-stabilized phosphaketenyl germylenes: synthesis and rearrangement patterns on photo-induced release of CO (Dipp = 2,6-iPr2C$_6$H$_3$).

electron-rich amino-functionalized Nacnac ligand variants ("N-nacnac", [HC{(Me$_2$N)C(R')N}$_2$]$^-$) and explored their complexation chemistry with tin as a Group 14 representative,[8] we sought to extend these studies to the lighter congener, germanium, focusing on potential chemical differences to their Nacnac counterparts. One aim was to investigate the impact of incorporating –NMe$_2$ groups into the ligand scaffold on the photochemical behaviour of the corresponding phosphaketenyl complexes, both experimentally and theoretically. Our efforts in this area are reported in the current manuscript.

In a similar manner to the preparation of the analogous chlorostannylene, the lithiated N-nacnac precursor [HC{(Me$_2$N)C(Dipp)N}$_2$]Li(OEt$_2$) undergoes salt metathesis with GeCl$_2$·dioxane, affording chlorogermylene **1** in moderate to good yield (66%; Scheme 2). **1** has been characterized by standard spectroscopic and analytical techniques, and its structure in the solid state has been determined by single crystal X-ray diffraction (Figure 1). This allows like-for-like comparison with previously reported chlorogermylenes stabilized by various Nacnac ligands, which differ only in the backbone C$_{imine}$-bound group (Table 1).[3a-c]

Scheme 2. Synthetic protocol for chlorogermylene **1** and hydridogermylene **2**.

Figure 1. Molecular structures of **1** (left) and **2** (right) in the solid state as determined by X-ray crystallography. Thermal ellipsoids have been set at 35% probability, with Dipp-substituents represented in the wireframe format, and hydrogen atoms omitted for clarity (apart from the Ge-bound hydride). Selected bond lengths (Å) and angles (°): (**1**) Ge1—Cl2 2.3490(4), Ge1—N3 1.9733(14), Ge1—N10 1.9680(13), N3—C4 1.347(2), C9—N10 1.358(2), C4—C8 1.414(2), C8—C9 1.397(2), C4—N5 1.367(2), C9—N23 1.368(2), N3—Ge1—N10 94.31(6), Cl2—Ge1—N3 94.92(4), Cl2—Ge1—N10 94.72(4); (**2**) Ge1—N1 2.0111(12), Ge1—N2 1.9922(12), N1—C1 1.3414(16), N2—C3 1.3447(16), C1—C2 1.4066(19), C2—C3 1.3925(19), C1—N3 1.3777(17), C3—N4 1.3796(17), N1—Ge1—N2 93.45(5).

Table 1. Crystallographically-determined structural parameters for Nacnac-stabilized chlorogermylenes of the type [HC{(R)C(Dipp)N}₂]GeCl.

R	d(Ge—Cl) (Å)	d(Ge—N) (Å)	∠(N-Ge-N) (°)	Distance of Ge above least squares NC₃N plane (Å)
H [3c]	2.302(1)	1.984(4) 1.972(4)	89.7(2)	0.276
Me [3a]	2.295(12)	1.988(2) 1.997(3)	90.89(10)	0.564
ᵗBu [3b]	2.2942(8)	1.9394(19) 2.036(2)	91.99(8)	0.599
NMe₂	**2.3490(4)**	**1.968(1) 1.973(1)**	**94.31(6)**	**0.550**

1 features similar (or slightly shorter) Ge—N distances to previously reported Nacnac systems featuring backbone H or alkyl substituents, but a distinctly longer Ge—Cl bond, and a significantly wider N—Ge—N angle (Table 1). Very similar structural observations have been made for the corresponding tin complex, [HC{(Me₂N)C(Dipp)N}₂]SnCl, in comparison to the related Nacnac system [HC{(Me)C(Dipp)N}₂]SnCl.[8] Spectroscopically, the chemical shift associated with the γ-CH proton is consistent with a degree of conjugation of the amino groups into the unsaturated backbone of the β-diketiminate ligand. Thus, the more upfield shifted signals measured for the N-nacnac complexes (δ_H = 4.26 and 4.04 ppm for [HC{(Me₂N)C(Dipp)N}₂]MCl (M = Ge, Sn) vs. 5.14 and 5.05 ppm for HC{(Me)C(Dipp)N}₂]MCl) are consistent with the well-documented effects of π-donor amino groups on alkene resonances.[3a,8,9] The extent of this effect is presumably tempered by steric factors which prevent the (planar) –NMe₂ groups from attaining perfect co-planarity with the C₃N₂ plane (the mean inter-plane torsion angle for **1** is 27.1°).

The synthetic versatility of **1** in the synthesis of related germylene compounds is readily demonstrated. Thus, hydrido-germylene **2** can easily be generated from **1** via a hydride-for-chloride substitution using K[HBEt₃] (Scheme 2) and its molecular structure confirmed by X-ray crystallography. The geometric differences between **2** and **1** are small, with the

germanium centre projected out of the C₃N₂ plane (by 0.646 Å) and the hydride ligand occupying the pseudo axial position.[10] Of interest spectroscopically, are the observations that the germanium-bound hydride is slightly more deshielded in **2** than in [HC{(Me)C(Dipp)N}₂]GeH (δ_H = 8.14 vs. 8.08 ppm) and that the Ge—H stretching frequency is somewhat higher (1755 vs. 1733 cm⁻¹).[4b] Both observations imply that the germanium centre bears a slightly higher partial positive charge in **2**,[10] which in turn suggests that the net effect of the backbone NMe₂ groups at the remote germanium centre (which is both coordinatively saturated and projected significantly out of the C₃N₂ plane) is as a σ electron-withdrawing group. On the other hand, the ¹H and ¹³C signals for the backbone γ-CH (δ_H = 4.22, δ_C = 78.2 ppm, cf. 4.92 and 97.8 ppm for [HC{(Me)C(Dipp)N}₂]GeH), suggest that (as with **1**) the effect of the NMe₂ groups on the more-or-less conjugated C₃ backbone is as a π electron donating group.

Similar substituent exchange chemistry can also be effected for the synthesis of the phosphaketenyl-germylene **3**, which is obtained in ca. 60% yield via the reaction between **1** and Na(PCO)(dioxane)ₓ (Scheme 3). **3** has been characterized by standard spectroscopic and analytical methods; particularly diagnostic are ³¹P and IR signatures for the Ge-PCO unit (δ_P = -317 ppm; ν(CO) = 1876 cm⁻¹) which are in line with previous examples of this functional group.[3c,6] While the molecular structure of **3** determined crystallographically (Figure 2) is also broadly in line with those of related systems, the ¹³C{¹H} NMR spectrum reveals a markedly upfield shifted resonance associated with the N-nacnac backbone CH group. The shifts measured for related compounds featuring backbone H, Me or

Scheme 3. Synthetic route to phosphaketenyl-substituted germylene **3** and imine-tethered N,P-heterocyclic germylene **4**.
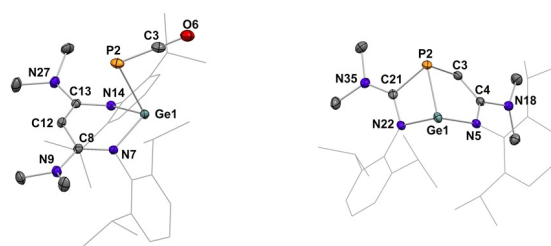

Figure 2. Molecular structures of **3** (left) and **4** (right) in the solid state as determined by X-ray crystallography. Thermal ellipsoids have been set at 35 % probability, with Dipp-substituents represented in the wireframe format, and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): (**3**) Ge1—P2 2.5470(6), P2—C3 1.684(5), C3—O6 1.187(6), Ge1—N7 1.9872(15), Ge1—N14 1.9652(15), Ge1—P2—C3 87.29(16), P2—C3—O6 179.11(10); (**4**) Ge1—P2 2.4323(9), Ge1—N5 1.938(3), Ge1—N22 2.038(3), P2—C3 1.803(3), P2—C21 1.883(3), C3—C4 1.383(4), C4—N18 1.394(4), C4—N5 1.387(4), C21—N35 1.335(4), C21—N22 1.328(4), Ge1—P2—C3 90.27(10), Ge1—P2—C21 74.75(10), C3—P2—C21 98.85(14), P2—Ge1—N5 88.14(8), P2—Ge1—N22 71.44(8), N5—Ge1—N22 99.30(10).

^{t}Bu groups fall in the range δ_C = 95.0-106.5 ppm, but that for **3** is observed at 81.3 ppm, consistent with the presence of a more electron rich backbone featuring pendant NMe$_2$ groups. In line with chloro- and hydrido-germylene complexes **1** and **2**, compound **3** features torsion angles between the amino-functions and the 5-membered ring chelate of 27.5° and 28.7°.
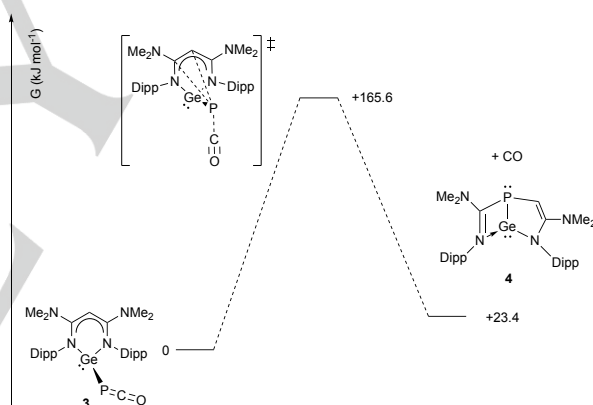
Broadband UV-photolysis of **3** over the course of 6 h, followed by recrystallization from pentane at -26°C yields the C-C insertion compound **4** (Scheme 3). Definitive characterization in this case relies heavily on X-ray crystallography (Figure 2), and the structure so obtained can be described in terms of a five-membered *N,P*-heterocyclic germylene, stabilized by an imine tether. As such, the isolation of **4** might shed some light on potential mechanisms for the formation of a related (dimeric) *N,P*-chelated germylene in the corresponding photolytic reaction of [HC{(^{t}Bu)C(Dipp)N}$_2$]Ge(PCO) (Scheme 1).[3c] The P-P bonded product (and diazabutadiene co-product) might be viewed as being generated from a species similar to **4** via homolytic cleavage of the P-C bond to the pendant imine function (with subsequent dimerization).

The structure of **4** is bicyclic, hinged about the Ge(1)-P(2) bond and with the angle between the least-squares planes of the two rings being 80.0°. The two Ge—N distances (1.938(3) and 2.038(3) Å) are consistent with previous reports of single and dative bonds, respectively. [11a-c] In addition, there is evidence for a significant π-conjugation across the N22—C21—N35 triatomic unit, as evidenced by (i) the very small dihedral angle between the –N(22)C$_2$ plane and that of the N22—C21—N35 unit (3.3°), and (ii) the negligible degree of pyramidalization of the two nitrogen atoms (sums of angles: N22, 358.9°; N35, 360.0°). As such, the two C—N distances involving C21 (d(C21—N35) = 1.335(4) Å; d(C21—N22) = 1.328(4) Å) are statistically identical. From a spectroscopic perspective, **4** gives rise to a single ^{31}P NMR resonance at δ_P = -50 ppm which shows two-bond coupling to the proton attached to C(3) ($^2J_{PH}$ = 33 Hz).

To shed a light on possible reaction pathways leading to the conversion of **3** to **4** we undertook DFT calculations at the PBE1PBE/Def2-TZVP level of theory. As a starting point, we considered the mechanistic hypothesis presented by Driess and co-workers, that initial photolytic loss of CO generates a transient germanium phosphinidene, which then rearranges via formal insertion into one of the backbone C-C bonds of the N-nacnac ligand.[3c] A number of different geometries were considered for the [HC{(Me$_2$N)C(Dipp)N}$_2$]GeP intermediate, the lowest energy of which features a Ge-P unit projected approximately perpendicular to the C$_3$N$_3$ plane, and which is converted via a very low energy transition state (ca. 6.1 kJ mol^{-1}) into **4** (see ESI). While the overall process is endoergic to the tune of +23.4 kJ mol^{-1} it is presumably driven by removal of the CO co-product. Whatismore, similar energetic profiles can be calculated for the corresponding derivatives featuring backbone H, Me or ^{t}Bu groups – albeit with slightly higher activation barriers (9.9, 16.8 and 19.6 kJ mol^{-1}, respectively).

We next considered the mechanism for the energetically expensive step, i.e. the CO loss from **3**. A linear transit carried out on the P-C(O) distance, however, revealed that stepwise elongation is accompanied by ever-closer approach to the phosphorus centre by the γ-carbon of the N-nacnac backbone. This structural distortion is consistent with the electron-deficient nature of the developing phosphinidene centre, and the electron-rich nature of the N-nacnac backbone (the NBO-calculated charge at the γ-C is -0.506). This trajectory for CO loss suggested to us that an alternative pathway for the *direct* conversion of **3** to **4** might involve concerted attack at P by the π-system centred at the γ-carbon accompanying CO loss (Scheme 4). Accordingly, we could locate a transition state (at +165.6 kJ mol^{-1}) corresponding to this process – which while relatively high in energy – is not inconsistent with the photolytic mode of activation of this chemistry. As such, we hypothesize that the overall transformation need not necessarily invoke the formation of a transient germanium phosphinidene intermediate. Intriguingly, the analogous linear transit carried out on the P-C(O) bond in [HC{(^{t}Bu)C(Dipp)N}$_2$]GePCO reveals a similar interaction with the γ-carbon (consistent with the finding that the final product in this case also involves C-C insertion), while the less electron-rich [HC{(H)C(Dipp)N}$_2$]GePCO system loses CO *without* involvement of the backbone π system – in line with the finding that the product in this case is the Ge$_2$P$_2$-containing "phosphindene dimer" (Scheme 1).[3c,6]

Scheme 4. Alternative (concerted) mechanism for the formation of **4** (Gibbs' energies in kJ mol^{-1}).

In summary we have developed the coordination chemistry of the N-nacnac family of ligands towards Ge^{II}, synthesizing chloride, hydride and phosphaketenyl systems (**1-3**). Electronically these systems feature a more electron rich β-diketiminate backbone – a feature which is not only signalled spectroscopically, but also of potential relevance in the photolytic reactivity of **3**, which proceeds via ejection of CO with concomitant insertion into one of the backbone C-C bonds.

Experimental Section

General details and the synthetic protocols for **2** and **4** are described in the ESI. X-ray crystal structure data have been deposited with the CCDC: 1528014 and 1849870-1849872.

Synthesis of **1**: A solution of N-nacnac-Li(OEt)$_2$ (1 mmol) in toluene (50 mL) was added to a solution (10 mL) containing

GeCl$_2$.dioxane (1.1 equiv.) in the same solvent at -78°C, and the resulting mixture warmed to room temperature with stirring overnight. Volatiles were subsequently removed *in vacuo*, and the resulting residue was washed with cold hexane (0°C) to yield the product as off-white spectroscopically pure solid (yield 0.38 g, 66 %). X-ray quality crystals were obtained from a concentrated toluene solution, layered with hexane, and stored at -26°C for several days. ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ$_H$ 1.08 (d, $^3J_{HH}$ = 6.8 Hz, 6H, (C$\underline{H}_3$)$_2$CH), 1.11 (d, $^3J_{HH}$ = 6.4 Hz, 6H, (C$\underline{H}_3$)$_2$CH), 1.29 (d, $^3J_{HH}$ = 6.8 Hz, 6H, (C$\underline{H}_3$)$_2$CH), 1.65 (d, $^3J_{HH}$ = 6.8 Hz, 6H, (C$\underline{H}_3$)$_2$CH), 2.25 (s, 12H, (C$\underline{H}_3$)$_2$N), 2.99 (sept, $^3J_{HH}$ = 6.7 Hz, 2H, (CH$_3$)$_2$C$\underline{H}$), 4.26 (s, 1H, methine CH), 4.53 (sept, $^3J_{HH}$ = 6.7 Hz, 2H, (CH$_3$)$_2$C$\underline{H}$), 7.04-7.18 (6H, aromatic CH) ppm. ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$): δ$_C$ 24.1, 24.2, 26.7, 27.9 ((C$\underline{H}_3$)$_2$CH), 28.3, 28.9 ((CH$_3$)$_2$C$\underline{H}$), 41.0 (C$\underline{H}_3$)$_2$N), 80.0 (methine CH), 124.4, 125.7 (*m*-CH of Dipp), 126.5 (*p*-CH of Dipp), 140.9, 145.0, 146.5 (aromatic carbons), 164.8 (imine quaternary C) ppm. EI-MS (*m/z*, %): 584.3, weak, [M]$^+$; accurate mass: calc. for C$_{19}$H$_{23}$ClGeN$_4$ ([M]$^+$) 584.2701, found 584.2720. Elemental microanalysis: calc. for C$_{31}$H$_{47}$ClGeN$_4$: C 63.78, H 8.11, N 9.60%, meas. C 63.84, H 8.16, N 9.46 %.

Synthesis of **3**: To a toluene suspension of NaPCO(dioxane)$_x$ complex (1.3 equiv.), a solution (20 mL) of **1** (0.2 mmol) in the same solvent was slowly added at -78°C. The reaction mixture was warmed to room temperature and stirred overnight, after which solvent was removed *in vacuo*, and the residual solid was washed with hexane (ca. 5 mL) to afford the spectroscopically pure product (Yield 0.076 g, 63 %). Storage of a saturated hexane solution of 3 at -26°C produced light yellow crystals suitable for X-ray crystallography. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ$_H$ 1.04 (d, $^3J_{HH}$ = 6.7 Hz, 6H, (C$\underline{H}_3$)$_2$CH), 1.09 (d, $^3J_{HH}$ = 6.8 Hz, 6H, (CH$_3$)$_2$CH), 1.33 (d, $^3J_{HH}$ = 6.6 Hz, 6H, (C$\underline{H}_3$)$_2$CH), 1.71 (d, $^3J_{HH}$ = 6.7 Hz, 6H, (C$\underline{H}_3$)$_2$CH), 2.21 (s, 12H, (C$\underline{H}_3$)$_2$N), 2.93 (sept, $^3J_{HH}$ = 6.7 Hz, 2H, (CH$_3$)$_2$C$\underline{H}$), 4.16 (s, 1H, methine CH), 4.47 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, (CH$_3$)$_2$C$\underline{H}$), 7.02 (d, $^3J_{HH}$ = 7.6 Hz, 2H, *m*-H of Dipp), 7.07 (t, $^3J_{HH}$ = 7.6 Hz, 2H, *p*-H of Dipp), 7.13 (d, $^3J_{HH}$ = 7.6 Hz, 4H, *m*-H of Dipp) ppm. ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$): δ$_C$ 24.1 (overlapping signals), 26.7, 28.3 ((C$\underline{H}_3$)$_2$CH), 30.5 (overlapping signals) ((CH$_3$)$_2$C$\underline{H}$), 41.0 ((C$\underline{H}_3$)$_2$N), 81.3 (d, methine CH, $^4J_{CP}$ = 9.2 Hz), 124.5, 125.7 (*m*-C of Dipp), 126.3 (*p*-C of Dipp), 141.1, 145.2, 146.3 (*o*-C and *ipso*-C of Dipp), 165.5 (d, through-space coupling with P, J_{CP} 4.2 Hz, imine quaternary C), 191.4 (d, $^1J_{CP}$ = 88 Hz, P$\underline{C}$O) ppm. ^{31}P{^{1}H} NMR (162 MHz, C$_6$D$_6$): δ$_P$ -317 ppm. IR (ATR, v$_{C-O}$/cm^{-1}): 1876. ESI-MS (*m/z*, %): 549.3, weak, [M - PCO]$^+$; accurate mass: calc. for C$_{31}$H$_{47}$GeN$_4$ ([M - PCO]$^+$) 549.3013, meas. 549.3028. Elemental microanalysis: calc. for C$_{32}$H$_{47}$GeN$_4$OP: C 63.28, H 7.80, N 9.22%, meas. C 63.42, H 7.96, N 9.18%.
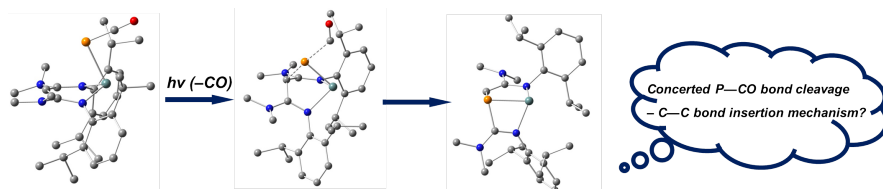
Acknowledgements

[1] Selected examples: a) H. V. R. Dias, Z. Wang, *J. Am. Chem. Soc.* **1997**, *119*, 4650–4655; b) S. R. Foley, C. Bensimon, D. S. Richeson, *J. Am. Chem. Soc.* **1997**, *119*, 10359–10363; c) S. P. Green, C. Jones, P. C. Junk, K. Lippert, A. Stasch, *Chem. Commun.* **2006**, 3978–3980; d) C. Jones, P. Rose, A. Stasch, *Dalton Trans.* **2008**, 2871–2878; e) L. Pu, M. M. Olmstead, P. P. Power, B. Schiemenz, *Organometallics* **1998**, *17*, 5602–5606; f) W. Leung, C. So, Y. Wu, H. Li, T. C. W. Mak, *Eur. J. Inorg. Chem.* **2005**, 513–521; g) J. Li, A. Stasch, C. Schenk, C. Jones, *Dalton Trans.* **2011**, *40*, 10448-10456; h) T. J. Hadlington, J. Li, C. Jones, *Can. J. Chem.* **2014**, *92*, 427–433; i) J. Berthe, J. M. Garcia, E. Ocando, T. Kato, N. Sa, F. P. Cossío, A. Baceiredo, *J. Am. Chem. Soc.* **2011**, *133*, 15930–15933.

[2] Selected examples: a) L. Pu, M. O. Senge, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **1998**, *120*, 12682–12683; b) M. Stender, A. D. Phillips, R. J. Wright, P. P. Power, *Angew. Chem. Int. Ed.* **2002**, *41*, 1785–1787; c) A. F. Richards, A. D. Phillips, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **2003**, *125*, 3204–3205; d) L. Pu, A. D. Phillips, A. F. Richards, M. Stender, R. S. Simons, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **2003**, *125*, 11626–11636; e) J. Schneider, K. M. Krebs, S. Freitag, K. Eichele, H. Schubert, L. Wesemann, *Chem. Eur. J.* **2016**, *22*, 9812–9826; f) M. Usher, A. V Protchenko, A. Rit, J. Campos, E. L. Kolychev, R. Tirfoin, S. Aldridge, *Chem. Eur. J.* **2016**, *22*, 11685–11698; g) J. Li, C. Schenk, C. Goedecke, G. Frenking, C. Jones, *J. Am. Chem. Soc.* **2011**, *133*, 18622–18625; h) J. Li, C. Schenk, F. Winter, H. Scherer, N. Trapp, A. Higelin, S. Keller, R. Pöttgen, I. Krossing, C. Jones, *Angew. Chem. Int. Ed.* **2012**, *51*, 9557–9561; i) N. Del Rio, A. Baceiredo, N. Saffon-Merceron, D. Hashizume, D. Lutters, T. Müller, T. Kato, *Angew. Chem. Int. Ed.* **2016**, *55*, 4753–4758.

[3] a) Y. Ding, H. W. Roesky, M. Noltemeyer, H. G. Schmidt, P. P. Power, *Organometallics* **2001**, *20*, 1190–1194; b) W. D. Woodul, A. F. Richards, A. Stasch, M. Driess, C. Jones, *Organometallics* **2010**, *29*, 3655–3660; c) S. Yao, Y. Xiong, T. Szilvási, H. Grützmacher, M. Driess, *Angew. Chem. Int. Ed.* **2016**, *55*, 4781–4785.

[4] a) Y. Ding, H. Hao, H. W. Roesky, M. Noltemeyer, H. G. Schmidt, *Organometallics* **2001**, *20*, 4806–4811; b) L. W. Pineda, V. Jancik, K. Starke, R. B. Oswald, H. W. Roesky, *Angew. Chem. Int. Ed.* **2006**, *45*, 2602–2605; c) A. Jana, D. Ghoshal, H. W. Roesky, I. Objartel, G. Schwab, D. Stalke, *J. Am. Chem. Soc.* **2009**, 1288–1293.

[5] W. D. Woodul, E. Carter, R. Müller, A. F. Richards, A. Stasch, M. Kaupp, D. M. Murphy, M. Driess, C. Jones, *J. Am. Chem. Soc.* **2011**, *133*, 10074–10077.

[6] Y. Wu, L. Liu, J. Su, J. Zhu, Z. Ji, Y. Zhao, *Organometallics* **2016**, *35*, 1593–1596.

[7] a) L. Liu, D. A. Ruiz, D. Munz, G. Bertrand, *Chem* **2016**, *1*, 147–153; b) M. M. Hansmann, R. Jazzar, G. Bertrand, *J. Am. Chem. Soc.* **2016**, *138*, 8356–8359.

[8] D. C. H. Do, A. Keyser, A. V Protchenko, B. Maitland, I. Pernik, H. Niu, E. L. Kolychev, A. Rit, D. Vidovic, A. Stasch, C. Jones, S. Aldridge, *Chem.-Eur. J.* **2017**, *23*, 5830–5841.

[9] E. Pretsch, P. Bühlmann, M. Badertscher in *Structure Determination of Organic Compounds* (eds. M. Badertscher, P. Bühlmann, E. Pretsch), Springer-Verlag, Berlin, 2009, Chp. 5.

[10] A. Caise, D. Jones, E. L. Kolychev, J. Hicks, S. Aldridge, *Chem.-Eur. J.* **2018**, in press (DOI: 10.1002/chem.201802603).

[11] a) I. L. Fedushkin, M. Hummert, H. Schumann, *Eur. J. Inorg. Chem.* **2006**, 3266–3273; b) A. Mcheik, N. Katir, A. Castel, H. Gornitzka, S. Massou, P. Rivière, T. Hamieh, *Eur. J. Inorg. Chem.* **2008**, 5397–5403;

c) S. P. Chia, Y. Li, R. Ganguly, C. W. So, *Eur. J. Inorg. Chem.* **2014**, 526–532.

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hv (–CO)

Concerted P—CO bond cleavage – C—C bond insertion mechanism?

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Dinh Cao Huan Do, Andrey V. Protchenko, Petra Vasko, Jésus Campos, Evgeny Kolychev, Simon Aldridge*

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N-nacnac stabilized tetrelenes: formation of an N,P-heterocyclic germylene via C—C bond insertion