

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

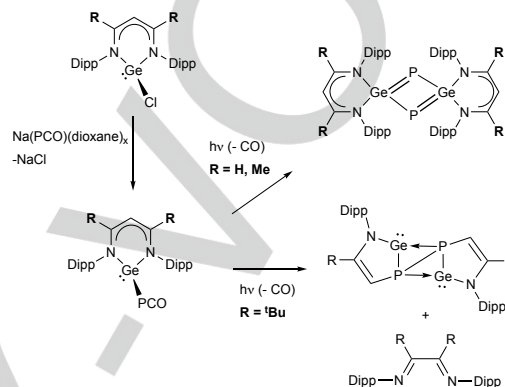
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Dedicated to Werner Uhl on the occasion of his 65th birthday

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. Transmetalation 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 chlorogermynes, $R(L)Ge^{II}Cl$, 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-j] 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 germaphosphinidene species.^[3c,6]

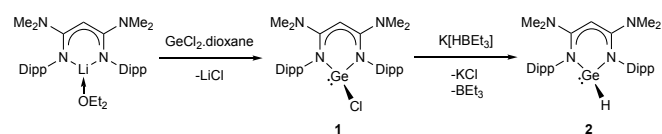
We were interested in the latter chemistry, not least because of its close relationship to the synthetic route used by the group of Bertrand to generate a “bottle-able” singlet phosphinidene.^[7a,b] In addition, it has been demonstrated that the steric/electronic profile of the Nacnac-backbone substituents exert a strong influence on the reactivity profile of the putative germaphosphinidene species generated on ejection of CO from Ge^{II} -PCO systems.^[3c,6] Having recently reported a series of novel



Scheme 1. Previously reported Nacnac-stabilized phosphaketenyl germynes: synthesis and rearrangement patterns on photo-induced release of CO (Dipp = 2,6-*i*Pr₂C₆H₃).

electron-rich amino-functionalized Nacnac ligand variants (“N-nacnac”, $[HC\{(Me_2N)C(R')N\}_2]^-$) 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 $[HC\{(Me_2N)C(Dipp)N\}_2]Li(OEt_2)$ 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 chlorogermynes 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**.

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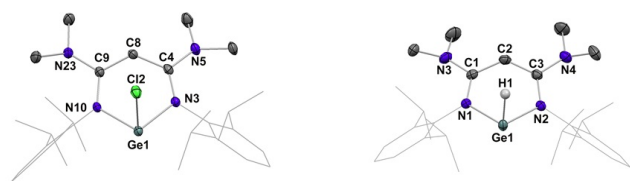


Figure 1. Molecular structures of **1** (left) and **2** (right) in the solid state as determined by X-ray crystallography. Thermal ellipsoids have been set at 35% probability, with Dipp-substituents represented in the wireframe format, and hydrogen atoms omitted for clarity (apart from the Ge-bound 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 chlorogermynes of the type [HC{(R)C(Dipp)N₂}₂GeCl].

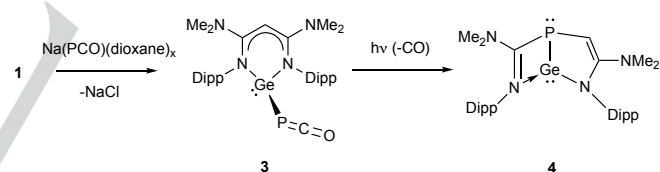
R	d(Ge—Cl) (Å)	d(Ge—N) (Å)	∠(N—Ge—N) (°)	Distance of Ge above least squares NC ₃ N ₂ plane (Å)
H ^[3c]	2.302(1)	1.984(4) 1.972(4)	89.7(2)	0.276
Me ^[3a]	2.295(12)	1.988(2) 1.997(3)	90.89(10)	0.564
^t Bu ^[3b]	2.2942(8)	1.9394(19) 2.036(2)	91.99(8)	0.599
NMe₂	2.3490(4)	1.968(1) 1.973(1)	94.31(6)	0.550

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)N₂}₂SnCl], in comparison to the related Nacnac system [HC{(Me)C(Dipp)N₂}₂SnCl].^[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 -diketiminato ligand. Thus, the more upfield shifted signals measured for the N-nacnac complexes ($\delta_{\text{H}} = 4.26$ and 4.04 ppm for [HC{(Me₂N)C(Dipp)N₂}₂]MCl (M = Ge, Sn) vs. 5.14 and 5.05 ppm for HC{(Me)C(Dipp)N₂}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)N₂}₂]GeH ($\delta_{\text{H}} = 8.14$ 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 ($\delta_{\text{H}} = 4.22$, $\delta_{\text{C}} = 78.2$ ppm, cf. 4.92 and 97.8 ppm for [HC{(Me)C(Dipp)N₂}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 phosphaketanyl-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 ($\delta_{\text{P}} = -317$ ppm; $\nu(\text{CO}) = 1876$ 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 phosphaketanyl-substituted germylene **3** and imine-tethered *N,P*-heterocyclic germylene **4**.

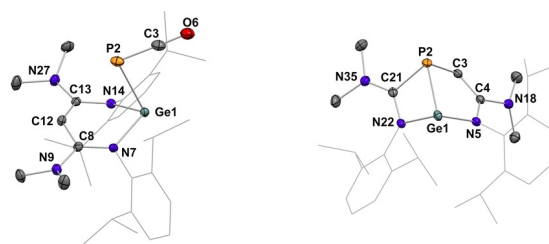


Figure 2. Molecular structures of **3** (left) and **4** (right) in the solid state as determined by X-ray crystallography. Thermal ellipsoids have been set at 35% probability, with Dipp-substituents represented in the wireframe format, and hydrogen atoms omitted for clarity. Selected bond lengths (Å) 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).

^tBu groups fall in the range $\delta_c = 95.0$ – 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 NMe₂ 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°.

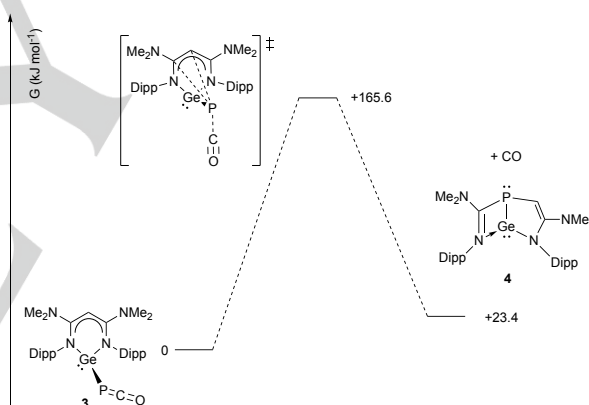
Broadband UV-photolysis of **3** over the course of 6 h, followed by recrystallization from pentane at -26°C yields the C-C insertion compound **4** (Scheme 3). Definitive characterization in this case relies heavily on X-ray crystallography (Figure 2), and the structure so obtained can be described 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(^tBu)C(Dipp)N]₂Ge(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)C₂ 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 ($d(\text{C21—N35}) = 1.335(4)$ Å; $d(\text{C21—N22}) = 1.328(4)$ Å) are statistically identical. From a spectroscopic perspective, **4** gives rise to a single ³¹P NMR resonance at $\delta_p = -50$ ppm which shows two-bond coupling to the proton attached to C(3) ($^2J_{\text{PH}} = 33$ 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((Me₂N)C(Dipp)N)₂]GeP intermediate, the lowest energy of which features a Ge-P unit projected approximately perpendicular to the C₃N₃ 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 ^tBu 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((^tBu)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]₂GePCO system loses CO *without* involvement of the backbone π system – in line with the finding that the product in this case is the Ge₂P₂-containing "phosphinidene 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 phosphaketonyl 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

GeCl₂.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. ¹H NMR (C₆D₆, 400 MHz): δ_H 1.08 (d, ³J_{HH} = 6.8 Hz, 6H, (CH₃)₂CH), 1.11 (d, ³J_{HH} = 6.4 Hz, 6H, (CH₃)₂CH), 1.29 (d, ³J_{HH} = 6.8 Hz, 6H, (CH₃)₂CH), 1.65 (d, ³J_{HH} = 6.8 Hz, 6H, (CH₃)₂CH), 2.25 (s, 12H, (CH₃)₂N), 2.99 (sept, ³J_{HH} = 6.7 Hz, 2H, (CH₃)₂CH), 4.26 (s, 1H, methine CH), 4.53 (sept, ³J_{HH} = 6.7 Hz, 2H, (CH₃)₂CH), 7.04–7.18 (6H, aromatic CH) ppm. ¹³C{¹H} NMR (100 MHz, C₆D₆): δ_C 24.1, 24.2, 26.7, 27.9 ((CH₃)₂CH), 28.3, 28.9 ((CH₃)₂CH), 41.0 (C(CH₃)₂N), 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 C₁₉H₂₃ClGeN₄ ([M]⁺) 584.2701, found 584.2720. Elemental microanalysis: calc. for C₃₁H₄₇ClGeN₄: 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. ¹H NMR (400 MHz, C₆D₆): δ_H 1.04 (d, ³J_{HH} = 6.7 Hz, 6H, (CH₃)₂CH), 1.09 (d, ³J_{HH} = 6.8 Hz, 6H, (CH₃)₂CH), 1.33 (d, ³J_{HH} = 6.6 Hz, 6H, (CH₃)₂CH), 1.71 (d, ³J_{HH} = 6.7 Hz, 6H, (CH₃)₂CH), 2.21 (s, 12H, (CH₃)₂N), 2.93 (sept, ³J_{HH} = 6.7 Hz, 2H, (CH₃)₂CH), 4.16 (s, 1H, methine CH), 4.47 (sept, ³J_{HH} = 6.8 Hz, 2H, (CH₃)₂CH), 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. ¹³C{¹H} NMR (100 MHz, C₆D₆): δ_C 24.1 (overlapping signals), 26.7, 28.3 ((CH₃)₂CH), 30.5 (overlapping signals) ((CH₃)₂CH), 41.0 ((CH₃)₂N), 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, ¹J_{CP} = 4.2 Hz, imine quaternary C), 191.4 (d, ¹J_{CP} = 88 Hz, PCO) ppm. ³¹P{¹H} NMR (162 MHz, C₆D₆): δ_P -317 ppm. IR (ATR, ν_{C-O}/cm⁻¹): 1876. ES-MS (*m/z*, %): 549.3, weak, [M - PCO]⁺; accurate mass: calc. for C₃₁H₄₇GeN₄ ([M - PCO]⁺) 549.3013, meas. 549.3028. Elemental microanalysis: calc. for C₃₂H₄₇GeN₄OP: C 63.28, H 7.80, N 9.22%, meas. C 63.42, H 7.96, N 9.18%.

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Keywords: germynes • β-diketiminates • phosphaketonyl • decarbonylation • inorganic bicyclic molecules

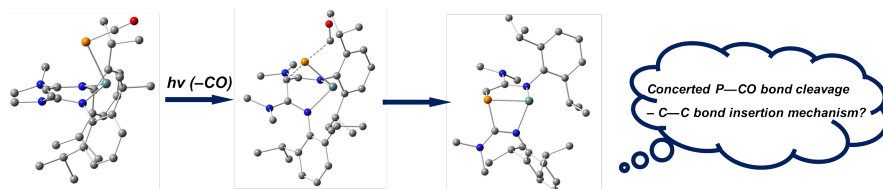
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COMMUNICATION



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

When #ElectrophilicPhosphorus meets #NucleophilicCarbon: The complexation chemistry of N-nacnac-stabilized germylenes provides insight into electronic divergence from conventional Nacnac- supported systems. In the case of a PCO-substituted system, UV-induced decarbonylation affords an unusual bicyclic N,P-heterocyclic germylene. This is proposed to occur *via* a C—C bond insertion initiated by interaction of P with the remarkably nucleophilic γ -carbon of the ligand backbone.