

Coordination Chemistry

A “Push–Pull” Stabilized Phosphinidene Supported by a Phosphine-Functionalized β -Diketiminato LigandSebastian Bestgen,^[a] Meera Mehta,^[a] Timothy C. Johnstone,^[b] Peter W. Roesky,^[c] and Jose M. Goicoechea^{*[a]}

Abstract: The use of a bis(diphenyl)phosphine functionalized β -diketiminato ligand, $[\text{HC}((\text{CH}_3)_2\text{C}_6\text{H}_4)_2\{\text{ortho-}[\text{P}(\text{C}_6\text{H}_5)_2]_2\text{C}_6\text{H}_4\text{N}\}_2]^-$ (PNac), as a support for germanium(II) and tin(II) chloride and phosphaketene compounds, is described. The conformational flexibility and hemilability of this unique ligand provide a versatile coordination environment that can accommodate the electronic needs of the ligated elements. For example, chloride abstraction from $[(\text{PNac})\text{EC}]$ ($\text{E} = \text{Ge}, \text{Sn}$) affords the cationic germyliumylidene

and stannylumylidene species $[(\text{PNac})\text{E}]^+$ in which the pendant phosphine arms associate more strongly with the Lewis acidic main group element centers, providing further electronic stabilization. In a similar fashion, chemical decarbonylation of the germanium phosphaketene $[(\text{PNac})\text{Ge}(\text{PCO})]$ with tris(pentafluorophenyl)borane affords a “push–pull” stabilized phosphinidene in which one of the phosphine groups of the ligand backbone associates with the low valent phosphinidene center.

Introduction

Since their discovery over 40 years ago, β -diketiminato (or NacNac) ligands have been employed extensively for the synthesis of metal and metalloid complexes from across the periodic table.^[1,2] One of the characteristics of this ligand scaffold that makes it an attractive support is the ease with which it can be modified. For example, variation of the N-substituents can be used to tune the steric demands and electronic properties of the ligand. Recently, there has been an effort to introduce additional donor capability at the pendant N-substituents including O-donor or S-donor groups.^[3–6] This, in turn, allows for the formation of flexible coordination pockets possessed with potentially hemilabile sites. We recently expanded this

class of ligands with the synthesis of a novel bis(diphenyl)-phosphine functionalized β -diketiminato ligand (PNac) which shows a wealth of coordination modes with transition metals.^[7] This highly versatile ligand can adapt to the electronic needs of the metals in question acting as a multidentate donor. As with other β -diketiminato ligands, this system provides a monoanionic, bidentate support for metal ions,^[2] however the introduction of additional heteroatom donor sites allows access to more complex coordination motifs, and potentially, a flexible electronic support that can respond to changes in the electronic needs of the complexed metal center.

Given the conformational flexibility of this ligand, and the presence of additional donor sites that can assist in the isolation of otherwise highly reactive species, we were intrigued to explore the use of this ligand for the synthesis of a series of germylene and stannylene complexes. Subsequent reactivity studies of these species show that the bis(diphenyl)phosphine functionalized β -diketiminato ligand can respond to changes in the coordination environment of the germanium(II) and tin(II) metal centers.

Results and Discussion

Deprotonation of the protonated ligand, (PNac)H, with potassium bis(trimethylsilyl)amide followed by addition of one equivalent of either $[\text{GeCl}_2(\text{dioxane})]$ or SnCl_2 affords the corresponding chloride complexes, $[(\text{PNac})\text{EC}]$ where $\text{E} = \text{Ge}$ (**1**), Sn (**2**), in moderate to high isolated yields (70–80%) as pictured in Scheme 1.

The ^1H NMR spectrum of **1** reveals the formation of a single product with a $\gamma\text{-H}$ resonance corresponding to the ligand backbone at 4.90 ppm. All other resonances in the ^1H and

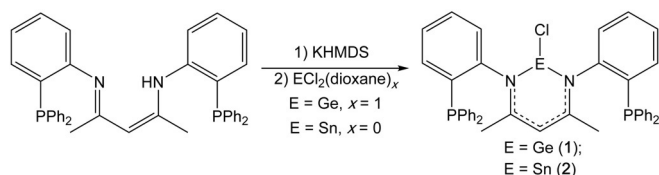
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Scheme 1. Synthesis of compounds 1 and 2.

$^{13}\text{C}\{^1\text{H}\}$ NMR spectra are as expected for a κ^2 - β -diketiminato ligand. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum reveals a singlet resonance at -20.4 ppm, which is shifted to slightly lower frequency than the protio-ligand (-14.5 ppm) and consistent with weak interactions arising between the two pendant phosphine arms and the germanium(II) center (this was also confirmed by single-crystal X-ray diffraction, vide infra).

By contrast, the NMR spectra recorded for solutions of crystals of **2** are more complex, revealing the presence to two isomers that are in a dynamic equilibrium. This can also be seen in the ^{31}P NMR spectrum where a singlet resonance at -19.7 ppm (accompanied by satellites due to coupling with ^{117}Sn and ^{119}Sn nuclei; $^1J_{\text{P-Sn}} = 342.0$ and 357.6 Hz) is accompanied by two doublets at -23.5 and -15.8 ppm (with weak phosphorus-phosphorus coupling of 4.7 Hz). This behavior is mirrored by the $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum which exhibits two resonances at -367 (d, $^1J_{\text{P-Sn}} = 260.1$ Hz) and -310 (t, $^1J_{\text{P-Sn}} = 354.3$ Hz). We postulate that the two isomers in solution are: 1) a species in which both pendant phosphines associate weakly with the tin(II) center (giving rise to a singlet in the $^{31}\text{P}\{^1\text{H}\}$ and a triplet in the $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectra); and 2) an isomer in which an asymmetrical coordination of the phosphine groups gives rise to a strong interaction between one arm and the tin(II) center whilst the second phosphine does not interact to any significant degree. On account of the stereochemically active lone-pair present on the tin(II) center, these two extremes would assume a five coordinate square pyramidal geometry, or a four-coordinate see-saw like structure, respectively. Variable-temperature ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR experiments conducted between 298 and 348 K revealed that both species interconvert (Figures S16 and S17).

Both **1** and **2** could be characterized by single-crystal X-ray diffraction and exhibit weak interactions between the pendant phosphine arms and the tetrel(II) element centers. In the case of **1** (Figure 1), the $\text{Ge}\cdots\text{P}$ interatomic distances differ significantly, $3.384(1)$ and $4.219(1)$ Å, indicating an asymmetric interaction of the phosphine arms. These are both significantly longer than a Ge-P single bond (2.27 – 2.32 Å),^[8,9] however the former is shorter than the sum of Van der Waals radii for the two elements (3.91 Å).^[10] This asymmetric association of the ligands in the solid-state contrasts with the observation of a single resonance in the ^{31}P NMR spectrum of **1**, and suggests that in solution, the association of the ligand arms is dynamic and time averaged. The structure of **2** (see Supporting Information) is also very similar and reveals short and long $\text{Sn}\cdots\text{P}$ contacts with interatomic distances of $3.475(1)$ and $4.385(2)$ Å. As with **1**, these values are longer than a Sn-P single bond (2.46 – 2.51 Å),^[8,9] while the shortest is smaller than the sum of Van der Waals radii (3.97 Å).^[10]

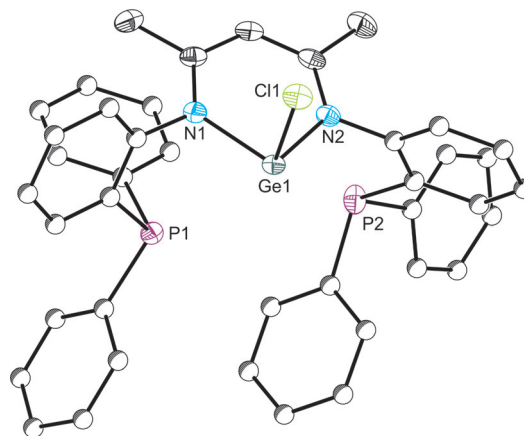
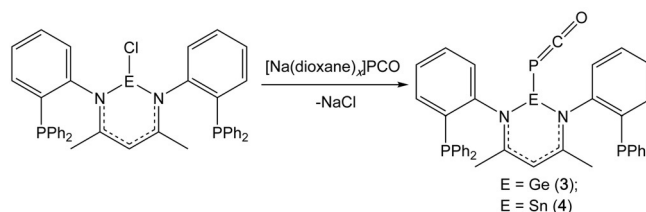


Figure 1. Molecular structure of **1** in the solid state. Anisotropic displacement ellipsoids set at 50% probability. All phenyl carbon atoms are pictured as spheres of arbitrary radius. Hydrogen atoms and solvent of crystallization are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge1-N1 $1.981(2)$, Ge1-N2 $1.972(2)$, Ge1-Cl1 $2.377(1)$, $\text{Ge1}\cdots\text{P1}$ $3.384(1)$, $\text{Ge1}\cdots\text{P2}$ $4.219(1)$; N2-Ge1-N1 $90.57(7)$, N1-Ge1-Cl1 $93.09(5)$, N2-Ge1-Cl1 $96.27(5)$, P1-Ge1-P2 $73.58(2)$.

The Ge-N and Sn-N bond distances in **1** and **2**, $1.972(2)/1.981(2)$ and $2.177(2)/2.185(2)$ Å, respectively, are in line with those observed for other comparable β -diketiminato germanium and tin chlorides.^[11–35] They compare favorably with compounds such as $[\text{HC}\{(\text{CH}_3)_2\text{C}(\text{Dipp})\text{N}_2\}_2\text{E}]\text{Cl}$ ($\text{E} = \text{Ge}, \text{Sn}$) in which the Ge-N and Sn-N bond distances are $1.988(2)/1.997(2)$ and $2.185(2)/2.180(2)$ Å, respectively.^[11]

Reaction of **1** and **2** with $[\text{Na}(\text{dioxane})_x]\text{PCO}$ affords the novel phosphaketene compounds, $[(\text{PNac})\text{E}(\text{PCO})]$ where $\text{E} = \text{Ge}$ (**3**), Sn (**4**) (Scheme 2), accompanied by elimination of sodium chloride. In both complexes, the phosphoethynolate ion (PCO^-) coordinates to the germanium and tin centers through the phosphorus atom. Related germanium(II) phosphaketene compounds featuring β -diketiminato ligands have been previously reported by Aldridge, Driess and Zhao.^[23,25,36] To the best of our knowledge, no analogous stannylene compounds have been reported to date.

The NMR spectra for **3** reveal the formation of a phosphaketene species as evidenced by the two doublet resonances observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at -21.8 and -326.9 ppm corresponding to the phosphine-functionalized β -diketiminato ligand and phosphaketene moieties, respectively. These exhibit a weak ^{31}P – ^{31}P coupling constant of 11.1 Hz. A resonance in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum for the phosphaketene was observed at 118.4 ppm, which exhibits a ^{13}C – ^{31}P coupling con-

Scheme 2. Synthesis of compounds **3** and **4**.

stant of 91.5 Hz, in line with other phosphorus bonded compounds of this type.^[37] As with that of **1**, the ¹H NMR spectrum of **3** reveals a single resonance corresponding to the γ-H position of the ligand backbone at 4.76 ppm indicating the formation of a single isomer (or rapid interconversion of isomers on the NMR timescale). Both **3** and **4** were found to rapidly decompose in solution; consequently, and due to the presence of two isomeric forms of **4** in solution, suitable NMR spectra could not be obtained for this compound although colorless to pale yellow crystals were found to readily precipitate from the reaction medium.

Compounds **3** and **4** were further characterized by single-crystal X-ray diffraction (Figure 2 and Supporting Information). Both exhibit linear phosphaketenes coordinated to the tetrel element center (∠P-C-O: 177.6(9) and 176.9(5)°, respectively) with Ge–PCO and Sn–PCO bonds (2.536(2) and 2.691(1) Å, respectively) that are in line with related species. The Ge–PCO bonds for known β-diketiminato germynes range between 2.476(1) and 2.547(1) Å.^[23,25,36] As with **1** and **2**, the single-crystal X-ray structures reveal a significant variation in the interatomic distances between the pendant phosphine arms of the ligand and the tetrel(II) centers. These values are 3.477(2) and 4.171(2) Å for **3** (cf. 3.384(1) and 4.219(1) Å for **1**), and 3.136(1) and 3.882(1) for **4** (3.475(1) and 4.385(2) for **2**). Of note is that these are significantly shorter for compound **4**, which suggests that the interaction of the phosphoethynolate ion with the tin(II) center is weaker than the corresponding interaction with the chloride ion in **2**. The Ge–N and Sn–N distances observed for **3** and **4**, 1.984(5)/1.993(4) and 2.207(3)/2.227(3) Å, respectively, are in line with those observed for **1** and **2** and other β-diketiminato compounds, cf. 1.971(2)/2.016(2) Å for [HC(tBuC)₂[(Dipp)N]₂]Ge(PCO).^[23]

Reaction of **1** and **2** with sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (Na[BarF₄]) permits the abstraction of a chlor-

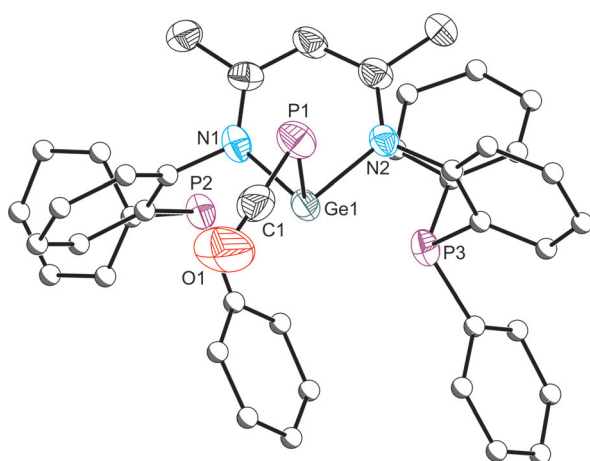
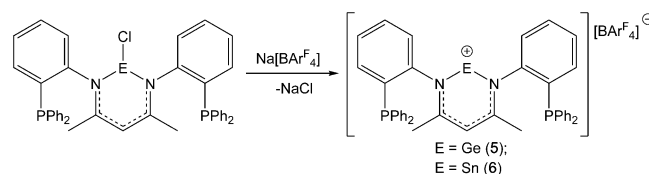


Figure 2. Molecular structure of **3** in the solid state. Anisotropic displacement ellipsoids set at 50% probability. All phenyl carbon atoms are pictured as spheres of arbitrary radius. Hydrogen atoms and solvent of crystallization are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge1–N1 1.993(4), Ge1–N2 1.984(5), Ge1–P1 2.536(2), P1–C1 1.567(8), C1–O1 1.188(11), Ge1–P2 4.171(2), Ge1–P3 3.477(2); N1–Ge1–N2 90.3(2), N2–Ge1–P1 95.24(15), N1–Ge1–P1 89.25(14), C1–P1–Ge1 91.7(3), O1–C1–P1 177.6(9), P2–Ge1–P3 70.72(4).

ide ion from the group 14 elements to afford salts [(PNac)E][BarF₄], where E = Ge (**5**), Sn (**6**) (Scheme 3). The reactions were monitored by ¹H and ³¹P{¹H} NMR spectroscopy, which reveal the formation of clean products with singlet chemical shifts in the ¹H NMR spectra at 4.53 and 4.36 ppm, for **5** and **6**, respectively, corresponding to the γ-H atoms of the ligand backbone. The ³¹P{¹H} NMR spectra reveal singlet resonances at –16.1 (**5**) and –14.2 ppm (**6**), which are moderately shifted from the chloride precursors. In both cases the spectra are consistent with the formation of a single isomer in which the two phosphine arms associate with the cationic tetrel(II) centers. This is best illustrated in the case of **6**, where the ³¹P{¹H} NMR resonance is accompanied by satellites due to coupling with ¹¹⁷Sn and ¹¹⁹Sn nuclei with ¹J_{P–Sn} values of 1139.1 and 1192.6 Hz. It is worth highlighting the significant increase in the phosphorus–tin coupling constant values, which treble relative to the chloride-containing precursor, indicating a significantly stronger interaction between the phosphine arms of the β-diketiminato ligand and the tin atom. The ¹¹⁹Sn{¹H} NMR spectrum of **6** reveals a triplet resonance centered at –505.1 ppm. No spectroscopic evidence was observed for a fluxional process such as that observed for **2**, indicating that in the case of the [(PNac)Sn]⁺ cation, the increased Lewis acidity of the metal center gives rise to a tighter association of the phosphine arms, as also highlighted by the increased coupling between nuclei. This was also confirmed by single-crystal X-ray diffraction. Related cationic germanium(II) complexes bearing β-diketiminato ligands have been previously synthesized using a related synthetic strategy.^[38,39]

The single-crystal X-ray structures of **5** and **6** reveal cationic β-diketiminato supported group 14 elements accompanied by weakly coordinating [BarF₄][–] anions (see Figure 3 and Supporting Information). In both cases, the phosphine arms of the ligand are more strongly associated with the central group 14 elements than in the chloride-containing precursors. The Ge–P bond lengths in **5** are 2.536(1) and 2.869(1) Å and are notably shorter than those observed for **1** (3.384(1) and 4.219(1) Å) whereas there is no significant change to the Ge–N distances. The same is also true of **6**, where the Sn–P distances, 2.761(1) and 2.916(1) Å, approach the values for single bonds (2.46–2.51 Å) and are notably shorter than those recorded for **2** (3.475(1) and 4.385(2) Å) and **4** (3.136(1) and 3.882(1) Å). In the case of **6**, the tin center adopts a square pyramidal geometry with a sum of bond angles about the tin(II) center of 307.4°. It is interesting to note that in the case of **6**, only one isomer is observed in solution (in contrast to **2** and **4**). This suggests that upon halide abstraction, the ligand associates more strongly with the tin(II) center and resolves dynamic behavior.



Scheme 3. Synthesis of compounds **5** and **6**.

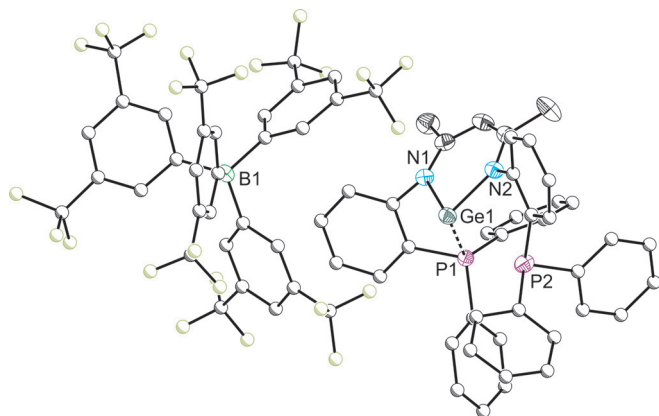


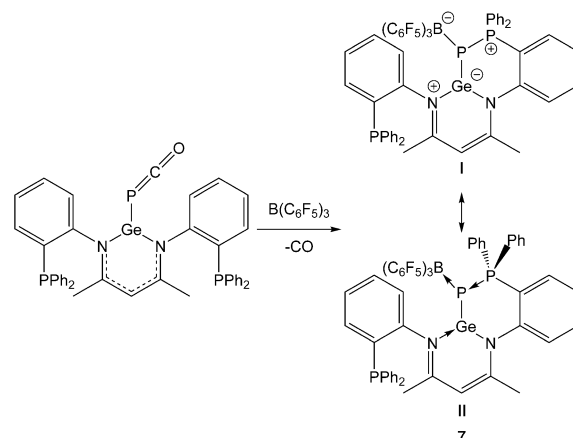
Figure 3. Molecular structure of **5** in the solid state. Anisotropic displacement ellipsoids set at 50% probability. All phenyl carbon and CF_3 atoms are pictured as spheres of arbitrary radius. Hydrogen atoms and disordered CF_3 groups are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge1–N1 2.052(2), Ge1–N2 1.975(2), Ge1...P1 2.536(1), Ge1...P2 2.869(1); N1–Ge1–N2 89.41(7), N1–Ge1–P1 72.61(5), N1–Ge1–P2 144.09(5), N2–Ge1–P1 110.41(5), N2–Ge1–P2 73.54(5), P1–Ge1–P2 83.89(2).

The reactivity of these Lewis acidic compounds is currently being explored, preliminary studies suggest that, given the increased Lewis acidity, the germyliumylidene cation **5** is significantly more reactive.

Intrigued by the geometric plasticity of this bis(diphenyl)-phosphine functionalized β -diketiminato ligand and its ability to stabilize reactive compounds in an intramolecular fashion, we explored the chemical decarbonylation of compound **3** using tris(pentafluorophenyl)borane. Analogous reactions with **4** led to decomposition. A number of transition metal and main group element phosphaketenes have been shown to undergo thermal or photolytic decarbonylation processes.^[37] These reactions are postulated to proceed via the formation of transient phosphinidenes which often dimerize to afford diphosphenes featuring P=P bonds. In selected cases, singlet and triplet phosphinidene compounds have been observed.^[40,41]

Reaction of **3** with $\text{B}(\text{C}_6\text{F}_5)_3$ afforded a novel species with three resonances in its $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. These were observed at 22.1, –19.8 and –123.8 ppm, with the first and last of these coupling to one another with a coupling constant of 538 Hz. The low frequency chemical shift of the latter of these resonances is significantly shifted relative to the phosphaketene precursor **3** and consistent with decarbonylation (Scheme 4). It is worth noting that a slight excess of $\text{B}(\text{C}_6\text{F}_5)_3$ is required for the stabilization of **7** in solution as the coordination appears to be reversible. No intermediates were observed in the reaction mixture. The $\text{B}(\text{C}_6\text{F}_5)_3$ -free species quickly undergoes further reactivity. In order to obtain a compositionally pure sample, excess $\text{B}(\text{C}_6\text{F}_5)_3$ was removed by washing orange crystals of **7** with hexane followed by removal of all volatiles under reduced pressure. The purity of this compound was confirmed by solid state NMR and elemental analysis investigations.

Orange crystals of this compound were obtained by slow diffusion of hexane into a toluene solution of the reaction mix-



Scheme 4. Synthesis of compound **7**.

ture. Single-crystal X-ray analysis confirmed the structure of the product as a “push–pull” stabilized phosphinidene, PNac-GeP(BCF) (**7**), in which the phosphorus atom of the parent phosphaketene interacts with BCF and with one of the phosphine arms of the β -diketiminato ligand (Figure 4). The P–P distance, 2.132(1) Å, is in line with the expected values for a single bond (2.14–2.22 Å), as is the P–B distance, 2.081(2) Å. All of the other bond metric data for this compound are in good agreement with those of the phosphaketene precursor, the Ge–P bond length (2.511(1) Å) is comparable to that observed for **3** (2.536(2) Å), as are the Ge–N bond lengths, 2.007(2)/2.024(2) Å (cf. 1.984(5)/1.993(4) for **3**).

Related “push–pull” stabilized phosphinidenes, the most common of which are Lewis-acid trapped phosphanylidene- σ^4 -phosphoranes ($\text{RP}=\text{PR}'_3$), have been reported in the chemical literature.^[42,43] The reaction of phosphanyl-phosphaketenes

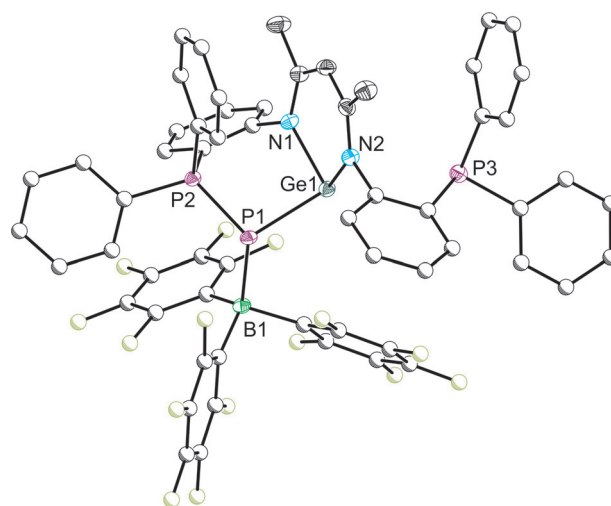


Figure 4. Molecular structure of **7** in the solid state. Anisotropic displacement ellipsoids set at 50% probability. All phenyl carbon atoms are pictured as spheres of arbitrary radius. Hydrogen atoms and solvent of crystallization are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge1–N1 2.007(2), Ge1–N2 2.024(2), Ge1–P1 2.511(1), P1–P2 2.132(1), P1–B1 2.081(2); N1–Ge1–N2 89.62(7), N1–Ge1–P1 97.44(5), N2–Ge1–P1 95.84(5), B1–P1–P2 112.20(6), B1–P1–Ge1 105.36(6), P2–P1–Ge1 94.52(2).

with strong Lewis bases (isocyanates, carbenes, phosphines) affords base-stabilized phosphinidenes,^[44] however, to our knowledge this is the first report in which an intramolecular interaction has been employed to trap such a species. This highlights the coordinative flexibility of the phosphine-functionalized β -diketiminato ligand.

Compound **7** can be described as a phosphonium borate bridged by a phosphine ($\sigma^3\lambda^3$ -phosphane) (**I**, Scheme 4) or, alternatively as a “push–pull” phosphinidene ($\sigma^3\lambda^1$ -phosphane) that is stabilized by donation from a phosphine and donation to a borane (**II**, Scheme 4). It is worth noting that we use the term “push–pull” phosphinidene to refer to a monovalent R–P compound which is stabilized by donor and acceptor interactions with a Lewis acid and a base.^[45] DFT calculations were conducted to establish the nature of the bonding interactions present in this species. The electron density (ρ), the Laplacian of the electron density ($\nabla^2\rho$), and the energy density ($E(r)$) at the bond critical points of the P–P and P–B bonds in **7** are more in line with dative interactions, such as the Ge–N bonds in the molecule, than with conventional covalent bonds, such as the C–C bonds in the molecule (see Supporting Information). Electronic structure **II** is also supported by population analyses based on the canonical molecular orbitals (Mulliken), natural bond orbitals (NPA), and topologically defined atomic basins (AIM) (Table 1). The relative atomic charges from all methods agree better with **II** than **I**. First, P2 and P3 have similar calculated charges, whereas structure **I** would result in P2 being much more positive than P3. Second, P1 is more negative than either P2 or P3, consistent with P1 being monovalent and P2 and P3 being trivalent. Although these data support the formulation of **7** as a “push–pull” stabilized phosphinidene, the reality of the bonding situation lies, as always, somewhere in between these two bonding extremes.

Table 1. Population analysis of the phosphorus atoms in **7**.^[a]

Atom ^[b]	Mulliken	NPA	AIM
P1	−0.11	−0.20	−0.31
P2	0.52	1.32	1.80
P3	0.46	0.92	1.66

[a] Full details in Supporting Information. [b] Atoms labeled as in Figure 4.

Conclusions

We have isolated several novel germylene and stannylene complexes featuring a phosphine-functionalized β -diketiminato ligand and shown that this novel supporting ligand plays an active role in the stabilization of electronically unsaturated species such as the cationic compounds $[(\text{PNac})\text{E}]^+$ ($\text{E} = \text{Ge}, \text{Sn}$) and the push–pull stabilized phosphinidene $(\text{PNac})\text{GeP}(\text{BCF})$. The germylumylidene and stannylumylidene compounds are interesting candidates for investigating their behavior towards nucleophiles and small molecule activation.

Experimental Section

General synthetic and analytical methods: All reactions and product manipulations were carried out under an inert atmosphere of argon or dinitrogen using standard Schlenk-line or glovebox techniques (MBraun UNILab glovebox maintained at <0.1 ppm H_2O and <0.1 ppm O_2). Pentane (pent; Sigma–Aldrich, HPLC grade, $\geq 99\%$), *n*-hexane (hex; Sigma–Aldrich, HPLC grade, $\geq 97\%$), benzene (Sigma–Aldrich, anhydrous, 99.8%) and toluene (Sigma–Aldrich; HPLC grade, 99.8%) were purified using an MBraun SPS-800 solvent system. Tetrahydrofuran (THF; Sigma–Aldrich, HPLC grade, $\geq 99.9\%$) was distilled over sodium metal/benzophenone. All dry solvents were stored under argon in gas-tight ampoules. Additionally, pentane, hexane and THF were stored over activated 3 Å molecular sieves. $[\text{D}_8]\text{THF}$ (Sigma–Aldrich, 99.5%) was dried over CaH_2 and vacuum distilled before use. C_6D_6 (Sigma–Aldrich, 99.5%) was stored over activated 3 Å molecular sieves and degassed prior to use. $(\text{PNac})\text{H}$, $[\text{Na}(\text{dioxane})_x]\text{PCO}$, $[\text{Na}(\text{BARF}_4)]$ and $\text{B}(\text{C}_6\text{F}_5)_3$ were prepared according literature procedures.^[7,46–48] The dioxane content in $[\text{Na}(\text{dioxane})_x]\text{PCO}$ was determined by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy using PPh_3 as internal standard. Potassium bis(trimethylsilyl)amide (KHMDs or KBTS; Sigma–Aldrich, 95%), $[\text{GeCl}_2(\text{dioxane})]$ (Sigma–Aldrich) and SnCl_2 (Acros Organics, 98%) were used without further purification.

NMR samples were prepared inside an inert atmosphere glovebox in NMR tubes fitted with a gas-tight valve. ^1H NMR spectra were recorded at either 499.9 MHz or 400.1 MHz on a Bruker AVIII 500 or a Bruker AVIII 400 NMR spectrometer, respectively. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded at either 125.8 MHz or 100.6 MHz on a Bruker AVII 500 fitted with a cryoprobe or a Bruker AVIII 400 NMR spectrometer, respectively. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded at 202.4 MHz or 162.0 MHz on a Bruker AVIII 500 or a Bruker AVIII 400 NMR spectrometer, respectively. ^{11}B (128.4 MHz), ^{19}F (376.5 MHz) and ^{119}Sn NMR (149.5 MHz) spectra were recorded at on a Bruker AVIII 400 NMR spectrometer. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra are reported relative to TMS and referenced to the most downfield residual solvent resonance where possible. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra are externally referenced to an 85% solution of H_3PO_4 in H_2O ($\delta = 0$ ppm). ^{11}B NMR spectra are externally referenced to a 15% $\text{BF}_3\cdot\text{OEt}_2$ solution in CDCl_3 . ^{19}F NMR spectra are externally referenced CFCl_3 . ^{119}Sn NMR spectra are externally referenced to SnMe_4 in CDCl_3 . SSNMR were run on a Bruker AVIIHD WB400 MHz NMR spectrometer. Samples were packed in 1.9 mm O.D. rotors.

For details of Density Functional Theory calculations please see Supporting Information.

Crystallographic data: Deposition numbers 195873, 195874, 195875, 195876, 195877, 195879, and 195880 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Synthesis of $[(\text{PNac})\text{GeCl}]$ (1**):** $(\text{PNac})\text{H}$ (200 mg, 0.32 mmol, 1.00 equiv.) and KHMDs (65 mg, 0.32 mmol, 1.00 equiv.) were weighted in a Schlenk tube and dissolved in THF (10 mL). The orange mixture was stirred for 1–2 hours at room temperature and subsequently dried under vacuum. In the glove box, $[\text{GeCl}_2(\text{dioxane})]$ (75 mg, 0.32 mmol, 1.00 equiv.) was added as a solid to the orange residue. Outside the box, toluene (10 mL) was added and the mixture was stirred overnight, during which it turned light yellow. The suspension was cannula filtered and concentrated (≈ 2 mL). Large colorless to pale yellow crystals were obtained within hours. After 2 days, crystals were separated from the mother liquor by decantation and dried under vacuum. Yield:

180 mg (78%, single crystals). Note: The product is quite soluble in toluene. Thus, the yield (based on crystalline material) varies depending on crystallization conditions and is usually higher than the yield reported here. ^1H NMR (C_6D_6 , 400.30 MHz): δ (ppm) = 1.36 (s, 6H; CH_3), 4.90 (s, 1H; CNCHCN), 6.81–6.94 (m, 8H; CH), 7.02–7.08 (m, 8H; CH), 7.17–7.25 (m, 6H; CH), 7.45–7.60 (m, 4H; CH), 7.72–7.82 (m, 2H; CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 100.67 MHz): δ (ppm) = 23.30 (CH_3), 100.01 (CNCHCN), 127.70 (CH), 128.30 (CH), 128.35 (CH), 128.49 (t, $^3J_{\text{C-P}} = 3.1$ Hz; CH), 128.78 (t, $^4J_{\text{C-P}} = 3.6$ Hz; CH), 129.15 (CH), 130.63 (CH), 133.63 (t, $^2J_{\text{C-P}} = 11.6$ Hz; CH), 134.85 (CH), 135.39 (t, $^3J_{\text{C-P}} = 12.3$ Hz; CH), 135.87 (dd, $J_{\text{C-P}} = 6.9$ Hz, 3.6 Hz; C_q), 137.13 (dd, $J_{\text{C-P}} = 8.8$ Hz, 5.9 Hz; C_q), 137.54 (dd, $J_{\text{C-P}} = 7.6$ Hz, 4.7 Hz; C_q), 149.03 (dt, $^2J_{\text{C-P}} = 24.6$ Hz, 12.1 Hz; C_q), 165.04 (CN). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 162.04 MHz): δ (ppm) = –20.4 (s). Elemental analysis calcd (%) for $[\text{C}_{41}\text{H}_{35}\text{ClGeN}_2\text{P}_2 \cdot 0.5 \text{C}_7\text{H}_8]$ (725.77 g mol $^{-1}$): C 69.25, H 5.09, N 3.63; Found C 68.98, H 5.15, N 3.52.

Synthesis of [(PNac)SnCl] (2): (PNac)H (315 mg, 0.51 mmol, 1.00 equiv.) and KHMDs (102 mg, 0.51 mmol, 1.00 equiv.) were weighed in a Schlenk tube and dissolved in THF (10 mL). The orange mixture was stirred for 1–2 hours at room temperature and subsequently dried under vacuum. In the glove box, SnCl_2 (97 mg, 0.51 mmol, 1.00 equiv.) was added as a solid to the orange residue. Outside the box, toluene (10 mL) was added and the mixture was stirred overnight, during which it turned light yellow. The suspension was cannula filtered and concentrated (≈ 2 mL). Large colorless to pale yellow crystals were obtained within hours. After 2 days, crystals were separated from the mother liquor by decantation and dried under vacuum. Yield: 280 mg (71%, single crystals). Note: The product is quite soluble in toluene. Thus, the yield (based on crystalline material) varies depending on crystallization conditions and is usually higher than the yield reported here. ^1H NMR (C_6D_6 , 400.30 MHz): δ (ppm) = 1.33 (s, 6H; CH_3 isomer 1), 1.43 (s, 3H total; CH_3 isomer 2), 1.64 (s, 3H; CH_3 isomer 2), 4.67 (s, 1H; CNCHCN isomer 1), 4.95 (s, 1H; CNCHCN isomer 2), 6.67–7.01 (m, 8H $\times 2$; CH), 7.01–7.11 (m, 10H $\times 2$; CH), 7.18–7.91 (m, 10H $\times 2$; CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 100.67 MHz): Due to the presence of two interconverting species, no ^{13}C spectra were recorded. $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 162.04 MHz): δ (ppm) = –23.5 (d, $^2J_{\text{P-Sn}} = 4.7$ Hz; $^{117/119}\text{Sn}$ satellites $^1J_{\text{P-Sn}} = 67.4$ Hz; isomer 2), –19.7 ($^{117/119}\text{Sn}$ satellites $^1J_{\text{P-Sn}} = 342.0$ Hz, $^1J_{\text{P-Sn}} = 357.6$ Hz; isomer 1), –15.8 (d, $^2J_{\text{P-P}} = 4.7$ Hz; $^{117/119}\text{Sn}$ satellites $^1J_{\text{P-Sn}} = 226.9$ Hz; isomer 2). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (C_6D_6 , 149.5 MHz): δ (ppm) = –368 (br; isomer 2), –311 (t, $^1J_{\text{P-Sn}} = 354$ Hz; isomer 1). Elemental analysis calcd (%) for $[\text{C}_{41}\text{H}_{35}\text{ClN}_2\text{P}_2\text{Sn} \cdot 0.5\text{C}_7\text{H}_8]$ (771.85 g mol $^{-1}$): C 65.35, H 4.81, N 3.43; Found C 65.45, H 4.84, N 3.53.

Synthesis of [(PNac)Ge(PCO)] (3): [(PNac)GeCl] (1) (50 mg, 0.06 mmol, 1.00 equiv.) and $[\text{Na}(\text{dioxane})_{2.5}]\text{PCO}$ (20 mg, 0.07 mmol, 1.15 equiv.) were weighed into a Schlenk flask and suspended in toluene (5 mL). The resulting mixture was stirred overnight. Subsequently, the mixture was filtered via cannula and concentrated to dryness. Typically, the target compound was used as prepared for further reactions, as it is prone to decomposition in solution. Colorless to pale yellow crystals can be obtained, which were separated from the mother liquor by decantation and dried under vacuum. ^1H NMR (C_6D_6 , 400.30 MHz): δ (ppm) 1.32 (s, 6H; CH_3), 4.76 (s, 1H; CNCHCN), 6.87–6.94 (m, 6H; CH), 7.01–7.08 (m, 10H; CH), 7.20–7.25 (m, 6H; CH), 7.47–7.55 (m, 4H; CH), 7.73–7.78 (m, 2H; CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 100.67 MHz): the sample was found to rapidly decompose preventing the collection of a suitable NMR spectrum, however a resonance could be observed at 188.40 (d, $^1J_{\text{C-P}} = 91.5$ Hz, PCO). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 162.04 MHz): δ (ppm) = –326.9 (t, $^1J_{\text{P-P}} = 11.1$ Hz), –21.8 (d, $^1J_{\text{P-P}} = 11.1$ Hz). Elemental analysis calcd (%) for

$[\text{C}_{42}\text{H}_{35}\text{GeN}_2\text{O}_3\text{P}_2]$ (749.31 g mol $^{-1}$): C 67.32, H 4.71, N 3.63; Found C 67.37, H 4.89, N 2.78.

Synthesis of [(PNac)Sn(PCO)] (4): [(PNac)SnCl] (2) (60 mg, 0.07 mmol, 1.00 equiv.) and $[\text{Na}(\text{dioxane})_{3.4}]\text{PCO}$ (40 mg, 0.10 mmol, 1.40 equiv.) were weighed into a Schlenk flask and suspended in toluene (5 mL). The resulting mixture was stirred overnight. Subsequently, the mixture was filtered via cannula and concentrated. Typically, the target compound was used as prepared for further reactions, as it is prone to rapid decomposition in solution. This decomposition precluded the collection of suitable NMR data. Colorless to pale yellow crystals can be obtained, which were separated from the mother liquor by decantation and dried under vacuum.

Synthesis of [(PNac)Ge][BAR $^{\text{F}}_4$] (5): [(PNac)GeCl] (1) (31.1 mg, 0.04 mmol, 1.00 equiv.) and $\text{Na}[\text{BAR}^{\text{F}}_4]$ (38 mg, 0.04 mmol) were added in a small Schlenk tube and dissolved in benzene (5 mL). The resulting suspension was gently heated and stirred overnight. Subsequently, the reaction mixture was filtered via cannula and concentrated to dryness. The solid residue was recrystallized from very concentrated benzene solutions or toluene solutions layered with *n*-pentane. Yield losses are attributed to the high solubility of **5** in these solvents. Yield: 32 mg (52%). ^1H NMR (C_6D_6 , 400.30 MHz): δ (ppm) 1.27 (s, 6H; CH_3), 4.53 (s, 1H; CNCHCN), 6.52–6.64 (m, 4H; CH), 6.64–6.75 (m, 2H; CH), 6.79–7.08 (m, 22H; CH), 7.65 (s, 4H; *p*-CH), 8.41 (m, 8H; *o*-CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 100.67 MHz): δ (ppm) 22.82 (s; CH_3), 103.07 (s; CNCHCN), 118.11 (sept, $^3J_{\text{C-F}} = 3.9$ Hz; $\text{C}^4\text{-BAR}^{\text{F}}_4$), 125.26 (q, $^1J_{\text{C-F}} = 272$ Hz; $\text{CF}_3\text{-BAR}^{\text{F}}_4$), 127.47 (t, $^1J_{\text{C-P}} = 22.2$ Hz; C-P), 128.79 (d, $^1J_{\text{C-P}} = 19.4$ Hz; C-P), 128.80 (s; *p*- C_{ph}), 129.33 (2 \times t, overlapping, $J_{\text{C-P}} = 8.6$ Hz; C_{ph}), 129.95 (qq, $^2J_{\text{C-F}} = 31.3$ Hz, $^4J_{\text{C-F}} = 2.7$ Hz; $\text{C}^3\text{-BAR}^{\text{F}}_4$), 131.42 (d, $^2J_{\text{C-P}} = 36$ Hz; C_{ph}), 132.79 (s; C_{ph}), 132.99 (t, $^3J_{\text{C-P}} = 6.9$ Hz; C_{ph}), 133.61 (t, $^3J_{\text{C-P}} = 7.5$ Hz; C_{ph}), 133.76 (s; C_{ph}), 135.46 (bs; $\text{C}^6\text{-BAR}^{\text{F}}_4$), 147.95 (t, $^2J_{\text{C-P}} = 9.0$ Hz; $\text{C}_q\text{-N}$), 162.79 (q, $^1J_{\text{C-B}} = 50.3$ Hz; $\text{C}^1\text{-BAR}^{\text{F}}_4$), 167.07 (s, C=N). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 162.04 MHz): δ (ppm) –16.1 (s). $^{19}\text{F}\{^1\text{H}\}$ NMR (C_6D_6 , 376.49 MHz): δ (ppm) –62.1 (s). $^{11}\text{B}\{^1\text{H}\}$ NMR (C_6D_6 , 128.37 MHz): δ (ppm) –5.9 (s). Elemental analysis calcd (%) for $[\text{C}_{73}\text{H}_{47}\text{BF}_4\text{GeN}_2\text{P}_2]$ (1553.54 g mol $^{-1}$): C 56.44, H 3.05, N 1.80; Found C 56.28, H 3.00, N 1.92.

Synthesis of [(PNac)Sn][BAR $^{\text{F}}_4$] (6): [(PNac)SnCl] (2) (20 mg, 0.02 mmol, 1.00 equiv.) and $\text{Na}[\text{BAR}^{\text{F}}_4]$ (23 mg, 0.02 mmol, 1.00 equiv.) were added in a small Schlenk tube and dissolved in benzene (5 mL). The resulting suspension was gently heated and stirred overnight. Subsequently, the reaction mixture was filtered via cannula and concentrated to dryness. The solid residue was recrystallized from very concentrated benzene solutions or toluene solutions layered with *n*-pentane. Yield losses are attributed to the high solubility of **6** in these solvents. Yield: 20 mg (48%). ^1H NMR (C_6D_6 , 400.30 MHz): δ (ppm) 1.26 (s, 6H; CH_3), 4.36 (s, 1H; CNCHCN), 6.47–6.63 (m, 4H; CH), 6.65–7.14 (m, 24H; CH), 7.66 (s, 4H; *p*-CH), 8.42 (m, 8H; *o*-CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 100.67 MHz): δ (ppm) 23.23 (s; CH_3), 100.51 (s; CNCHCN), 118.11 (sept, $^3J_{\text{C-F}} = 3.2$ Hz; $\text{C}^4\text{-BAR}^{\text{F}}_4$), 125.00 (q, $^1J_{\text{C-F}} = 272$ Hz; $\text{CF}_3\text{-BAR}^{\text{F}}_4$), 126.00 (t, $^1J_{\text{C-P}} = 23.3$ Hz; C-P), 127.53 (s; *p*- C_{ph}), 127.60 (d, $^1J_{\text{C-P}} = 21.9$ Hz; C-P), 129.40 (t, $^3J_{\text{C-P}} = 4.7$ Hz; C_{ph}), 129.60 (t, $^3J_{\text{C-P}} = 4.8$ Hz; C_{ph}), 129.95 (qq, $^2J_{\text{C-F}} = 31.5$ Hz, $^4J_{\text{C-F}} = 2.8$ Hz; $\text{C}^3\text{-BAR}^{\text{F}}_4$), 131.70 (d, $^2J_{\text{C-P}} = 24.5$ Hz; C_{ph}), 132.76 (s; C_{ph}), 133.82 (s; C_{ph}), 133.33 (t, $^3J_{\text{C-P}} = 6.8$ Hz; C_{ph}), 133.62 (t, $^3J_{\text{C-P}} = 7.2$ Hz; C_{ph}), 135.47 (bs; $\text{C}^6\text{-BAR}^{\text{F}}_4$), 149.57 (t, $^2J_{\text{C-P}} = 7.7$ Hz; $\text{C}_q\text{-N}$), 162.81 (q, $^1J_{\text{C-B}} = 49.7$ Hz; $\text{C}^1\text{-BAR}^{\text{F}}_4$), 166.87 (s, C=N). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 162.04 MHz): δ (ppm) –14.2 (s), $^{117/119}\text{Sn}$ satellites (d, $^1J_{\text{P-Sn}} = 1139$ Hz; d, $^1J_{\text{P-Sn}} = 1192$ Hz). $^{19}\text{F}\{^1\text{H}\}$ NMR (C_6D_6 , 376.49 MHz): δ (ppm) –62.1 (s). $^{11}\text{B}\{^1\text{H}\}$ NMR (C_6D_6 , 128.37 MHz): δ (ppm) –5.9 (s). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (C_6D_6 , 149.5 MHz): δ (ppm) –505 (t, $^1J_{\text{P-Sn}} = 1191$ Hz). Elemental analysis calcd (%) for $[\text{C}_{73}\text{H}_{47}\text{BF}_4\text{N}_2\text{P}_2\text{Sn}]$

(1600.19 g mol⁻¹): C 54.81, H 2.96, N 1.75; Found C 54.86, H 3.05, N 1.84.

Synthesis of [(PNac)GeP(B(C₆F₅)₃)] (7): [(PNac)Ge(PCO)] (3) (70 mg, 0.09 mmol, 1.00 equiv) was dissolved in toluene and added to a Schlenk charged with a stir bar. To this solution, B(C₆F₅)₃ (57 mg, 0.11 mmol, 1.2 equiv) was added resulting in a color change from yellow to orange. The solution was allowed to react overnight and under ambient conditions. The mother liquors were layered with *n*-hexane and slow diffusion yield orange crystals in Yield: 80 mg (69% single crystals). *Note:* A slight excess of B(C₆F₅)₃ is required as the coordination appears to be reversible. The B(C₆F₅)₃-free species quickly undergoes further reactivity. Given the functional nature of this species a clean ¹³C NMR could not be obtained. Excess B(C₆F₅)₃ was removed by washing orange crystals of **7** with hexane (3 × 20 mL) followed by removal of all volatiles under reduced pressure. Presence of **7** was confirmed by soli-state NMR and elemental analysis investigations. ¹H NMR (C₆D₆, 400.30 MHz): δ (ppm) 0.51 (s, 3H; CH₃), 1.04 (s, 3H; CH₃), 3.28 (qd, *J* = 7.0, 2.2 Hz, 1H; CNCHCN), 8.13–7.19 (m, 11H; CH), 7.13–6.08 (m, 17H; CH). ³¹P{¹H} NMR (C₆D₆, 162.04 MHz): δ (ppm) 22.10 (d, ¹*J*_{P-P} = 532 Hz, 1P; Ph₂PP), –19.81 (s, 1P; Ph₂P), –123.84 (dm, ¹*J*_{P-P} = 538 Hz; GeP). ¹⁹F{¹H} NMR (C₆D₆, 376.50 MHz): δ (ppm) –127.50 (b, 4F; *o*-C₆F₅), –132.42 (m, 2F; *o*-C₆F₅), –164.45 (bs, 3F; *p*-C₆F₅), –164.54 (bs, 6F; *m*-C₆F₅). ¹¹B{¹H} NMR (C₆D₆, 128.39 MHz): δ (ppm) –13.39 (s, B(C₆F₅)). ³¹P{¹H} NMR (SS, 161.87 MHz): δ (ppm) 21.96 (d, ¹*J*_{P-P} = 399 Hz; Ph₂PP), 19.28 (d, ¹*J*_{P-P} = 472 Hz; Ph₂PP), –16.48 (s; Ph₂P), –18.61 (s; Ph₂P), –112.86 (bm; GeP). ¹⁹F{¹H} NMR (SS, 376.22 MHz): δ (ppm) –42.36 (s; C₆F₅), –43.83 (s; C₆F₅), –50.46 (s; C₆F₅), –81.54 (s; C₆F₅), –90.46 (s; C₆F₅), –121.52 (s; C₆F₅), –129.39 (s; C₆F₅), –129.89 (s; C₆F₅), –162.96 (s; C₆F₅), –200.85 (s; C₆F₅), –208.37 (s; C₆F₅), –240.78 (s; C₆F₅), –279.84 (s; C₆F₅). ¹¹B{¹H} NMR (SS, 128.39 MHz): δ (ppm) –12.31. Elemental analysis calcd (%) for [C₅₉H₃₅BF₁₅GeN₂P₃C₇H₈] (1325.42 g mol⁻¹): C 59.81, H 3.15, N 2.38; Found C 59.56, H: 3.15, N: 2.33.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: phosphathenolate • phosphine • phosphinidene • β-diketimine • tris(pentafluorophenyl)borane

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