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The Reactivity of Phosphagermaallene Tip(*t*-Bu)Ge═C═PMes* with Doubly and Triply Bonded Nitrogen Compounds

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Phosphagermaallene Tip(*t*-Bu)Ge═C═PMes* (**1**; Mes* = 2,4,6-tri-*tert*-butylphenyl, Tip = 2,4,6-triisopropylphenyl) gives, with N-benzylidenemethylamine and pivalonitrile, [2+2] cycloadditions between the Ge═C double bond and the C═N and C≡N unsaturations, leading to the formation of the corresponding four-membered heterocycles **2** and **9**. With N-*tert*-butyl-α-phenylnitrone and benzonitrile oxide, [2+3] cycloadditions occur to form the five-membered ring derivatives **6** and **7**. By treatment of **1** with derivatives which possess weak acidic hydrogens in α of the C═N or C≡N multiple bond, two types of reactions were observed: an ene reaction with methyl(benzylideneamino)acetate and a 1,2 addition with acetonitrile to afford azadienyl(germyl)ether (**4**) and 3-germa-1-phosphapropene (**8**), respectively. In the case of benzonitrile, phosphagermaallene **1** behaves as a 1,3-dipole, to give, via a cyclic phosphagermacarbene intermediate, the tricyclic derivative **10**.

Introduction

Alkenes and allenes are among the most important compounds in organic chemistry: they are the precursors of many derivatives and organic functions by the addition of various reagents on the C═C double bond. Their heavier analogues E═E′ and E═C═E′ (E, E′ = Si, Ge, Sn, N, P, As) have only been postulated as transient intermediates for a long time. However, heavier heteroallenes, such as phosphaallenes —P═C═X[1] (X = C, N, P, As, O, S) and some metallaallenes >Si═C═C<[1−3] or >Ge═C═C<,[1,4] can be successfully synthesized as stable derivatives by the use of bulky substituents, which kinetically stabilize the reactive double bonds. With two different heavy elements of groups 14 and 15, only one transient phosphasilaallene, Ph(Tip)Si═C═PMes*[5] (Mes* = 2,4,6-tri-*tert*-butylphenyl, Tip = 2,4,6-triisopropylphenyl), and two phosphagermaallenes, the transient Mes_2Ge═C═PMes*[6] and the stable and isolable Tip(*t*-Bu)Ge═C═PMes*,[7] have been reported. These compounds are particularly interesting since they present several possibilities of reactions: by the P═C double bond or by the lone pair at phosphorus like —P═C═X derivatives and by the extremely reactive Si═C or Ge═C double bond like sila- and germaallenes >Si═C═C< and >Ge═C═C<. A behavior of silylene >Si: or germylene >Ge: can also be envisaged if the E═C double bond (E = Si, Ge) would cleave as in SiCN[8] and SnCN[9]

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(1) For reviews on heteroallenes, see: (a) Escudié, J.; Ranaivonjatovo, H.; Rigon, L. *Chem. Rev.* **2000**, *100*, 3639–3696. (b) Eichler, B.; West, R. *Adv. Organomet. Chem.* **2001**, *46*, 1–46. (c) Escudié, J.; Ranaivonjatovo, H. *Organometallics* **2007**, *26*, 1542–1559. (d) Appel, R. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Thieme: Stuttgart, Germany, 1990; pp 157−219. (e) Yoshifuji, M. *Dalton Trans.* **1998**, 3343–3349.

(2) (a) Miracle, G.; Ball, J. L.; Powell, D. R.; West, R. *J. Am. Chem. Soc.* **1993**, *115*, 11598–11599. (b) Trommer, M.; Miracle, G. E.; Eichler, B. E.; Powell, D. R.; West, R. *Organometallics* **1997**, *16*, 5737–5747. (c) Eichler, B. E.; Miracle, G. E.; Powell, D. R.; West, R. *Main Group Met. Chem.* **1999**, *22*, 147–162. (d) Ichinohe, M.; Tanaka, T.; Sekiguchi, A. *Chem. Lett.* **2001**, *30*, 1074–1075. (e) Spirk, S.; Belaj, F.; Albering, J. H.; Pietschnig, R. *Organometallics* **2010**, *29*, 2981–2986.

(3) For transient >Si═C═C<, see: (a) Kunai, A.; Matsuo, Y.; Ohshita, J.; Ishikawa, M.; Aso, Y.; Otsubo, T.; Ogura, F. *Organometallics* **1995**, *14*, 1204–1212 and references therein. (b) Kerst, C.; Ruffolo, R.; Leigh, W. J. *Organometallics* **1997**, *16*, 5804–5810. (c) Kerst, C.; Rogers, C. W.; Ruffolo, R.; Leigh, W. J. *J. Am. Chem. Soc.* **1997**, *119*, 466–471.

(4) (a) Eichler, B. E.; Powell, D. R.; West, R. *Organometallics* **1998**, *17*, 2147–2148. Eichler, B. E.; Powell, D. R.; West, R. *Organometallics* **1999**, *18*, 540–545. (b) Kishikawa, K.; Tokitoh, N.; Okazaki, R. *Organometallics* **1997**, *16*, 5127–5129. (c) Tokitoh, N.; Kishikawa, K.; Okazaki, R. *Chem. Lett.* **1998**, *27*, 811–812.

(5) Rigon, L.; Ranaivonjatovo, H.; Escudié, J.; Dubourg, A.; Declercq, J.-P. *Chem.—Eur. J.* **1999**, *5*, 774–781.

(6) Ramdane, H.; Ranaivonjatovo, H.; Escudié, J.; Mathieu, S.; Knouzi, N. *Organometallics* **1996**, *15*, 3070–3075.

(7) (a) El Harouch, Y.; Gornitzka, H.; Ranaivonjatovo, H.; Escudié, J. *J. Organomet. Chem.* **2002**, *643*−*644*, 202–208. (b) Ouhsaine, F.; André, E.; Sotiropoulos, J.-M.; Escudié, J.; Ranaivonjatovo, H.; Gornitzka, H.; Saffon, N.; Miqueu, K.; Lazraq, M. *Organometallics* **2010**, *29*, 2566–2578.

(8) (a) Takeda, N.; Suzuki, H.; Tokitoh, N.; Okazaki, R.; Nagase, S. *J. Am. Chem. Soc.* **1997**, *119*, 1456–1457. (b) Takeda, N.; Kajiwara, T.; Suzuki, H.; Okazaki, R.; Tokitoh, N. *Chem.—Eur. J.* **2003**, *9*, 3530–3543. (c) Abe, T.; Iwamoto, T.; Kabuto, C.; Kira, M. *J. Am. Chem. Soc.* **2006**, *128*, 4228–4229.

(9) Grützmacher, H.; Freitag, S.; Herbst-Irmer, R.; Sheldrick, G. M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 437–438.

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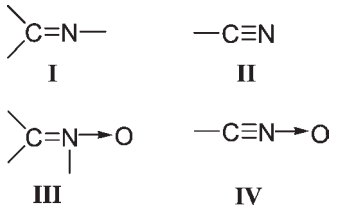
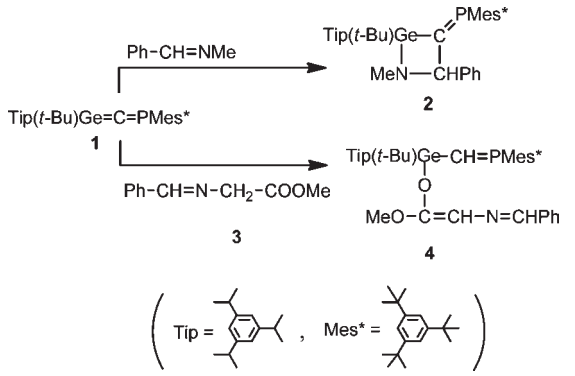
Chart 1



Scheme 1



derivatives. Despite their high potential in organometallic synthesis, the reactivity of $>E_{14}=C=E_{15}-$ derivatives has been poorly studied until now: in the case of >Si=C=P—, only the reaction with MeOH[5] and, in that of >Ge=C=P–, only the reactions with MeOH,[6] MeLi,[6] water,[6] aldehydes,[7] and ketones,[7] and chalcogens[10] have been reported. All of these reactions occur exclusively via the E_{14}=C double bond. By contrast, dimerization observed with transient species involves both E_{14}=C and P=C double bonds.[5,6]

We present here the reactivity of phosphagermaallene Tip(*t*-Bu)Ge=C=PMes* (**1**) toward doubly and triply bonded nitrogen compounds such as imines (**I**), nitriles (**II**), a nitrone (**III**), and a nitrile oxide (**IV**) (Chart 1).

Results and Discussion

Imines. We have studied the reactivity of **1** with two imines which present different substitution patterns on the nitrogen atom: PhCH=NMe, for which a [2+2] cycloaddition between the C=N and Ge=C or P=C double bonds is expected, and PhCH=N—CH_2—COOMe. From the latter, various reactions could occur: [2+2] cycloadditions involving the C=N or the C=O double bonds and an ene reaction with the CH_2 unit.

In fact, phosphagermaallene **1** reacts with the N-benzylidenemethylamine by an exclusive [2+2] cycloaddition between the Ge=C and C=N double bonds, leading to the formation of the corresponding four-membered ring 1-aza-2-germacyclobutane (**2**; Scheme 1). The P=C double bond is not involved in the reaction, as shown by the low-field chemical shift in the ^{31}P NMR spectrum (258.4 ppm, $^3J_{HP}$ = 13.6 Hz). The ^{1}H and ^{13}C NMR data for the *CH*Ph moiety (δ^1H = 5.05 ppm, $^3J_{PH}$ = 13.6 Hz; δ^{13}C = 80.89 ppm, $^2J_{CP}$ = 19.3 Hz) confirm the regiochemistry of this reaction, with the nitrogen atom bonded to the germanium atom, in agreement with the polarity $Ge^{\delta+}=C^{\delta-}$. Despite the high ring strain

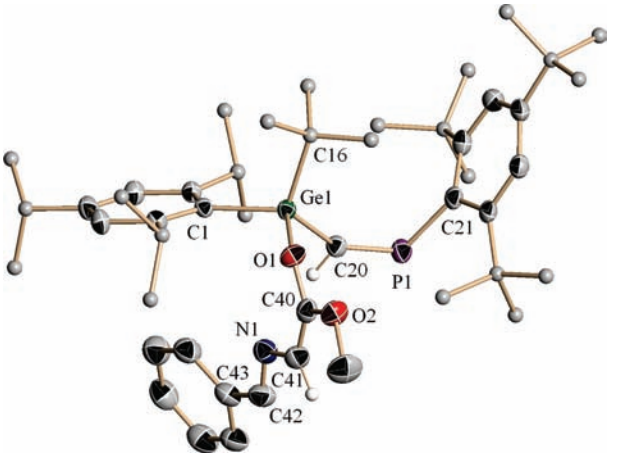


Figure 1. Structure of **4**. Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms are omitted; *t*-Bu and *i*-Pr groups are simplified for clarity. Selected bond lengths (Å) and bond angles (deg): Ge1−C20 1.961(2), Ge1−C1 1.995(2), Ge1−C16 1.983(2), C20−P1 1.671(2), P1−C21 1.856(2), Ge1−O1 1.833(2), O1−C40 1.320(2), C40−C41 1.348(3), C41−N1 1.389(2), N1−C42 1.286(2), Ge1−C20−P1 148.9(1), C20−P1−C21 111.9(1), Ge1−O1−C40 135.1(2), C40−C41−N1 120.5(2), C41−N1−C42 118.5(2), N1−C42−C43 122.7(2).

in the formed four-membered heterocycle, derivative **2** is perfectly stable, probably owing to the steric protection caused by the bulky substituents on the germanium and phosphorus atoms.

By contrast, when the methyl group on the nitrogen atom is replaced by the CH_2COOMe group, a totally different reaction is observed: the addition of methyl-(benzylideneamino)acetate (**3**) to phosphagermaallene (**1**) leads only to the formation of the azadienyl(germyl)-ether (**4**) by an ene reaction (Scheme 1). The structure of **4** was evidenced by a doublet at low field in the ^{31}P NMR spectrum (δ = 324.3 ppm, $^2J_{PH}$ = 21.6 Hz) characteristic for a Ge—CH=P moiety; the carbon atom doubly bonded to the phosphorus was observed at 162.71 ppm with a $^1J_{PC}$ coupling constant of 69.6 Hz. The formation of the *Z* isomer for the P=CH unsaturation was only proved by an X-ray structural analysis (Figure 1) since the values of the $^2J_{PH}$ and $^1J_{PC}$ coupling constants in the CH=PMes* unit are not significantly different for *Z* and *E* isomers in compounds of the type GeC(H)=P—.[11] This study additionally revealed the stereochemistry of the 2-azadiene structure PhCH=N—CH=C< with a *Z* configuration for the C=C double bond and *E* for the C=N one.

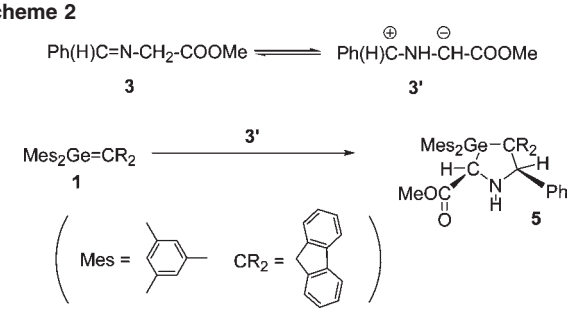
In **2** and **4**, the methyls of each *i*-Pr of the Tip group are diastereotopic. For compound **4**, two doublets and two singlets are observed in ^{1}H and ^{13}C NMR spectra, respectively, for the *o*-*i*-Pr groups. By contrast, in the cyclic compound **2**, four doublets and four singlets are found due to a nonequivalence of the *o*-*i*-Pr groups caused by the hindered rotation of the Tip group around the Ge−C(ipso) bond, consecutive to the greater steric hindrance. In **2** and **4**, the *o*-*t*-Bu groups of Mes* resonate as two signals (2s in ^{1}H NMR and 2d in ^{13}C NMR) due also to the hindered rotation of the Mes* group.

The results obtained from these two imines demonstrate that the ene reaction is preferred to the cycloaddition when

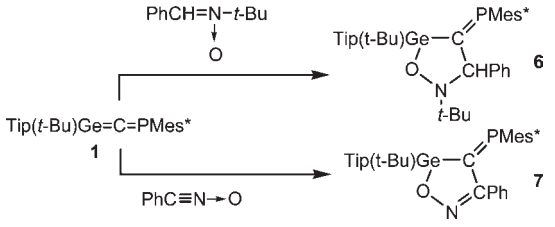
(10) Ouhsaine, F.; Ranaivonjatovo, H.; Escudié, J.; Saffon, N.; Lazraq, M. *Organometallics* **2009**, *28*, 1973–1975.

(11) For example, in $Me_3GeC(H)$=PMes*, the $^2J_{PH}$ coupling constants are 23.5 (*Z*) and 26.4 (*E*) and the $^1J_{P=C}$ coupling constants are 56.0 (*Z*) and 67.4 (*E*). Goede, S. J.; Bickelhaupt, F. *Chem. Ber.* **1991**, *124*, 2677–2684.

Scheme 2



Scheme 3



an electron withdrawing group (e.g., methoxycarbonyl) is present in the α position of the C=N unsaturation.

Whereas a similar [2+2] cycloaddition was observed between germene $Mes_2Ge{=}CR_2$ and N-benzylideneethylamine[12] (by the Ge=C and C=N double bonds), a completely different reaction occurred with the iminoester **3**[13] (Scheme 2). In this case, the five-membered heterocycle **5** was formed by a [2+3] cycloaddition between the germene and the 1,3-dipole azomethine ylide **3′** formed from **3** by a prototropic shift probably assisted by the germene.[14]

1,3-Dipoles. A nearly quantitative [2+3] cycloaddition, involving the Ge=C double bond, occurs between **1** and the 1,3-dipolar derivative N-*tert*-butyl-α-phenylnitrone, leading to the formation of the five-membered ring 1-oxa-2-aza-5-germacyclopentane (**6**; Scheme 3). The ^{31}P NMR study of the crude reaction mixture ($\delta^{31}P$ = 337.0 ppm) shows the presence of only one isomer. The $^3J_{PH}$ coupling constant (22.6 Hz) corroborates the expected regiochemistry of the reaction with the CH(Ph) moiety of the nitrone bonded to the central carbon atom of the GeCP unit. This CH presents expected chemical shifts in ^1H and ^{13}C NMR spectra with large PH and PC coupling constants (δ^1H = 5.16 ppm, d, $^3J_{PH}$ = 22.6 Hz, $\delta^{13}C$ = 78.04 ppm, d, $^2J_{CP}$ = 50.5 Hz). These spectral findings were confirmed by an X-ray study (Figure 2), which demonstrated the formation of the *Z* isomer at the level of the P=C double bond and additionally showed that the phenyl group is placed in front of the *tert*-butyl group less bulky than the Tip group. In the formed five-membered ring, four atoms, O1, Ge1, C31, and C24, are about in the same plane, the nitrogen atom being out by 0.72 Å. Like in compounds **4**, **8**, and **10** (see further), the Ge−C bonds are slightly elongated in **6** (Ge1−C31 = 1.992(2) Å,

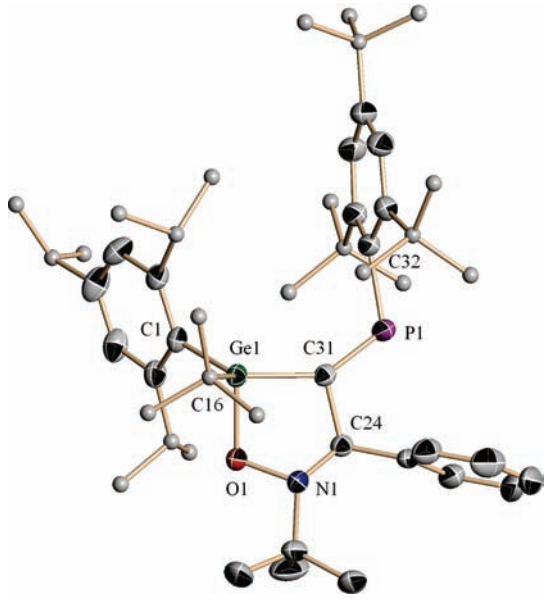
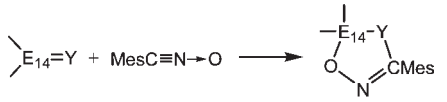


Figure 2. Structure of **6**. Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms and a non-coordinating Et_2O molecules are omitted; *t*-Bu and *i*-Pr groups are simplified for clarity. Selected bond lengths (Å) and bond angles (deg): Ge1−C31 1.992(2), Ge1−C1 2.008(2), Ge1−C16 2.034(2), C31−C24 1.567(3), C24−N1 1.481(3), N1−O1 1.473(2), O1−Ge1 1.821(2), C31−P1 1.679(2), P1−C32 1.852(2), Ge1−C31−C24 103.9(2), C31−C24−N1 108.1(2), C24−N1−O1 103.9(2), N1−O1−Ge1 106.4(1), O1−Ge1−C31 87.8(1), C31−P1−C32 115.9(1), P1−C31−Ge1 144.6(2).

Scheme 4



E_{14} = Si, Ge, Sn; Y = C<, C=C<, S

Ge1−C1 = 2.008(2) Å, and particularly Ge1−C16 = 2.034(2) Å) in relation to the standard ones (1.94−1.98 Å).[15a,b] P=C (1.679(2) Å) double bond[15c] and P−C (1.852(2) Å) single bond lengths are in the normal range.

To determine whether a [2+3] addition process is also realizable with other 1,3-dipoles, such as nitrile oxides, the phosphagermaallene (**1**) was allowed to react with PhC≡N→O, generated in situ from N-hydroxy-benzimoyl chloride. A similar cycloadduct, the 1-oxa-2-aza-5-germacyclopent-2-ene (**7**), was formed in 72% yield (Scheme 3) and was characterized by low-field shifts in ^{31}P NMR (296.7 ppm) and ^{13}C NMR spectra (175.63 ppm, $^2J_{CP}$ = 25.5 Hz for C=N and 182.71 ppm, $^1J_{CP}$ = 69.8 Hz for C=P). Mass spectrometry displays the molecular peak and a fragment corresponding to Tip(*t*-Bu)GeO, consistent with the proposed regiochemistry. However, cycloadduct **7** is a thermally stable compound, and no cycloreversion by a [5]→[2+3] process, leading to transient germanone Tip(*t*-Bu)GeO, has been observed, even by refluxing in toluene.

It is worth noting that a related behavior was reported by Tokitoh in the case of various doubly bonded and aromatic heavier group 14 derivatives E_{14}=Y (E_{14} = Si,

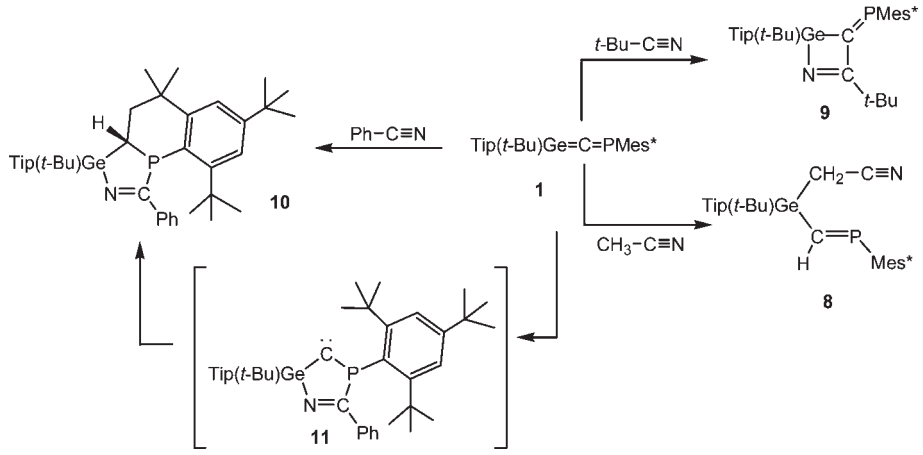
(12) Lazraq, M.; Escudié, J.; Couret, C.; Satgé, J.; Soufiaoui, M. *Organometallics* **1991**, *10*, 1140–1143.

(13) Ech-Cherif El Kettani, S.; Escudié, J.; Couret, C.; Ranaivonjatovo, H.; Lazraq, M.; Soufiaoui, M.; Gornitzka, H.; Cretiu Nemes, G. *Chem. Commun.* **2003**, 1662–1663.

(14) The high reactivity of germenes towards acidic hydrogens is well established. For reviews on germenes, see: (a) Baines, K. M.; Stibbs, W. G. *Adv. Organomet. Chem.* **1996**, *39*, 275–324. (b) Escudié, J.; Couret, C.; Ranaivonjatovo, H. *Coord. Chem. Rev.* **1998**, *178*−*180*, 565–592. (c) Escudié, J.; Ranaivonjatovo, H. *Adv. Organomet. Chem.* **1999**, *44*, 113–174.

(15) (a) Baines, K. M.; Stibbs, W. G. *Coord. Chem. Rev.* **1995**, *145*, 157–200. (b) Holloway, C. E.; Melnik, M. *Main Group Met. Chem.* **2002**, *25*, 185–266. (c) Fischer, R. C.; Power, P. P. *Chem. Rev.* **2010**, *110*, 3877–3923.

Scheme 5



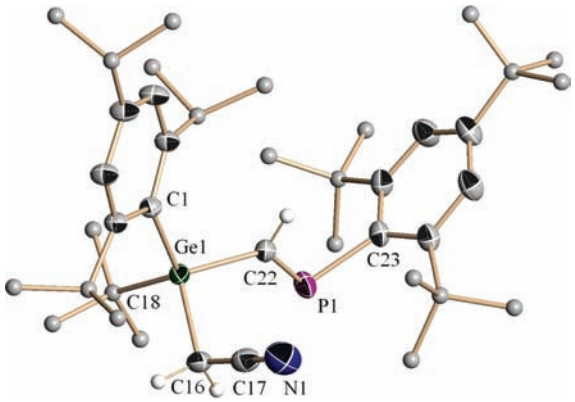


Figure 3. Structure of **8**. Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms and a disorder of a *t*-Bu group are omitted; *t*-Bu and *i*-Pr groups are simplified for clarity. Selected bond lengths (Å) and bond angles (deg): Ge1−C1 1.985(2), Ge1−C18 1.991(2), Ge1−C16 2.004(2), C16−C17 1.439(2), C17−N1 1.148(2), Ge1−C22 1.955(2), C22−P1 1.661(2), P1−C23 1.856(2), Ge1−C22−P1 126.85(7), C22−P1−C23 101.15(7).

Y = C<,[16] S;[17] E_{14} = Ge, Y = C<,[18] C=C<,[19] S;[20] E_{14} = Sn, Y = C<,[21] S[22]) with the structurally close mesitonitrile oxide MesC≡N→O, giving the corresponding five-membered sila-, germa-, and stanna-heterocycles (Scheme 4), respectively.

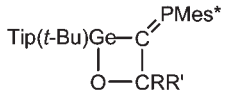
Nitriles. We have examined the behavior of phosphagermaallene **1** with three different nitriles such as acetonitrile, which has mobile hydrogens in the α of the triple bond, and two nitriles without such hydrogen atoms and bearing an alkyl or an aryl group.

With acetonitrile, a 1,2 addition of a C−H bond onto the Ge=C double bond occurs, leading only to the formation of the 3-germa-1-phosphapropene (**8**; Scheme 5), as indicated by the ^{31}P NMR spectrum, which displays a signal at 322.5 ppm with a $^{2}J_{PH}$ coupling constant of 23.7 Hz characteristic of the HC=PMes* unit. Unexpectedly, the diastereotopic protons of the $CH_2C{\equiv}N$ fragment resonate as only one singlet in ^{1}H NMR, corresponding to two hydrogen atoms. The X-ray study of **8** proves the formation of the *E* isomer (Figure 3).

With pivalonitrile, only a [2+2] cycloaddition was observed between the Ge=C double bond and the nitrile function, leading to the formation of 1-aza-2-germacyclobut-1-ene (**9**) with an exocyclic P=C double bond (Scheme 5). Probably owing to a good steric protection caused by bulky Tip and *t*-Bu groups, the Ge−N bond, generally easily hydrolyzable, is relatively insensitive in **9**, which can be handled in the air for a short period of time. Cycloadduct **9** was characterized by a very low-field shift in ^{13}C NMR for the sp^2 carbon atom bonded to nitrogen (δ = 196.08 ppm, $^{2}J_{PC}$ = 28.4 Hz), which proves the regiochemistry of the reaction. A similar very low-field shift (198.41 ppm) was reported for the closely related four-membered ring derivative obtained in the reaction of $Mes_2Ge{=}CR_2$ with pivalonitrile.[23] The endocyclic sp^2 carbon atom doubly bonded to the phosphorus resonates at 181.81 ppm with a large $^{1}J_{CP}$ coupling constant (103.5 Hz). Signals in the range of 162.71−194.45 ppm are observed for carbon atoms in the Ge—C=P unit of **2**, **4**, **6**, **7**, **8**, and **9**. The resonances at lower fields (194.45 (**2**), 192.51 (**6**), 182.71 (**7**), and 181.81 (**9**) ppm) correspond to those for cyclic compounds, whereas those at higher fields (162.71 (**4**) and 175.75 (**8**) ppm) are due to those for acyclic ones. In ^{1}H NMR, acyclic derivative **8** presents similar data to those of acyclic germylether **4** (two doublets for *o*-*i*-Pr due to the free rotation of the Tip group); four-membered ring compound **9** has similar characteristics to those of **2** (four doublets for *o*-*i*-Pr of the Tip group and two singlets for *o*-*t*-Bu of the Mes* group due to their hindered rotation). In the less sterically encumbered acyclic derivative **8**, a unique singlet is even observed for the *o*-*t*-Bu of the Mes* group, showing its free rotation on the NMR time scale. The chemical shifts of phosphorus (δ ^{31}P), of the central carbon atom bonded to phosphorus and to germanium (δ $^{13}C_{GeCP}$), and of the carbon atom bonded to the nitrogen atom

(16) Tokitoh, N.; Shinohara, A.; Matsumoto, T.; Sasamori, T.; Takeda, N.; Furukawa, Y. *Organometallics* **2007**, *26*, 4048–4053.
(17) Suzuki, H.; Tokitoh, N.; Nagase, S.; Okazaki, R. *J. Am. Chem. Soc.* **1994**, *116*, 11578–11579.
(18) (a) Nakata, N.; Takeda, N.; Tokitoh, N. *J. Am. Chem. Soc.* **2002**, *124*, 6914–6920. (b) Nakata, N.; Takeda, N.; Tokitoh, N. *Organometallics* **2003**, *22*, 481–489.
(19) Tokitoh, N.; Kishikawa, K.; Okazaki, R. *Chem. Lett.* **1998**, *27*, 811–812.
(20) Tokitoh, N.; Matsumoto, T.; Manmaru, K.; Okazaki, R. *J. Am. Chem. Soc.* **1993**, *115*, 8855–8856.
(21) Mizuhata, Y.; Takeda, N.; Sasamori, T.; Tokitoh, N. *Chem. Lett.* **2005**, *34*, 1088–1089.
(22) Saito, M.; Tokitoh, N.; Okazaki, R. *J. Am. Chem. Soc.* **2004**, *126*, 15572–15582.
(23) Ech-Cherif El Kettani, S.; Lazraq, M.; Ranaivonjatovo, H.; Escudié, J.; Couret, C.; Gornitzka, H.; Merceron, N. *Organometallics* **2004**, *23*, 5062–5065.

Table 1. NMR data for the obtained and related compounds

Compd	δ ^{31}P (J_{PH}, Hz)	δ $^{13}C_{GeCP}$ ($^{1}J_{CP}$, Hz)	Compd	δ ^{31}P (J_{PH}, Hz)	δ $^{13}C_{GeCP}$ ($^{1}J_{CP}$, Hz)	δ $^{13}C_{CN}$ (J_{CP}, Hz)
 a) R = H, R' = Ph [7a] b) R = R' = Ph [7a] c) CRR' = 9-fluorenylidene [7a] d) R = H, R' = MeCH=CH [7b] e) R = H, R' = PhCH=CH [7b]	a) 253.8 ($^{3}J_{PH}$ = 14.0) b) 328.2 - c) 314.0 - d) 257.9 ($^{3}J_{PH}$ = 15.2) e) 254.3 ($^{3}J_{PH}$ = 15.8)	a) 193.31 ($^{1}J_{CP}$ = 75.3) b) 195.61 ($^{1}J_{CP}$ = 71.7) c) 193.50 ($^{1}J_{CP}$ = 60.9) d) 197.24 ($^{1}J_{CP}$ = 73.0) e) 196.73 ($^{1}J_{CP}$ = 73.0)	**2** **4** **6** **7** **8** **9** **10**	258.4 ($^{3}J_{PH}$ = 13.6) 324.3 - 337.0 ($^{3}J_{PH}$ = 22.6) 296.7 - 322.5 ($^{2}J_{PH}$ = 23.7) 219.6 - 5.4 -	194.45 ($^{1}J_{CP}$ = 75.2) 162.71 ($^{1}J_{CP}$ = 69.6) 192.51 ($^{1}J_{CP}$ = 59.6) 182.71 ($^{1}J_{CP}$ = 69.8) 175.75 ($^{1}J_{CP}$ = 74.1) 181.81 ($^{1}J_{CP}$ = 103.5) 23.23 ($^{1}J_{CP}$ = 21.5)	80.89 ($^{2}J_{CP}$ = 19.3) 146.63 - 78.04 ($^{2}J_{CP}$ = 50.5) 175.63 ($^{2}J_{CP}$ = 25.5) 120.66 - 196.08 ($^{2}J_{CP}$ = 28.4) 176.38 ($^{1}J_{CP}$ = 25.5)

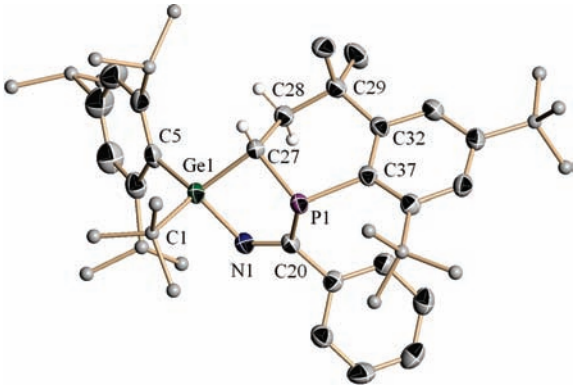
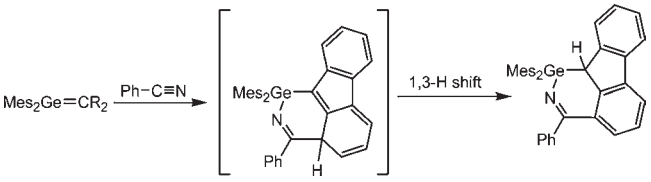


Figure 4. Structure of **10**. Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms and disorders of a *t*-Bu and an *i*-Pr group are omitted; *t*-Bu and *i*-Pr groups are simplified for clarity. Selected bond lengths (Å) and bond angles (deg): Ge1−C1 1.996(3), Ge1−C5 1.975(3), Ge1−C27 1.997(3), Ge1−N1 1.899(2), N1−C20 1.276(3), C20−P1 1.899(3), P1−C27 1.827(3), C27−C28 1.524(4), C28−C29 1.539(4), C29−C32 1.549(4), C32−C37 1.415(4), C37−P1 1.841(3), Ge1−C27−P1 99.4(2), C27−P1−C20 92.2(2), P1−C20−N1 118.7(2), C20−N1−Ge1 112.3(2), N1−Ge1−C27 93.1(1), C27−P1−C37 105.7(2).

(δ $^{13}C_{CN}$), together with relevant coupling constants for some 1-oxa-2-germacyclobutanes and for the synthesized products, are listed in Table 1.

While a [2+2] cycloaddition could be expected in the reaction of phosphagermaallene with benzonitrile, like in the case of pivalonitrile, a completely different and unexpected reaction occurred. The ^{31}P NMR spectrum of the crude reaction mixture showed a unique signal at 5.4 ppm, a relatively high-field shift, characteristic for three-coordinated phosphorus atoms, thus indicating that the P=C double bond has been involved in the reaction. The stability toward oxygen and moisture of the isolated product suggests that the Ge=C double bond has also reacted. The structure of the adduct **10** (Scheme 5) was determined by an X-ray study (Figure 4). The formation of this tricyclic derivative can reasonably be explained by the intermediate formation of the cyclic phosphagermacarbene (**11**; a PGeHC carbene, analogous to the well-known NHCs), followed by insertion of the carbenic carbon atom into the C−H bond of an *ortho tert*-butyl group of the Mes* group. Such insertions of a carbene into a C−H bond are well-known.[24] Transient carbene **11** would be formed by a [3+2] cycloaddition between the Ge=C=P moiety of the phosphagermaallene, behaving as a 1,3-dipole, and the C≡N triple bond. We must note that such behavior of 1,3-dipole has never been observed for other heteroallenes of the type E_{14}=C=C, E_{14}=C=E_{15}, or E_{15}=C=E_{15}.

Scheme 6



Despite the presence of three chiral centers, only one diastereoisomer was formed. The X-ray study shows that the two six-membered rings (the ring with phosphorus and the ring substituted by two *t*-Bu groups) are nearly in the same plane. The P1−C20 bond length (1.899(3) Å) is longer than the two other P−C bonds (P1−C27 = 1.827(3) Å and P1−C37 = 1.841(3) Å). The five-membered ring presents an envelope geometry with the P1, C20, N1, and Ge1 atoms in the same plane.

Monitoring the reaction by ^{31}P NMR between −80 °C and room temperature did not allow detection of the transient carbene **11**, which probably rearranges immediately after its formation to the final product **10**. We attempted to chemically characterize **11** by trapping reactions; however, as its lifetime seems to be very short, the trapping agent must be added to the phosphagermaallene solution before the addition of benzonitrile. The problem is the high reactivity of the Ge=C double bond, which complicates the choice of the trapping agent. Triphenylphosphine, an efficient reagent for silyl(phosphino)carbenes[24,25] and inert toward phosphagermaallene **1**, failed to trap the intermediate carbene **11**, perhaps because of the weak stability in solution of the latter as well as of the steric overcrowding around the carbene center.

(24) Reviews: (a) Doyle, M. P.; Duffy, R.; Ratnikov, M.; Zhou, L. *Chem. Rev.* **2010**, *110*, 704–724. (b) Ritleng, V.; Sirlin, C.; Pfeffer, M. *Chem. Rev.* **2002**, *102*, 1731–1770. (c) Kakiuchi, F.; Murai, S. *Acc. Chem. Res.* **2002**, *35*, 826–834. (d) Jia, C.; Kitamura, T.; Fujiwara, Y. *Acc. Chem. Res.* **2001**, *34*, 633–639.

Scheme 7

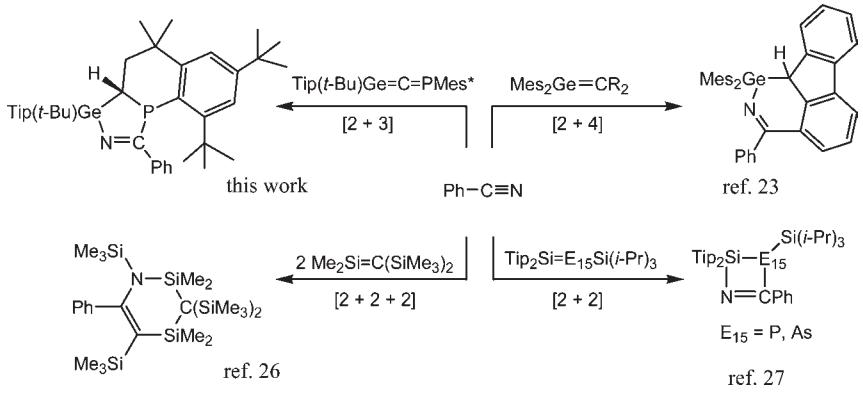


Table 2. Crystal Data for Compounds **4** and **6**

	4	**6**
empirical formula	$C_{48}H_{72}GeNO_2P$	$C_{49}H_{76}GeNOP$, $(C_4H_{10}O)_{0.5}$
fw	798.65	835.77
temp	193(2) K	193(2) K
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	9.2525(1)	10.9509(2)
b (Å)	11.0188(2)	12.2987(2)
c (Å)	23.1235(3)	19.9337(3)
α (deg)	98.915(1)	97.910(1)
β (deg)	95.089(1)	99.636(1)
γ (deg)	93.842(1)	105.745(1)
vol	2311.99(6) Å^3	2499.67(7) Å^3
Z	2	2
abs coeff	0.733 mm^{-1}	0.676 mm^{-1}
reflns collected	37910	55247
independent reflns	11955 [R(int) = 0.0358]	9151 [R(int) = 0.0389]
abs correction	Multiscan	Multiscan
min/max transm	0.820/0.865	0.806/0.874
data/restraints/params	11 955/5/495	9151/31/547
goodness-of-fit on F^2	1.023	1.033
final R indices [$I > 2\sigma(I)$]	R1 = 0.0380 wR2 = 0.0899	R1 = 0.0343 wR2 = 0.0829
R indices (all data)	R1 = 0.0519 wR2 = 0.0960	R1 = 0.0454 wR2 = 0.0901
largest diff. peak and hole	0.688 and −0.277 e Å^{-3}	0.621 and −0.422 e Å^{-3}

Table 3. Crystal Data for Compounds **8** and **10**

	8	**10**
empirical formula	$C_{40}H_{64}GeNP$	$C_{45}H_{66}GeNP$
fw	662.50	724.57
temp	193(2) K	193(2) K
cryst syst	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a (Å)	21.710(16)	10.5721(2)
b (Å)	9.831(8)	12.6065(3)
c (Å)	19.999(15)	17.4404(4)
α (deg)	90	81.459(1)
β (deg)	113.189(9)	86.387(1)
γ (deg)	90	68.519(2)
vol	3924(5) A^3	2138.87(9) A^3
Z	4	2
abs coeff	0.847 mm^{-1}	0.782 mm^{-1}
reflns collected	101 060	44 342
independent reflns	19 550 [R(int) = 0.0516]	7822 [R(int) = 0.0664]
abs correction	multiscan	multiscan
min/max transm	0.659/0.812	0.819/0.939
data/restraints/params	19 550/9/408	7822/9/446
goodness-of-fit on F^2	1.011	1.015
final R indices [$I > 2\sigma(I)$]	R1 = 0.0409, wR2 = 0.0967	R1 = 0.0436, wR2 = 0.0972
R indices (all data)	R1 = 0.0775, wR2 = 0.1132	R1 = 0.0662, wR2 = 0.1082
largest diff. peak and hole	0.676 and −0.926 e A^{-3}	0.627 and −0.443 e A^{-3}

The reaction of benzonitrile with phosphagermaallene **1** is completely different than that occurring with the germene $Mes_2Ge{=}CR_2$, for which a [2+4] cycloaddition was observed between the C≡N triple bond and the Ge=C—C=C dienic system (involving the fluorenylidene group), followed by rearomatization via a 1,3-H shift (Scheme 6).[23]

With regard to other heavier heteroalkenes, a [2+2+2] cycloadduct of PhC≡N with the silene $Me_2Si{=}C(SiMe_3)_2$[26] has been reported so far, while the $Si{=}E_{15}$ (E_{15} = P, As) double bond in phospha- and arsa-silenes $Tip_2Si{=}E_{15}Si(i\text{-}Pr)_3$ reacts with the C≡N triple bond of benzonitrile[27] to furnish [2+2]-cycloaddition products. We summarized these differences in Scheme 7.

By contrast, the transient silene $Me_2Si{=}CH_2$[28] generated by the pyrolysis of the corresponding silacyclobutane undergoes an insertion reaction into a C−H bond of acetonitrile, similar to that observed with germene $Mes_2Ge{=}CR_2$[23] and phosphagermaallene Tip(*t*-Bu)Ge=C=PMes*.

In conclusion, phosphagermaallene **1** displays very rich and varied reactivity since it gives selectively, depending on the reagents, cycloaddition, insertion, or ene reactions via the Ge=C double bond or behaves as a 1,3-dipole involving both Ge=C and C=P double bonds. In most of the cases, only the Ge=C double bond of **1** is involved, and the ene reaction or 1,2 addition of C−H is preferred to [2+2] cycloaddition when both reactions are possible. The reactivity of the cumulative Ge=C double bond of **1** and that of the isolated Ge=C double bond of germene $Mes_2Ge{=}CR_2$ are somewhat different, particularly toward benzonitrile and

(25) The carbene $Me_3Si\text{-}C\text{-}PR_2$ (R = cyclohexyl) rather similarly substituted as **11** (phosphino and silyl groups on the carbon atom instead of phosphino and germyl groups) has been successfully trapped by Ph_3P and other phosphines. Goumri-Magnet, S.; Polishchuk, O.; Gornitzka, H.; Marsden, C.; Baceiredo, A.; Bertrand, G. *Angew. Chem., Int. Ed.* **1999**, *38*, 3727-3729.

(26) Wiberg, N.; Preiner, G.; Schieda, O. *Chem. Ber.* **1981**, *114*, 3518–3532.

(27) Driess, M.; Pritzkow, H.; Rell, S.; Winkler, U. *Organometallics* **1996**, *15*, 1845–1855.

(28) Bush, R. D.; Golino, C. M.; Roark, D. N.; Sommer, L. H. *J. Organomet. Chem.* **1973**, *59*, C17–C20.

methyl(benzylideneamino)acetate. Compared with other unsaturated compounds of group 14 elements, phosphagermaallene Tip(*t*-Bu)Ge═C═PMes* has been shown an unprecedented example of cycloaddition in the reaction with benzonitrile, while similar behavior was observed in the case of acetonitrile. The 1,3-dipole behavior of **1**, a new mode of reaction for a heteroallene, allows the formation of a cyclic phosphagermacarbene intermediate, a novel type of cyclic carbene (PGeHC). Further investigations on the chemical reactivity of phosphagermaallene **1** towards a large variety of unsaturated reagents are now in progress.

Experimental Section

All experiments were carried out in flame-dried glassware under a nitrogen and argon atmosphere using high-vacuum-line techniques. Solvents were dried and freshly distilled using an SPS-5MB system. NMR spectra were recorded (with $CDCl_3$ as solvent) on a Bruker Avance 300 spectrometer at the following frequencies: ^{1}H, 300.13 MHz; ^{13}C, 75.47 MHz (reference TMS); ^{31}P, 121.51 MHz (reference H_3PO_4). Melting points were determined on a Wild Leitz-Biomed apparatus. Mass spectra were obtained on a Hewlett-Packard 5989A spectrometer by EI at 70 eV and on a Nermag R10−10 spectrometer by CI. Elemental analyses were performed by the Service de Microanalyse de l'Ecole de Chimie de Toulouse. NMR spetra have been elucidated using COSY, HMBC, and HSQC techniques.

X-Ray Structure Determinations for 4, 6, 8, and 10. All data were collected at low temperatures using an oil-coated shock-cooled crystal on a Bruker-AXS APEX II diffractometer with Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods,[29] and all non-hydrogen atoms were refined anisotropically using the least-squares method on F^2.[30] For crystal data, see Tables 2 and 3.

Synthesis of 1. Phosphagermaallene **1** was synthesized as previously described[7] via the addition of a solution of 1.7 M *tert*-butyllithium in pentane (0.6 mL) to a solution of fluorophosphagermapropene Tip(*t*-Bu)Ge(F)—C(Cl)═PMes* (0.676 g, 1 mmol) in diethylether (10 mL) cooled to −78 °C. A ^{31}P NMR analysis (δ 249.9 ppm) showed the nearly quantitative formation of phosphagermaallene **1**. Solutions of **1** containing LiF were used directly without further purification.

Synthesis of 2. To a solution of phosphagermaallene **1** (1 mmol) in diethyl ether (10 mL) was added N-benzylidenemethylamine (0.119 g, 1 mmol) at −78 °C, and the mixture was stirred at room temperature for 3 h. After filtration, volatiles were removed under a vacuum, and the residue was dissolved in pentane. The saturated solution was stored at −20 °C to give a yellow crystalline product (0.59 g, 80%, mp 156 °C). ^{1}H NMR (300.13 MHz): δ 1.16 and 1.53 (2s, 2 × 9H, *o*-CMe_3 of Mes*); 1.25, 1.27, 1.36, and 1.41 (4d, $^3J_{HH}$ = 6.6 Hz, 4 × 3H, *o*-CH*MeMe*′); 1.32 (s, 9H, $GeCMe_3$); 1.35 (d, $^3J_{HH}$ = 6.6 Hz, 6H, *p*-CH*MeMe*′); 1.44 (s, 9H, *p*-CMe_3 of Mes*); 2.45 (s, 3H, NMe); 2.85 and 3.34 (2sept, $^3J_{HH}$ = 6.6 Hz, 2 × 1H, *o*-C*H*MeMe′); 2.97 (sept, $^3J_{HH}$ = 6.6 Hz, 1H, *p*-C*H*MeMe′); 5.05 (d, $^3J_{PH}$ = 13.6 Hz, 1H, PhC*H*); 6.61−6.64 (m, 2H, Ph); 6.96 and 7.42 (2s, 2 × 1H, *m*-CH of Mes*); 7.01−7.08 (m, 3H, Ph); 7.11 and 7.14 (2s, 2 × 1H, *m*-CH of Tip). ^{13}C NMR (75.47 MHz): δ 23.75, 24.64, 25.99, and 26.53 (*o*-CH*MeMe*′); 23.83 and 23.96 (*p*-CH*MeMe*′); 29.73 (GeC*Me*$_3$); 31.56 (*p*-C*Me*$_3$ of Mes*); 32.40 (d, $^3J_{CP}$ = 3.2 Hz, Ge*C*Me_3); 32.83 (d, $^4J_{CP}$ = 8.7 Hz) and 33.08 (d, $^4J_{CP}$ = 6.0 Hz) (*o*-C*Me*$_3$ of Mes*); 33.98 (NMe); 34.03 (*p*-*C*HMeMe′); 34.80 (*p*-*C*Me_3 of Mes*); 36.02 and 36.17 (*o*-*C*HMeMe′); 37.44 and 38.10 (*o*-*C*Me_3 of Mes*); 80.89 (d, $^2J_{CP}$ = 19.3 Hz, Ph*C*H); 120.91, 121.54, 121.56, and 121.96 (*m*-CH of Tip and Mes*); 136.32 (d, $^3J_{CP}$ = 4.5 Hz, *ipso*-C of Tip); 138.53 (d, $^1J_{CP}$ = 73.5 Hz, *ipso*-C of Mes*); 141.21 (d, $^3J_{CP}$ = 6.2 Hz, *ipso*-C of Ph); 148.74 (*p*-C of Mes*); 149.21 (*p*-C of Tip); 152.63 and 152.72 (d, $^2J_{CP}$ = 3.9 Hz) (*o*-C of Mes*); 152.90 and 153.59 (*o*-C of Tip); 194.45 (d, $^1J_{CP}$ = 75.2 Hz, C═P). ^{31}P NMR (121.51 MHz): δ 258.4 (d, $^3J_{HP}$ = 13.6 Hz). MS (*m*/*z*, %): 742 (M + H, 1), 685 (M − *t*-Bu + H, 15), 566 (M − PhCH═NMe − *t*-Bu + H, 5), 510 (M − PhCH═NMe − 2*t*-Bu + 2H, 5), 377 (Mes*P═C═CHPh − H, 8), 275 (Mes*P − H, 25), 233 (TipGe − *i*-Pr − H, 20), 118 (PhCH═NMe−H, 15), 57 (*t*-Bu, 100). Anal. Calcd for $C_{46}H_{70}GeNP$ (740.63): C, 74.60; H, 9.53%. Found: C, 74.72; H, 9.44%.

Synthesis of 4. A solution of methyl(benzylidene)aminoacetate (0.177 g, 1 mmol) in diethyl ether (5 mL) was added dropwise to a solution of phosphagermaallene **1** (1 mmol) in diethyl ether (10 mL) at −78 °C. The mixture was allowed to warm to room temperature, was stirred for 12 h, and then was filtered. The solvents were removed and replaced with pentane (10 mL), to give a yellow precipitate (0.58 g, 73%, mp 172 °C). ^{1}H NMR (300.13 MHz): δ 0.74 (s, 9H, $GeCMe_3$), 1.14 and 1.21 (2d, $^3J_{HH}$ = 6.6 Hz, 2 × 6H, *o*-CH*MeMe*′), 1.27 and 1.29 (2d, $^3J_{HH}$ = 6.6 Hz, 2 × 3H, *p*-CH*MeMe*′), 1.37 (s, 9H, *p*-CMe_3 of Mes*), 1.49 and 1.57 (2s, 2 × 9H, *o*-CMe_3 of Mes*), 2.91 (sept, $^3J_{HH}$ = 6.6 Hz, 1H, *p*-C*H*MeMe′), 3.15 (broad signal, 2H, *o*-C*H*MeMe′), 3.62 (s, 3H, OMe), 5.80 (s, 1H, CH═C), 7.08−7.17 (m, 5H, Ph), 7.10 (s, 2H, *m*-CH of Tip), 7.34 and 7.37 (2s, 2 × 1H, *m*-CH of Mes*), 7.87 (s, 1H, CH═N), 7.89 (d, $^2J_{PH}$ = 21.6 Hz, CH═P). ^{13}C NMR (75.47 MHz): δ 23.76 and 24.03 (*p*-CH*MeMe*′); 25.59 and 25.83 (*o*-CH*MeMe*′); 27.80 (GeC*Me*$_3$); 29.35 (GeCMe_3); 31.40 (*p*-C*Me*$_3$ of Mes*); 34.01 (*p*-*C*HMeMe′); 34.23 (d, $^4J_{CP}$ = 8.8 Hz) and 34.71 (d, $^4J_{CP}$ = 7.5 Hz; *o*-C*Me*$_3$ of Mes*); 34.87 (*p*-*C*Me_3 of Mes*); 38.45 and 38.86 (*o*-*C*Me_3 of Mes*); 54.24 (OMe); 99.76 (*C*H═C); 121.39 and 122.55 (*m*-CH of Mes*); 122.40 (*m*-CH of Tip); 126.97, 127.59, and 128.28 (*o*-, *m*-, and *p*-CH of Ph); 133.06 (*ipso*-C of Tip); 138.50 (*ipso*-C of Ph); 141.93 (d, $^1J_{CP}$ = 74.8 Hz, *ipso*-C of Mes*); 146.63 (CH═N); 149.41 (*p*-C of Tip); 149.79 (*p*-C of Mes*); 153.73 and 154.69 (*o*-C of Mes*); 154.70 (*o*-C of Tip); 160.15 (CH═*C*); 162.71 (d, $^1J_{CP}$ = 69.6 Hz, CH═P). ^{31}P NMR (121.51 MHz): δ 324.3 (brs). MS (*m*/*z*, %): 799 (M, 1), 742 (M − *t*-Bu, 5), 623 (M − PhCH═N—CH═COOMe, 40), 597 (M − Tip + H, 25), 565 (M − PhCH═N—CH═COOMe − *t*-Bu − H, 15), 509 (M − PhCH═N—CH═COOMe − 2*t*-Bu, 35), 333 (Ge(*t*-Bu)Tip − H, 10), 275 (Mes*P − H, 20), 233 (TipGe − *i*-Pr − H, 15), 57 (*t*-Bu, 100). IR (KBr, cm^{-1}): 1630 (C═N). Anal. Calcd for $C_{48}H_{72}GeNO_2P$ (798.66): C, 72.19; H, 9.09%. Found: C, 72.23; H, 9.26%.

Synthesis of 6. To a solution of phosphagermaallene **1** (1 mmol) in diethyl ether (10 mL) was added at −78 °C N-*tert*-butyl-α-phenylnitrone (0.177 g, 1 mmol) dissolved in 10 mL of THF. The color of the solution changed from brown to yellow. The mixture was allowed to warm to room temperature and stirred for 2 h. After this time, the solvent was removed under reduced pressure, and the residue was dissolved in 30 mL of pentane. Lithium salts were filtered off, and the solvents partially removed under vacuum conditions to generate a saturated solution. Storage of the solution at −20 °C afforded colorless crystals of **6** (0.61 g, 76%, mp 166 °C). ^{1}H NMR (300.13 MHz): δ 0.62 and 1.17 (2d, $^3J_{HH}$ = 6.6 Hz, 2 × 6H, *o*-CH*MeMe*′), 1.08 and 1.34 (2s, 2 × 9H *o*-CMe_3 of Mes*), 1.14 (s, 9H, $NCMe_3$), 1.21 (d, $^3J_{HH}$ = 6.6 Hz, 6H, *p*-CH*Me*$_2$), 1.27 (s, 9H, *p*-CMe_3 of Mes*), 1.31 (s, 9H, $GeCMe_3$), 2.82 (sept, $^3J_{HH}$ = 6.6 Hz, 1H, *p*-C*H*Me$_2$), 3.29 (brs, 2H, *o*-C*H*MeMe′), 5.16 (d, $^3J_{PH}$ = 22.6 Hz, 1H, PhC*H*), 6.89 (s, 2H, *m*-CH of Tip), 7.20−7.22 (m, 2H, *p*-CH of Ph and one *m*-CH of Mes*), 7.29−7.33 (m, 3H, *m*-CH of Ph and one *m*-CH of Mes*), 7.58 (d, $^3J_{HH}$ = 6.9 Hz, 2H, *o*-CH of Ph). ^{13}C NMR (75.47 MHz): δ 23.84 (*p*-CH*Me*$_2$), 25.52 and 25.94 (*o*-CH*MeMe*′), 27.32 (NC*Me*$_3$), 30.57 (GeC*Me*$_3$), 31.17 (*p*-C*Me*$_3$ of Mes*), 33.05 (d, $^4J_{CP}$ = 7.2 Hz) and 33.30 (d, $^4J_{CP}$ = 6.0 Hz; *o*-C*Me*$_3$ of Mes*), 33.86 (*p*-*C*HMe$_2$), 34.16 (*o*-*C*HMeMe′), 34.84 (*p*-*C*Me_3 of Mes*), 36.44 (Ge*C*Me_3), 38.36 and 38.44 (*o*-*C*Me_3 of Mes*), 60.53 (N*C*Me_3), 78.04 (d, $^2J_{CP}$ = 50.5 Hz, Ph*C*H), 122.00 (*m*-CH of Tip), 122.33 and 122.89 (*m*-CH of Mes*),

(29) SHELXS-97: Sheldrick, G. M. *Acta Crystallogr*. **1990**, *A46*, 467−473.
(30) Sheldrick, G. M. *SHELXL-97*; University of Göttingen: Göttingen, Germany, 1997.

126.45 (*p*-CH of Ph), 127.64 (*m*-CH of Ph), 130.22 (d, $^4J_{CP}$ = 4.1 Hz, *o*-CH of Ph), 131.75 (*ipso*-C of Tip), 131.75 (d, $^1J_{CP}$ = 75.5 Hz, *ipso*-C of Mes*), 147.13 (d, $^3J_{CP}$ = 13.0 Hz, *ipso*-C of Ph), 149.58 (*p*-C of Tip), 149.80 (*p*-C of Mes*), 152.14 (d, $^2J_{CP}$ = 4.5 Hz) and 152.45 (d, $^2J_{CP}$ = 6.6 Hz; *o*-C of Mes*), 154.88 (*o*-C of Tip), 192.51 (d, $^1J_{CP}$ = 59.6 Hz, C=P). ^{31}P NMR (121.51 MHz): δ 337.0 (d, $^3J_{PH}$ = 22.6 Hz). MS (*m*/*z*, %): 799 (M, 5), 728 (M − N(*t*-Bu), 5), 670 (M − *t*-Bu − N(*t*-Bu) − H, 5), 598 (M − Tip +2H, 5), 555 (M − Mes* + H, 1), 333 (Ge(*t*-Bu)Tip − H, 10), 275 (Mes*P − H, 25), 233 (TipGe − *i*-Pr − H, 15), 57 (*t*-Bu, 100). Anal. Calcd for $C_{49}H_{76}$GeNOP (798.71): C, 73.69; H, 9.59%. Found: C, 73.81; H, 9.62%.

Synthesis of 7. A solution of N-hydroxy-benzimoyl chloride (0.155 g, 1 mmol) in 20 mL of diethyl ether was added dropwise to a solution of phosphagermaallene **1** (1 mmol) in 10 mL of diethyl ether and 7 mL of triethylamine (about 50-fold molar excess) over a period of 1 h, while maintaining the temperature between −80 and −70 °C. The reaction mixture was allowed to warm to room temperature, and stirring was continued at room temperature for 6 h. The solvent was removed under vacuum conditions and the residue extracted with pentane (40 mL). The filtrate was concentrated under vacuum conditions until **7** was precipitated of as a yellow powder (0.53 g, 72% mp 118 °C). ^{1}H NMR (300.13 MHz): δ 0.69 and 1.24 (2d, $^3J_{HH}$ = 6.6 Hz, 2 × 6H, *o*-CH*MeMe*′), 1.15 and 1.41 (2s, 2 × 9H *o*-CMe$_3$ of Mes*), 1.28 and 1.30 (2d, $^3J_{HH}$ = 6.6 Hz, 2 × 3H, *p*-CH*MeMe*′), 1.32 (s, 9H, *p*-CMe$_3$ of Mes*), 1.35 (s, 9H, GeCMe$_3$), 2.82 (sept, $^3J_{HH}$ = 6.6 Hz, 1H, *p*-C*H*MeMe′), 3.31 (brs, 2H, *o*-C*H*MeMe′), 7.10−7.19 (m, 5H, Ph), 7.11 (s, 2H, *m*-CH of Tip), 7.35 and 7.39 (2s, 2 × 1H, *m*-CH of Mes*). ^{13}C NMR (75.47 MHz): δ 23.80 and 23.81 (*p*-CH*MeMe*′); 25.55 and 25.97 (*o*-CH*MeMe*′); 30.60 (GeC*Me*$_3$); 31.15 (*p*-C*Me*$_3$ of Mes*); 33.02 (d, $^4J_{CP}$ = 7.0 Hz) and 33.25 (d, $^4J_{CP}$ = 6.2 Hz; *o*-C*Me*$_3$ of Mes*); 33.88 (*p*-*C*HMeMe′); 34.11 (*o*-*C*HMeMe′); 34.80 (*p*-*C*Me$_3$ of Mes*); 36.35 (Ge*C*Me$_3$); 38.41 and 38.48 (*o*-*C*Me$_3$ of Mes*); 121.50 and 122.65 (*m*-CH de Mes*); 122.68 (*m*-CH de Tip); 127.57, 128.56, and 128.23 (*o*-, *m*- and *p*-CH of Ph); 134.56 (*ipso*-C of Tip); 135.47 (d, $^1J_{CP}$ = 73.9 Hz, *ipso*-C of Mes*); 138.89 (*ipso*-C of Ph); 149.43 (*p*-C of Tip); 149.88 (*p*-C of Mes*); 153.56 and 154.65 (*o*-C of Mes*); 154.89 (*o*-C of Tip); 175.63 (d, $^2J_{CP}$ = 25.5 Hz, C=N); 182.71 (d, $^1J_{CP}$ = 69.8 Hz, C=P). ^{31}P NMR (121.51 MHz): δ 296.7. MS (*m*/*z*, %): 742 (M + H, 1), 685 (M − *t*-Bu + H, 5), 629 (M − 2*t*-Bu + 2H, 5), 510 (M − PhCNO − 2*t*-Bu + 2H, 5), 350 (Tip(*t*-Bu)GeO, 5), 289 (Mes* PC + H, 12), 277 (TipGe, 45), 231 (Mes* − Me + H, 30), 57 (*t*-Bu, 100). IR (KBr, cm^{-1}): 1596 (C=N). Anal. Calcd for $C_{45}H_{66}$GeNOP (740.58): C, 72.98; H, 8.98%. Found: C, 72.80; H, 8.79%.

Synthesis of 8. One equivalent of acetonitrile (0.041 g, 1 mmol) was added to a solution of **1** (1 mmol) in 10 mL of diethyl ether, cooled to −78 °C. The reaction mixture gradually turned from brown to light yellow after overnight stirring at room temperature. LiF was then filtered off, and the solvents were removed under vacuum conditions. Recrystallization of the crude material from pentane at −20 °C afforded white crystals of **8** (0.52 g, 78%, mp 178 °C). ^{1}H NMR (300.13 MHz): δ 1.00 and 1.20 (2d, $^3J_{HH}$ = 6.9 Hz, 2 × 6H, *o*-CH*MeMe*′), 1.22 (d, $^3J_{HH}$ = 6.9 Hz, 6H, *p*-CH*Me*$_2$), 1.30 (s, 9H, *p*-CMe$_3$ of Mes*), 1.36 (s, 9H, GeCMe$_3$), 1.51 (s, 18H, *o*-CMe$_3$ of Mes*), 2.25 (s, 2H, CH$_2$CN), 2.77 (sept, $^3J_{HH}$ = 6.9 Hz, 2H, *o*-C*H*MeMe′), 2.83 (sept, $^3J_{HH}$ = 6.9 Hz, 1H, *p*-C*H*Me$_2$), 6.97 (s, 2H, *m*-CH of Tip), 7.33 (s, 2H, *m*-CH of Mes*), 7.88 (d, $^2J_{PH}$ = 23.7 Hz, CH=P). ^{13}C NMR (75.47 MHz): δ 7.60 (d, $^3J_{CP}$ = 11.5 Hz, *C*H$_2$CN), 23.71 (*p*-CH*Me*$_2$), 25.16 and 25.70 (*o*-CH*MeMe*′), 28.80 (d, $^4J_{CP}$ = 4.8 Hz, GeC*Me*$_3$), 28.90 (GeC*Me*$_3$), 31.27 (*p*-C*Me*$_3$ of Mes*), 33.89 (*p*-*C*HMe$_2$), 34.01 (d, $^4J_{CP}$ = 7.5 Hz, *o*-C*Me*$_3$ of Mes*), 34.80 (*p*-*C*Me$_3$ of Mes*), 35.16 (*o*-*C*HMeMe′), 37.97 (*o*-*C*Me$_3$ of Mes*), 120.66 (C≡N), 121.56 (*m*-CH of Mes*), 122.44 (*m*-CH of Tip), 129.99 (d, $^3J_{CP}$ = 6.5 Hz, *ipso*-C of Tip), 144.32 (d, $^1J_{CP}$ = 69.9 Hz, *ipso*-C of Mes*), 149.59 (*p*-C of Mes*), 149.93 (*p*-C of Tip), 152.67 (*o*-C of Mes*), 154.92 (*o*-C of Tip), 175.75 (d, $^1J_{CP}$ = 74.1 Hz, CH=P). ^{31}P NMR (121.51 MHz): δ 322.5 (d, $^2J_{PH}$ = 23.7 Hz). MS (*m*/*z*, %): 663 (M, 5), 621 (M − CH$_2$CN − 2H, 5), 607 (M − *t*-Bu + H, 30), 566 (M − *t*-Bu − CH$_2$CN, 5), 509 (M − 2*t*-Bu − CH$_2$CN, 15), 418 (M − Mes*, 5), 377 (M − Mes* − CH$_2$CN − H, 5), 346 (M − Mes*P − CH$_2$CN − H, 5), 275 (Mes*P − H, 15), 233 (GeTip − *i*-Pr − H, 15), 57 (*t*-Bu, 100). IR (KBr, cm^{-1}): 2232 (C≡N). Anal. Calcd for $C_{40}H_{64}$GeNP (662.51): C, 72.52; H, 9.74%. Found: C, 72.72; H, 9.70%.

Synthesis of 9. A mixture of phosphagermaallene **1** (1 mmol) in 10 mL of diethyl ether and pivalonitrile (0.083 g, 1 mmol) was heated overnight at 70 °C in a sealed tube. After the filtration to remove LiF and evaporation of solvents under reduced pressure, crystallization from pentane at −20 °C afforded 0.55 g (78%) of **9** (mp 183 °C). ^{1}H NMR (300.13 MHz): δ 0.68 (s, 9H, NCCMe$_3$); 1.00, 1.12, 1.24, and 1.45 (4d, $^3J_{HH}$ = 6.6 Hz, 4 × 3H, *o*-CH*MeMe*′); 1.31 (s, 9H, GeCMe$_3$); 1.33 and 1.34 (2d, $^3J_{HH}$ = 6.6 Hz, 2 × 3H, *p*-CH*MeMe*′); 1.36 (s, 9H, *p*-CMe$_3$ of Mes*); 1.61 and 1.66 (2s, 2 × 9H, *o*-CMe$_3$ of Mes*); 2.97 (sept, $^3J_{HH}$ = 6.6 Hz, 1H, *p*-C*H*MeMe′); 3.19 and 3.59 (2sept, $^3J_{HH}$ = 6.6 Hz, 2 × 1H, *o*-C*H*MeMe′); 6.95 and 7.10 (2s, 2 × 1H, *m*-CH of Tip); 7.35 and 7.41 (2s, 2 × 1H, *m*-CH of Mes*). ^{13}C NMR (75.47 MHz): δ 23.91 and 23.94 (*p*-CH*MeMe*′); 24.08, 25.17, 25.78, and 25.86 (*o*-CH*MeMe*′); 28.45 (NCC*Me*$_3$); 28.93 (GeC*Me*$_3$); 31.37 (*p*-C*Me*$_3$ of Mes*); 33.64 (d, $^4J_{CP}$ = 6.7 Hz) and 33.85 (d, $^4J_{CP}$ = 6.1 Hz; *o*-C*Me*$_3$ of Mes*); 33.99, 34.15, and 34.29 (*o*- and *p*-*C*HMeMe′); 34.96 (*p*-*C*Me$_3$ of Mes*); 37.93 and 38.27 (*o*-*C*Me$_3$ of Mes*); 121.12 and 121.55 (*m*-CH of Tip); 121.97 and 122.14 (*m*-CH of Mes*); 131.90 (d, $^3J_{CP}$ = 3.2 Hz, *ipso*-C of Tip); 142.02 (d, $^1J_{CP}$ = 86.5 Hz, *ipso*-C of Mes*); 149.97 and 150.16 (*p*-C of Mes* and Tip); 153.50, 153.78, 154.62, and 155.06 (*o*-C of Mes* and Tip); 181.81 (d, $^1J_{CP}$ = 103.5 Hz, C=P); 196.08 (d, $^2J_{CP}$ = 28.4 Hz, C=N). ^{31}P NMR (121.51 MHz): δ 219.6. MS (*m*/*z*, %): 705 (M, 2), 648 (M − *t*-Bu, 25), 622 (M − *t*-BuCN, 5), 510 (M − 2*t*-Bu − *t*-BuCN + 2H, 15), 275 (Mes*P − H, 20), 84 (*t*-BuCN + H, 5), 57 (*t*-Bu, 100). IR (KBr, cm^{-1}): 1597 (C=N). Anal. Calcd for $C_{43}H_{70}$GeNP (704.59): C, 73.30; H, 10.01%. Found: C, 73.39; H, 9.95%.

Synthesis of 10. To a solution of **1** (1 mmol) in diethyl ether (10 mL) was added benzonitrile (0.103 g, 1 mmol) at −78 °C. The mixture was stirred at room temperature for 3 h. The solvents were removed under reduced pressure, and the remaining brownish powder was extracted with 50 mL of pentane. Concentration of the solution to 10 mL, followed by the slow evaporation of the solvent, provided 0.45 g (62%) of **10** (mp 188 °C). ^{1}H NMR (300.13 MHz): δ 1.17, 1.18, 1.29, and 1.56 (4d, $^3J_{HH}$ = 6.6 Hz, 4 × 3H, *o*-CH*MeMe*′); 1.32 (d, $^3J_{HH}$ = 6.6 Hz, 6H, *p*-CH*MeMe*′); 1.35 and 1.71 (2s, 2 × 9H, CMe$_3$); 1.40 (s, 3H, C*Me*Me′); 1.42 (s, 12H, GeCMe$_3$ and CMe*Me*′); 1.84 (m, 1H, C*H*H′); 2.20 (m, 1H, CH*H*′); 2.47 and 3.12 (2sept, $^3J_{HH}$ = 6.6 Hz, 2 × 1H, *o*-C*H*MeMe′); 2.61 (m, 1H, CHP); 2.94 (sept, $^3J_{HH}$ = 6.6 Hz, 1H, *p*-C*H*MeMe′); 6.74 (d, $^3J_{HH}$ = 7.5 Hz, 2H, *o*-CH of Ph); 7.00 (t, $^3J_{HH}$ = 7.5 Hz, 1H, *p*-CH of Ph); 7.08 and 7.11 (2s, 2 × 1H, *m*-CH of Tip); 7.25 (t, $^3J_{HH}$ = 7.5 Hz, 2H, *m*-CH of Ph); 7.43 (brs, 2 × 1H, arom CH). ^{13}C NMR (75.47 MHz): δ 23.23 (d, $^1J_{CP}$ = 21.5 Hz, CHP); 23.63 and 23.88 (*p*-CH*MeMe*′); 25.31, 25.55, 26.15, and 27.73 (*o*-CH*MeMe*′); 29.15 (d, $^3J_{CP}$ = 1.0 Hz, Ge*C*Me$_3$); 30.12 (d, $^4J_{CP}$ = 5.6 Hz, GeC*Me*$_3$); 31.21 and 33.17 (d, $^4J_{CP}$ = 12.1 Hz; C*Me*$_3$); 33.43 and 33.66 (C*MeMe*′); 33.92 (*p*-*C*HMeMe′); 34.72 and 37.63 (*o*-*C*HMeMe′); 34.97 and 38.10 (d, $^3J_{CP}$ = 1.6 Hz; *C*Me$_3$); 37.25 (d, $^3J_{CP}$ = 1.4 Hz, *C*MeMe′); 37.60 (*C*HH′); 119.58 (d, $^3J_{CP}$ = 2.0 Hz, *o*-CH of Ph); 121.12 and 123.03 (*m*-CH of Tip); 121.85 (d, $^3J_{CP}$ = 8.2 Hz) and 122.60 (arom CH); 123.02 (d, $^1J_{CP}$ = 28.8 Hz, P−C$_{arom}$); 123.22 (*p*-CH of Ph); 128.39 (*m*-CH of Ph); 129.86 (d, $^3J_{CP}$ = 4.3 Hz, *ipso*-C of Tip); 149.17 and 150.95 (*C*CMe$_3$); 150.18 (*p*-C of Tip); 153.25 (d, $^2J_{CP}$ = 6.5 Hz, *ipso*-C of Ph); 153.25 and

154.96 (*o*-C of Tip); 155.28 (d, $^2J_{CP}$ = 23.4 Hz, *C*CMeMe′); 176.38 (d, $^1J_{CP}$ = 25.5 Hz, C═N). ^{31}P NMR (121.51 MHz): δ 5.4. MS (*m*/*z*, %): 725 (M, 2), 623 (M − PhCN + H, 10), 566 (M − *t*-Bu − PhCN + H, 10), 333 (Tip(*t*-Bu)Ge − H, 8), 277 (TipGe, 100), 57 (*t*-Bu, 80). IR (KBr, cm^{-1}): 1604 (C═N). Anal. Calcd for $C_{45}H_{66}GeNP$ (724.58): C, 74.59; H, 9.18%. Found: C, 74.47; H, 9.28%.

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Supporting Information Available: CIF files for **4**, **6**, **8**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.