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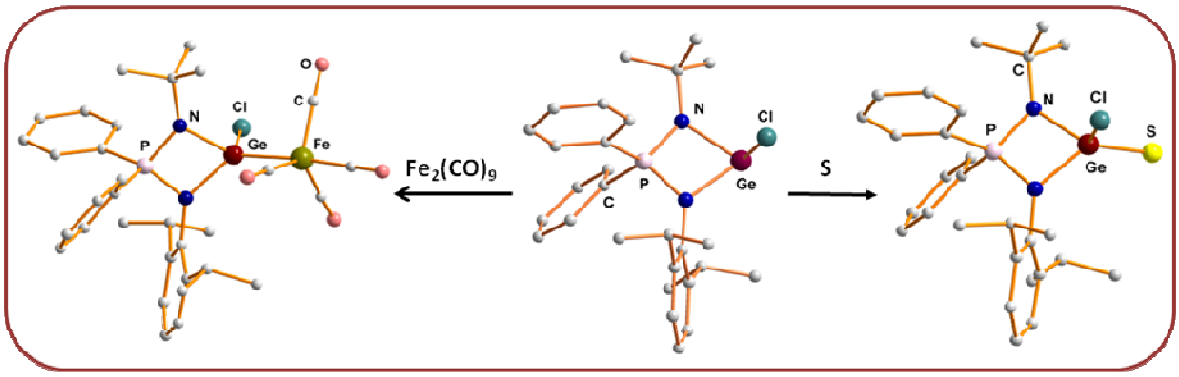
Graphical Abstract

Concise access to iminophosphonamide stabilized heteroleptic germylenes: Chemical reactivity and structural investigation

*Billa Prashanth and Sanjay Singh**



A heteroleptic three coordinate germylene monochloride, its adduct with a Lewis acid, and germaacid-chloride & –ester derivatives with sulfur and selenium have been reported

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ARTICLE TYPE

Concise access to iminophosphonamide stabilized heteroleptic germylenes: Chemical reactivity and structural investigation

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Influence of a sterically demanding iminophosphonamide ligand, [(2,6-*i*Pr$_2$C$_6$H$_3$N)P(Ph$_2$)(N*t*Bu)]H (**LH**) on the synthesis and stability of a heteroleptic germylene monochloride, [(2,6-*i*Pr$_2$C$_6$H$_3$N)P(Ph$_2$)(N*t*Bu)]GeCl (**1**) and its reaction chemistry has been discussed. Complex **1** behaves as a Lewis base to form adduct with Fe(CO)$_4$, as [(2,6-*i*Pr$_2$C$_6$H$_3$N)P(Ph$_2$)(N*t*Bu)]Ge(Cl)Fe(CO)$_4$ (**2**). Reaction of **1** with KO*t*Bu or AgOSO$_2$CF$_3$ affords Ge(II) compounds, [(2,6-*i*Pr$_2$C$_6$H$_3$N)P(Ph$_2$)(N*t*Bu)]GeR (R = O*t*Bu (**3**), OSO$_2$CF$_3$ (**4**)). Treatment of complex **1** with elemental sulfur or selenium leads to heavier analogues of germaacid chlorides, [(2,6-*i*Pr$_2$C$_6$H$_3$N)P(Ph$_2$)(N*t*Bu)]Ge(E)Cl (E = S (**5**), Se (**6**)). Similarly, compound **3** on reaction with elemental sulfur or selenium produces heavier analogues of germaesters, [(2,6-*i*Pr$_2$C$_6$H$_3$N)P(Ph$_2$)(N*t*Bu)]Ge(E)O*t*Bu (E = S (**7**), Se (**8**)). Complexes **1**−**8** were characterized using multinuclear NMR, EI-MS and solid state structures of the complexes **1**-**3**, **5** and **7** have been elucidated using single crystal X-ray diffraction.

Introduction

The first germylene (R$_2$Ge) was isolated in 1974 by Lappert et al., (R = N(SiMe$_3$)$_2$, CH(SiMe$_3$)$_2$, N(SiMe$_3$)(CMe$_3$))[1] and later the N-heterocyclic germylenes (NHGe) emerged as stable 6 valence electron neutral divalent compounds of Ge with a vacant *p*-orbital.[2] If this vacant *p*-orbital at the germanium centre can be engaged into donor-acceptor interaction through a donor atom of the supporting bidentate ligand that would give rise to heteroleptic three coordinated germylenes with 8 valence electrons.[3] The use of monoanionic [N,N']-chelating ligands have facilitated the isolation of three coordinated heteroleptic metallylenes not only for Ge but also for other elements of group 14.[4,5] {Carbon has been an exception so far as a three coordinated heteroleptic compound is not yet known.} As shown in Chart 1, the six membered β-diketiminate (**A**),[4,5] five membered aminotroponiminate (ATI) (**B**)[6] and four membered amidinate and guanidinate (**C**)[4,5] ligands have provided an opportunity to investigate the effect of heteroatom ring sizes and donor ability of the ligand in stabilization of tricoordinate Ge(II) centres in these compounds. The iminophosphonamides have similar attributes as ligands as compared to amidinates or guanidinates however, due to the longer P−N (vs. the C−N bonds in type **A**, **B** or **C** in Chart 1) bond length and the wider N−P−N bite angle (vs. the N−C−N bite angle) the iminophosphonamides would make flexible chelate rings and can provide potential alternative to the popular amidinate or guanidinate ligands.[7,8]

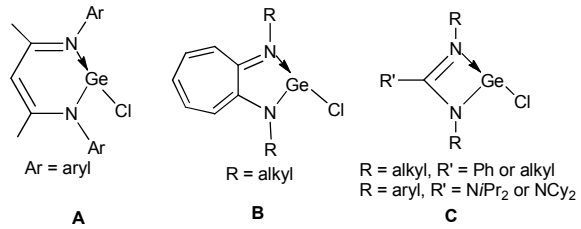

Chart 1 Notable examples of tricoordinate germylene monochlorides: Six membered (**A**), five membered (**B**) and four membered (**C**) metallacycles.

While the synthesis and reactivity of heteroleptic germylenes of types **A** and **B** have been explored in detail, the chemistry of germylenes of type **C** and similar four membered metallacyles have been relatively less explored.[4-6] The heavy ketones of germanium with RR'Ge=E moiety (E = O, S, Se, and Te)[9], germaacidchloride complexes [{HC{(MeC)(C$_6$H$_5$N)}$_2$]Ge(E)Cl[10] & [HC{MeCN(2,6-*i*Pr$_2$C$_6$H$_3$)}$_2$]Ge(E)Cl[11] (E = S, Se), heavier germacarboxylic acids [HC{MeCN(2,6-*i*Pr$_2$C$_6$H$_3$)}$_2$]Ge(E)OH] (E = S, Se)[12] and a sulfur analogue of carboxylic acid [HC{MeCN(2,6-*i*Pr$_2$C$_6$H$_3$)}$_2$]Ge(S)SH,[13] are some of the key molecules based on six membered chelates. Nagendran and co-workers have recently used type **B** complex based on ATI ligand to prepare heavier germathioacid halides, [(R)$_2$ATI]Ge(E)X (E = S, Se; X = Cl, F; R = *i*Bu, *t*Bu), germathio/seleno/telluro derivatives [(R)$_2$ATI]Ge(E)R' (R = *i*Bu, *t*Bu; R' = O*t*Bu, pyrrole, E = S, Se, Te).[14-18]

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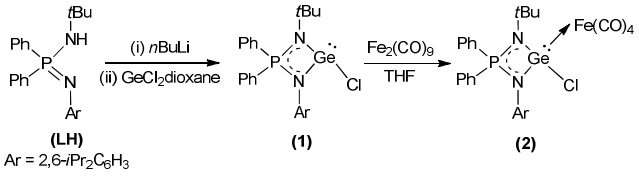
† Electronic supplementary information (ESI) available: Multinuclear NMR spectrum of compound **1**-**8**, HMQC and HMBC spectra of compound **7**. CCDC reference number 1402721-1402725 for compounds **1-3, 5** and **8**, respectively are available. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

Four membered metallyenes of germanium (type **C**) with amidinates and guanidinates have seen rapid development of their chemistry.[4,5] The amidinate and guanidinate stabilized Ge(I) dimers,[19-21] L'Ge(I)Ge(I)L' and amidinate stabilized bisgermylene oxide and sulfide[22] have been the recent important breakthrough. The adducts of Lewis acidic metal fragments with germylenes[23-25] and terminal chalcogenido germanium complexes with alkylamidinates are also noteworthy.[26] Similarly, Sen et al. reported the dimeric germathioacid chloride, $[PhC(NtBu)_2Ge(\mu\text{-}S)Cl]_2$ due to high reactivity of the intermediate $[PhC(NtBu)_2]Ge(S)Cl$ units that undergo rapid [2+2] cycloaddition.[27] Prior to the present work, the known complexes of Ge(II) with iminophosphonamide ligands were only $[(RO)_2P(NSiMe_3)_2]GeCl$ and $[(RO)(Me_3SiO)P(NSiMe_3)_2]GeCl$, (R = *i*Pr).[28] Based on these facts, the motivation to the present work lies in exploring the chemistry of heteroleptic germylene monochloride, $[(2,6\text{-}iPr_2C_6H_3N)P(Ph_2)(NtBu)]GeCl$ (**1**). Therefore, the reaction chemistry of **1** in the synthesis of other heteroleptic germylene derivatives, reaction with a Lewis acid fragment, $Fe(CO)_4$ and oxidation reaction with S and Se to prepare heavy germaacid–chlorides and –esters have been discussed.

Results and discussion

Spectroscopic characterization of complexes 1-8

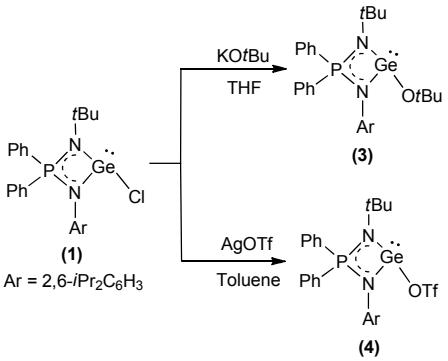
Treatment of the lithium complex **L**Li, generated *in situ* by reacting **LH** with *n*BuLi (**L** = $(2,6\text{-}iPr_2C_6H_3N)P(Ph_2)(NtBu)$), with one equivalent of $GeCl_2$·dioxane in Et_2O smoothly formed the germylene monochloride complex, $[(2,6\text{-}iPr_2C_6H_3N)P(Ph_2)(NtBu)]GeCl$ (**1**) in moderate yield (Scheme 1). Complex **1** is off-white crystalline solid that is soluble in solvents such as Et_2O, toluene, and THF. Germylenes due to the availability of a stereochemically active lone pair of electrons have the ability to coordinate a Lewis acidic transition metal species allowing formation of a donor-acceptor adduct.[3] To probe the donor ability of **1,** its reaction with $Fe_2(CO)_9$ was performed which afforded the adduct, $[(2,6\text{-}iPr_2C_6H_3N)P(Ph_2)(NtBu)]Ge(Cl)Fe(CO)_4$ (**2**) in good yield (Scheme 1). Compounds **1** and **2** have long shelf life, no decomposition was observed up to two months when stored in a argon filled glove box. However, compounds **1** and **2** decompose immediately after exposure to air and moisture.



Scheme 1 Synthesis of iminophosphonamide supported germylene monochloride complex **1** and its Lewis acid adduct **2**.

The EI mass spectrum of **1** showed a peak at *m/z* 539.1488 that corresponds to $[M]^+$ and another signal was observed at *m/z* 505.1878 for $[M\text{-}Cl]^+$. For compound **2**, the mass spectrum showed the molecular ion peak $[M+H]^+$ at *m/z* 709.0754 and the peaks at *m/z* 539.1456 and 505.1847 were attributed to $[M\text{-}Fe(CO)_4]^+$ and $[M\text{-}Fe(CO)_4\text{-}Cl]^+$, respectively. The IR spectrum of **2** showed three distinct active CO stretching bands at 2040 (st, CO), 1968 (m, CO), 1926 (st, CO) cm^{-1} that are expected for a trigonal bipyramidal based local symmetry (C_{3v}) around the Fe atom of the $Fe(CO)_4$ moiety where one of the axial position should be occupied by the Ge atom. The ^1H NMR spectrum of **1** and **2** showed that the two *i*Pr groups of the ligand are magnetically non-equivalent and the two methyl groups of each *i*Pr group are diastereotopic.[29] This pattern is also supported by the presence of two broad septets for $CHMe_2$ at 2.99 and 4.36 ppm for **1** and 3.16 and 4.16 ppm for **2**. The methyl groups of both the *i*Pr moiety appear as four doublets (0.22, 0.63, 1.05 and 1.46 ppm for **1**) and (0.05, 0.49, 1.12 and 1.25 ppm for **2**). A signal in ^{13}C NMR spectrum of **2** at 214.7 ppm is assigned to the *C*O carbons[23,24] and other signals were as expected for the ligand. The $^{31}P\{^1H\}$ NMR spectrum of compounds **1** and **2** showed signals at 47.2 (**1**), and 52.2 (**2**) ppm respectively, and these values are significantly shifted downfield as compared to the ligand, $[(2,6\text{-}iPr_2C_6H_3N)P(Ph_2)(NtBu)]H$ (**LH**) (-16.6 ppm).[8]

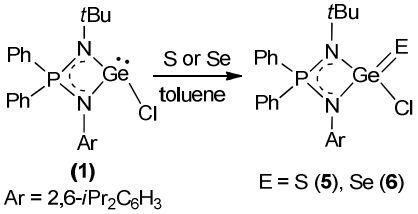
With the objective to extend the reaction chemistry of complex **1** to prepare other Ge(II) derivatives and to test the suitability of iminophosphonamide as a ligand with germanium centre we performed salt metathesis on **1** with KO*t*Bu and $AgOSO_2CF_3$ to obtain the anticipated complexes, $[(2,6\text{-}iPr_2C_6H_3N)P(Ph_2)(NtBu)]GeOtBu$ (**3**) and $[(2,6\text{-}iPr_2C_6H_3N)P(Ph_2)(NtBu)]GeOSO_2CF_3$ (**4**) in good yields (Scheme 2). The formation of complexes **2-4** clearly explained the robustness of the metal ligand interaction and at the same time allowed the germanium centre to participate in further reactions. The EI mass spectrum of complex **3** gave a signal, *albeit* in low intensity, at *m/z* 503.1851 assigned to $[M\text{-}OtBu]^+$ and for **4** the peak at *m/z* 653.1266 was due to $[M]^+$. The ^1H NMR features for **3** are similar to those observed for compounds **1** and **2** with typical *i*Pr pattern of two septets for $CHMe_2$ groups and four doublets for the methyl groups of two *i*Pr moieties present on the ligand. Two sharp singlets for **3** at 1.36 and 1.83 ppm are respectively, due to the *t*Bu group of the ligand and O*t*Bu on germanium. The O*t*Bu carbons were seen at 32.8 and 75.9 ppm in its ^{13}C NMR spectrum and the ligand *t*Bu carbons were observed at 33.3 and 55.3 ppm. The $^{31}P\{^1H\}$ NMR spectrum of **3** showed a signal at 39.0 ppm and for **4** it appeared at 62.1 ppm. The ^{19}F NMR spectrum of complex **4** revealed a signal at -77.4 ppm for the triflate group.[30]



Scheme 2 Salt metathesis on **1** to form the germylene monoalkoxide **3** and the germylene monotriflate **4**.

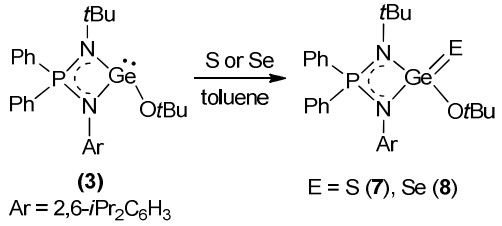
In addition to the adduct formation and salt metathesis reactions the reaction chemistry of complex **1** has also been elaborated in the oxidation of divalent Ge centre with heavier chalcogens. Thus, the reaction of **1** with one equivalent of elemental sulfur afforded

the germathioacid chloride [(2,6-*i*Pr$_2$C$_6$H$_3$N)P(Ph$_2$)(N*t*Bu)]Ge(S)Cl (**5**), formation of which was confirmed by multinuclear NMR spectroscopy and X-ray crystallography. Contrary to the previous report on oxidation of Ge(II) centre by S where the intermediate germathione analogue (>Ge=S) undergoes [2+2] cycloaddition to afford the dimeric complex[27] [PhC(N*t*Bu)$_2$Ge(μ-S)Cl]$_2$, the oxidation of Ge(II) in compound **1** was not followed by the [2+2] cycloaddition and the monomeric complex **5** was the final stable product. Using a similar procedure as that for **5**, its selenium analogue [(2,6-*i*Pr$_2$C$_6$H$_3$N)P(Ph$_2$)(N*t*Bu)]Ge(Se)Cl (**6**), was synthesized under heating condition (Scheme 3).



Scheme 3 Synthesis of heavier analogues of germaacid chlorides **5** and **6**.

The mass spectrum of compound **5** showed a peak at *m/z* 569.1334 that corresponds to $[M+H]^+$ and the peak at 537.1467 was due to $[M-S]^+$. For compound **6**, a peak at *m/z* 619.2278 was attributed to $[M+H]^+$ and another signal observed at *m/z* 583.2417 was assigned as $[M-Cl]^+$. The NMR features for compounds **5** and **6** are similar to those observed for the free ligand, [(2,6-*i*Pr$_2$C$_6$H$_3$N)P(Ph$_2$)(N*t*Bu)]H (**LH**) however, the chemical shifts were considerably different, specially in the $^{31}P\{^1H\}$ NMR. Therefore, a typical isopropyl pattern of one septet for *CH*Me$_2$ (3.09 ppm for **5** and 3.05 ppm for **6**) and one doublet for methyl groups of *i*Pr (0.88 ppm for **5** and 0.92 ppm for **6**) were observed. The $^{31}P\{^1H\}$ NMR spectrum of complexes **5** and **6** showed a resonance at 37.5 and 36.2 ppm, respectively and these values are significantly shifted downfield as compared to its germylene monochloride precursor **1** (47.2 ppm) or the ligand [(2,6-*i*Pr$_2$C$_6$H$_3$N)P(Ph$_2$)(N*t*Bu)]H (**LH**) (-16.6 ppm).



Scheme 4 Synthesis of heavier analogues of germaesters **7** and **8**.

In a manner similar to the synthesis of complexes **5** and **6**, the reaction of **3** with one equivalent of elemental sulfur or selenium in toluene afforded the germathioester [(2,6-*i*Pr$_2$C$_6$H$_3$N)P(Ph$_2$)(N*t*Bu)]Ge(S)O*t*Bu (**7**) and germaselenoetser [(2,6-*i*Pr$_2$C$_6$H$_3$N)P(Ph$_2$)(N*t*Bu)]Ge(Se)O*t*Bu (**8**). The mass spectrum of compound **7** showed a peak at *m/z* 610.2121 that corresponds to $[M+H]^+$ and the peak at *m/z* 577.2296 is due to $[M-S]^+$. The mass spectrum of compound **8** showed a peak at *m/z* 656.1664 that corresponds to $[M]^+$ and the peak at *m/z* 577.2399 is due to $[M-Se]^+$. Unlike complexes **5** and **6**, the ^1H NMR features of **7** and **8** resemble its precursor **3** and the same can be ascribed to the presence of two magnetically non-equivalent *i*Pr groups with two septets for C*H*Me$_2$ and four doublets for the diastereotopic methyls on CH*Me*$_2$. Additionally, a singlet (1.35 ppm for **7** and 1.36 ppm for **8**) was assigned to the *t*Bu group of the ligand and another singlet was assigned to the O*t*Bu group (1.60 ppm for **7** and 1.63 ppm for **8**). The ^{13}C NMR signals for *t*Bu (32.8 and 55.0 ppm for **7**; 32.9 and 55.2 ppm for **8**) and *t*BuO (32.2 and 75.3 ppm for **7**; 32.4 and 75.7 ppm for **8**) were consistent with its precursor **3**. The $^{31}P\{^1H\}$ NMR spectrum of complexes **7** and **8** showed a resonance at 42.3 and 43.6 ppm respectively, which is shifted downfield as compared to the germylene tertbutoxide **3** (39.0 ppm).

Single crystal X-ray structural description of complexes 1-3, 5 and 8

The unambiguous composition of compounds **1**−**3**, **5** and **8** have been confirmed by single crystal X-ray structural anlysis. Selected crystal data and data collection parameters are listed in Table 1.

Crystals suitable for X-ray diffraction of compound [(2,6-*i*Pr$_2$C$_6$H$_3$N)P(Ph$_2$)(N*t*Bu)]GeCl (**1**) were obtained from Et$_2$O. Compound **1** crystallizes in the monoclinic crystal system with *Cc* space group. The Ge(II) centre in complex **1** adopts pyramidal geometry where one of the vertices is occupied by a lone pair. The Ge(1)−Cl(1) distance in compound **1** (2.338(1) Å) is longer when compared with that of the amidinate complexes, [PhC(N*t*Bu)$_2$]GeCl (2.257(2) Å),[19] [*t*BuC(N-2,6-*i*Pr$_2$C$_6$H$_3$)$_2$]GeCl (2.174(2) Å)[20] and guanidinate complex, [Cy$_2$NC(N-2,6-*i*Pr$_2$C$_6$H$_3$)$_2$]GeCl (2.245(3) Å).[31] The Ge−N bond lengths in **1** (1.980(3) and 1.992(3) Å) are slightly shorter than that in [PhC(N*t*Bu)$_2$]GeCl (2.060(2) Å).[19] The N(1)−Ge(1)−N(2) bite angle (73.08(2)°) in **1**, as expected, is wider than the corresponding angle in the amidinates [PhC(N*t*Bu)$_2$]GeCl (63.22(11)°),[19] [*t*BuC(N-2,6-*i*Pr$_2$C$_6$H$_3$)$_2$]GeCl (65.25(14)°)[20] and the guanidinate complex, [Cy$_2$NC(N-2,6-*i*Pr$_2$C$_6$H$_3$)$_2$]GeCl (65.76(13)°).[31]

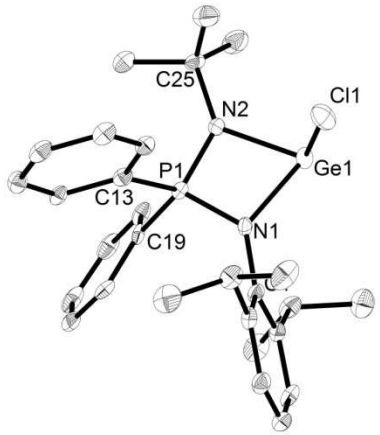


Fig 1. Single crystal X-ray structure **1**. All hydrogen atoms have been omitted for clarity. Thermal ellipsoids have been drawn at 50% probability. Selected bond lengths [Å] and bond angles [°]: P(1)–N(1) 1.622(3), P(1)–N(2) 1.612(3), P(1)–C(13) 1.806(2), P(1)–C(19) 1.811(2), C(1)–N(1) 1.437(2), C(25)–N(2) 1.490(2), Ge(1)–N(1) 1.980(3), Ge(1)–N(2) 1.992(3), Ge(1)–Cl(1) 2.338(1); N(1)–P(1)–N(2) 94.00(1), C(13)–P(1)–C(19) 106.45(1), N(1)–Ge(1)–N(2) 73.08(2), N(1)–Ge(1)–Cl(1) 97.01(1), N(2)–Ge(1)–Cl(1) 102.18(1).

This data on Ge−Cl and Ge−N bond lengths and the wider N−Ge−N bond angle is indicative of electron rich backbone in the iminophosphonamide ligand as compared to amidinates and guanidinates. These changes could also be due to different N−P−N angle in the present case versus the N−C−N angle of amidinates and guanidinates.[8,7] This strong chelation of the iminophosphonamide supposedly locates more electron density at the Ge(II) centre thus shortening the Ge−N bonds and weakening the Ge−Cl bond.

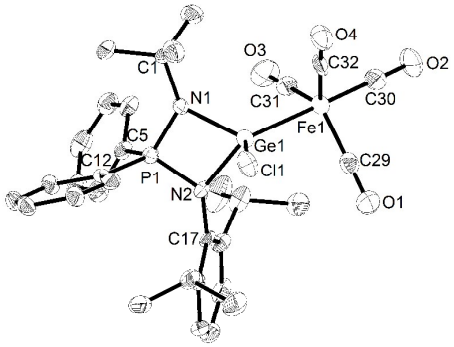


Fig 2. Single crystal X-ray structure of **2**. All hydrogen atoms have been omitted for clarity. Thermal ellipsoids have been drawn at 50% probability. Selected bond lengths [Å] and bond angles [°]:P(1)–N(1) 1.608(4), P(1)–N(2) 1.626(3), C(1)–N(1) 1.477(2), C(17)–N(2) 1.437(6), Ge(1)−N(1) 1.902(4), Ge(1)−N(2) 1.906(3), Ge(1)−Cl(1) 2.205(3), Ge(1)−Fe(1) 2.270(2); N(1)−P(1)−N(2) 92.34(3), N(1)−Ge(1)−N(2) 75.55(1), N(1)−Ge(1)−Cl(1) 105.01(3), N(2)−Ge(1)−Cl(1) 100.34(4), Fe(1)−Ge(1)−Cl(1) 112.38(3), Fe(1)−Ge(1)−N(1) 124.27(3), Fe(1)−Ge(1)−N(2) 132.25(3), Ge(1)−Fe(1)−C(30) 172.97(3), C(31)−Fe(1)−C(32) 118.64(2), C(29)−Fe(1)−C(31) 128.74(2), C(29)−Fe(1)−C(32) 112.25(1), C(29)−Fe(1)−C(30) 93.52(5), C(29)−Fe(1)−Ge(1) 85.83(2).

Single crystals of [(2,6-*i*Pr$_2$C$_6$H$_3$N)P(Ph$_2$)(N*t*Bu)]Ge(Cl)Fe(CO)$_4$ (**2**) were obtained from toluene. Compound **2** crystallizes in the triclinic system with $P\bar{1}$ space group. Solid state structure of **2** corroborates with that predicted based on the spectroscopic data and reveals a distorted tetrahedral arrangement around germanium(II) centre comprising of two nitrogen atoms, a chlorine atom and an Fe atom of the Fe(CO)$_4$ fragment. The Fe centre in **2** is five coordinated in a slightly distorted trigonal bipyramidal structure (Figure 2). The previously known 1:1 adducts of heteroleptic germylene with Fe(CO)$_4$ includes the amidinate complexes, [*t*BuC(N*i*Pr)$_2$]Ge(Cl)Fe(CO)$_4$ and [PhC(N*t*Bu)$_2$]Ge(Cl)Fe(CO)$_4$.[23] The acute bond angle of N(1)−Ge(1)−N(2) (75.55 (1)º) in **2** is little wider than that in **1** (73.08(2)º). The average Ge−N and the Ge−Cl bond length in **2** (1.904 Å) and (2.205(3) Å) respectively, are shorter than the corresponding values in **1** (1.986 Å) and (2.338(1) Å). The prediction from IR spectrum of **2**, for a tbp based geometry around Fe centre, was also confirmed in the single crystal X-ray data. The germylene donor fragment in **2** occupies an axial position of this tbp arrangement with the C(30)−Fe(1)−Ge(1) axial angle of 172.97(3)º. The angles in the equatorial plane of this distorted tbp structure are: C(29)−Fe(1)−C(31) 128.74(2)°, C(29)−Fe(1)−C(32) 112.25(1)°, and of C(31)−Fe(1)−C(32) 118.64(2)°. The Ge−Fe bond distance 2.270(2) Å is similar to that found in [PhC(N*t*Bu)$_2$]Ge(Cl)Fe(CO)$_4$ (2.278(1) Å)[23] and slightly shorter than 2.34(4) Å seen in the Ge(I) dimer, [PhC(N*t*Bu)$_2$](Fe(CO)$_4$)Ge−Ge(Fe(CO)$_4$)[PhC(N*t*Bu)$_2$].[24]

Crystals of complex [(2,6-*i*Pr$_2$C$_6$H$_3$N)P(Ph$_2$)(N*t*Bu)]GeO*t*Bu (**3**) suitable for X-ray diffraction were grown from its toluene solution at 4 ºC. Compound **3** crystallizes in the monoclinic system with space group $P2_1/n$. Complex **3** is the first example of a germylene alkoxide where Ge(II) centre is part of a four membered heterocyclic ring. The [N,N']-chelation of the iminophosphonamide ligand with the germanium atom is similar to that found in its precursor **1**. Thus, the Ge(II) centre in **3** adopts a distorted tetrahedral geometry with a lone pair of electrons located at one of the vertices. The Ge-N bonds in **3** are comparable (avg 2.017 Å) to those in **1** (avg 1.986 Å). However, the N−Ge−O bond angles in **3** (94.90(1) and 94.20 (3)º are narrower than the N−Ge−Cl bond angles (97.01(1) and 102.18(1)°) in **1**. It is to be noted that the Ge−O distance (1.848(3) Å) in **3** is slightly longer than that observed for [HC{MeCN(2,6-*i*Pr$_2$C$_6$H$_3$)}$_2$]GeO*t*Bu (1.827(14) Å)[32] and [HC{MeCN(2,6-*i*Pr$_2$C$_6$H$_3$)}$_2$]GeOH (1.828(1) Å).[33]

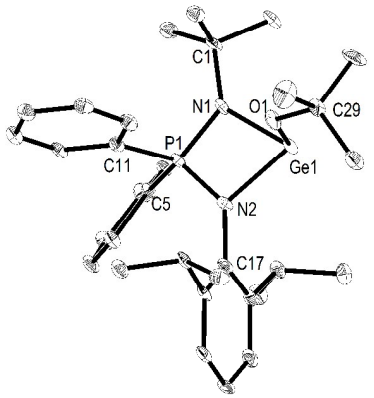


Fig 3. Single crystal X-ray structure of **3**. All hydrogen atoms have been omitted for clarity. Thermal ellipsoids have been drawn at 50% probability. Selected bond lengths [Å] and bond angles [°]: P(1)–N(1) 1.609(4), P(1)–N(2) 1.604(3), P(1)–C(5) 1.803(5), P(1)–C(11) 1.816(7), C(1)–N(1) 1.475(1), C(17)–N(2) 1.427(1), Ge(1)−N(1) 2.020(4), Ge(1)−N(2) 2.014(2), Ge(1)−O(1) 1.848(3), O(1)−C(29) 1.432(2); N(1)−P(1)−N(2) 95.11(1), N(1)−Ge(1)−N(2) 71.96(1), N(1)−Ge(1)−O(1) 94.90(1), N(2)−Ge(1)−O(1) 94.20(3), Ge(1)−O(1)−C(29) 122.40(1).

Compound [(2,6-*i*Pr$_2$C$_6$H$_3$N)P(Ph$_2$)(N*t*Bu)]Ge(S)Cl (**5**) crystallizes in monoclinic system with $P2_1/c$ space group. Compound **5** is the first example of a monomeric germathioacid chloride with Ge in a four membered heterocyclic ring. The previously reported germathioacid chloride stabilized by an amidinate ligand undergoes [2+2] cycloaddition reaction to form the dimer [PhC(N*t*Bu)$_2$Ge(μ-S)Cl]$_2$.[27] Similarly, the dianionic bis(amido)silyl ligands also led to the [2+2] cycloaddition dimers: [{*i*Pr$_2$Si(N-2,6-*i*Pr$_2$C$_6$H$_3$)$_2$}Ge(μ-S)]$_2$, [{*i*Pr$_2$Si(N-SiPh$_3$)$_2$}Ge(μ-S)]$_2$[33a] and [{[(4-*i*PrC$_6$H$_4$)$_3$SiN]$_2$Si(tolyl)$_2$}Ge(μ-S)]$_2$.[33b] The solid state structure of **5** reveals that the Ge(IV) centre is bonded to iminophosphonamide ligand in a [N,N']-chelate fashion and the other sites are occupied by chlorine and sulfur atoms resulting in a distorted tetrahedral geometry at the germanium centre (Figure 4). The Ge–S bond length of (2.048(2) Å) was found to be identical with [{HC(CMeNAr)$_2$}]Ge(S)Cl (2.053(6) Å)[11] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) and shorter when compared to that of the sulfur bridged dimer, [PhC(N*t*Bu)$_2$Ge(μ-S)Cl]$_2$ (2.209(4) Å)[27]

suggesting a double bond character in the Ge−S bond. The Ge−Cl bond length in **5** (2.209(2) Å) is slightly shorter when compared to its parent molecule **1** (2.338(1) Å). The Ge−N bond distances in **5** (1.912(3) and 1.905(3) Å) are also slightly shorter than that in **1** (1.980(3) and 1.992(3) Å). The N(1)−Ge(1)−N(2) bond angle in **5** (76.31(2)°) is slightly wider than the corresponding angle observed in **1** (73.08(2)°).

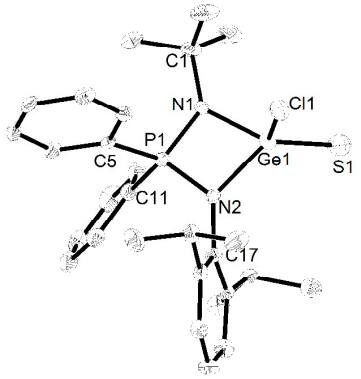


Fig 4. Single crystal X-ray structure of **5**. All hydrogen atoms have been omitted for clarity. Thermal ellipsoids have been drawn at 50% probability. Selected bond lengths [Å] and bond angles [°]:P(1)–N(1) 1.630(3), P(1)–N(2) 1.644(3), P(1)–C(5) 1.805(2), P(1)–C(11) 1.804(2), C(1)–N(1) 1.497(2), C(17)–N(2) 1.458(2), Ge(1)–N(1) 1.912(3), Ge(1)–N(2) 1.905(3), Ge(1)–Cl(1) 2.209(1), Ge(1)−S(1) 2.048(2); N(1)–P(1)–N(2) 92.16(1), N(1)–Ge(1)–N(2) 76.31(2), C(5)–P(1)–C(11) 106.59(1), Cl(1)–Ge(1)–S(1) 113.22(1).

Crystals of complex [(2,6-iPr$_2$C$_6$H$_3$N)P(Ph$_2$)(NtBu)]Ge(Se)OtBu (**8**) suitable for single crystal X-ray structural analysis were grown at 4 ºC from toluene. Compound **8** is the first example of a germaselenoester with Ge as part of a four membered ring. Compound **8** crystallizes in monoclinic system with space group $P2_1$/c. Solid state structure of **8** showed tetracoordinated Ge centre in a distorted tetrahedral environment of two nitrogen atoms, selenium atom and O of the tBuO group (Figure 5). The Ge(1)−Se(1) bond distance (2.200(3) Å) in **8** is comparable to that found in [(R)$_2$ATI]Ge(Se)OtBu (2.219(7) Å for R = iBu; 2.2180(1) Å for R = tBu)[15] and the Ge=Se distance in a selenoketone, Tbt(Tip)Ge=Se (2.180(2) Å).[34] The average Ge−N distance in compound **8** (1.926 Å) is shorter than that found in [(2,6-iPr$_2$C$_6$H$_3$N)P(Ph$_2$)(NtBu)]GeCl (**1**) (1.986 Å) and [(2,6-iPr$_2$C$_6$H$_3$N)P(Ph$_2$)(NtBu)]GeOtBu (**3**) (2.017 Å). The Ge−O bond length (1.782(4) Å) has also shortened compared to its precursor **3** (1.848(3) Å). The Se−Ge−O angle (121.12 (1)º) in **8** is comparable to the corresponding angle in [(R)$_2$ATI]Ge(Se)OtBu (R = iBu or tBu) (123.2(1)º and 123.39(9)º)[15] and [HC{MeCN(2,6-iPr$_2$C$_6$H$_3$)}$_2$]Ge(Se)OH (121.4(1)º).[12b]

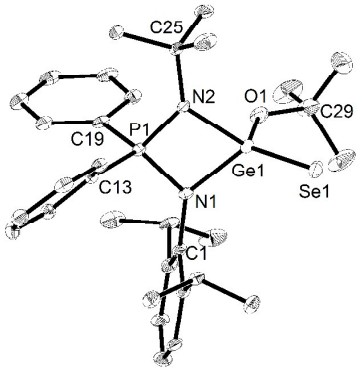


Fig 5. Single crystal X-ray structure of **8**. All hydrogen atoms and toluene molecule have been omitted for clarity. Thermal ellipsoids have been drawn at 50% probability. Selected bond lengths [Å] and bond angles [°]: P(1)–N(1) 1.628(1), P(1)–N(2) 1.627(4), P(1)–C(13) 1.797(5), P(1)–C(19) 1.805(6), C(1)–N(1) 1.443(2), C(25)–N(2) 1.482(1), Ge(1)−N(1) 1.928(5), Ge(1)−N(2) 1.925(2), Ge(1)−Se(1) 2.200(3), Ge(1)−O(1) 1.782(4), O(1)−C(29) 1.428(1); N(1)−P(1)−N(2) 95.11(1), N(1)−Ge(1)−N(2) 71.96(1), Se(1)−Ge(1)−O(1) 121.12(1), N(1)−Ge(1)−O(1) 94.90(1), N(2)−Ge(1)−O(1) 94.20(1), N(1)−Ge(1)−Se(1) 124.15(3), N(2)−Ge(1)−Se(1) 123.50(4), Ge(1)−O(1)−C(29) 122.40(1).

Table 1 Crystallographic data and refinement parameters for compounds **1-3, 5** and **8**.

Compound	**1**	**2**	**3**	**5**	**8**·C$_7$H$_8$
Chemical formula	$C_{28}H_{36}N_2PGeCl$	$C_{32}H_{36}N_2PGeClFeO_4$	$C_{32}H_{45}N_2PGeO$	$C_{28}H_{36}N_2PGeSCl$	$C_{39}H_{53}N_2PGeOSe$
Molar mass	539.6	707.5	577.3	571.7	748.4
Crystal system	monoclinic	triclinic	monoclinic	triclinic	monoclinic
Space group	*Cc*	*P*$\bar{1}$	$P2_1/n$	*P*$\bar{1}$	$P2_1/c$
T[K]	100(2)	100(2)	100(2)	100(2)	100(2)
a [Å]	16.9536(3)	9.6544(5)	9.1120(3)	10.1608(5)	23.5042(3)
b [Å]	9.0581(2)	12.5176(2)	21.7986(6)	10.4339(3)	8.9246(2)
c [Å]	35.2533(3)	16.7548(9)	15.3863(2)	14.9957(4)	20.4702(3)
α[°]	90.00	68.117(3)	90.00	103.237(3)	90.00
β [°]	94.174(3)	83.597(4)	95.351(3)	95.103(4)	109.724(2)
γ[°]	90.00	71.997(2)	90.00	113.163(3)	90.00
V [Å^3]	5399.40(3)	1786.92(2)	3042(7)	1394.05(1)	4042.01(2)
Z	8	2	4	2	4
D(calcd.) [g·cm^{-3}]	1.33	1.31	1.26	1.36	1.23
μ(Mo-K_α) [mm^{-1}]	1.312	1.401	1.086	1.346	1.727
Index range	$-20 \le h \le 20$	$-11 \le h \le 10$	$-10 \le h \le 10$	$-12 \le h \le 12$	$-28 \le h \le 28$
	$-10 \le k \le 10$	$-15 \le k \le 15$	$-26 \le k \le 26$	$-12 \le k \le 12$	$-10 \le k \le 10$
	$-42 \le l \le 42$	$-19 \le l \le 20$	$-18 \le l \le 18$	$-18 \le l \le 18$	$-24 \le l \le 24$

Reflections collected	25911	18364	17781	12709	34873
Independent reflections	9725	6463	5570	5104	7388
Data/restraints/parameters	9725/2/609	6463/0/386	5570/0/344	5104/0/313	7388/0/417
$R1$, $wR2$ [$I>2\sigma(I)$][a]	0.0346, 0.0780	0.057, 0.120	0.084, 0.205	0.075, 0.147	0.055, 0.147
$R1$, $wR2$ (all data)[a]	0.042, 0.0811	0.112, 0.138	0.106, 0.230	0.124, 0.180	0.061, 0.151
GOF	1.031	0.930	1.015	1.011	1.036

[a] $R1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$. $wR2 = [\Sigma w(|Fo^2| - |Fc^2|)^2/\Sigma w|Fo^2|^2]^{1/2}$

Conclusions

In conclusion we have demonstrated the ability of iminophosphonamide to strongly chelate with the Ge(II) centres and form robust heteroleptic germylene complexes. Further reactions on the germylene complexes in formation of Lewis acid adduct, metathesis and oxidation reactions illustrate the usefulness of the germylene complexes. Synthesis of the unknown germaacid chlorides, germacarboxylic acids, esters and anhydrides are the immediate future prospects of the present work and these studies are currently underway.

Experimental section

General procedures

All syntheses were carried out under an inert atmosphere of dinitrogen in oven dried glassware using standard Schlenk techniques, and other manipulations were accomplished in an Ar filled glove box. Solvents were purified by MBRAUN solvent purification system MB SPS-800. All chemicals were purchased from commercial sources used without further purification. Compound [(2,6-*i*Pr$_2$C$_6$H$_3$N)P(Ph$_2$)(N*t*Bu)]H (**LH**) was prepared as reported in the literature.[8] ^{1}H, ^{13}C, ^{31}P{^{1}H} NMR spectra were recorded with a Bruker Avance DPX 400 MHz spectrometer. High resolution mass spectrometry was performed with Waters SYNAPT G2S.

X-ray crystallography for compounds 1-3, 5 and 8

Single crystal X-ray diffraction data **1** and **2** were collected on a Bruker *AXS KAPPA APEX-II* CCD diffractometer (Monochromatic MoKα radiation) equipped with Oxford cryosystem 700 plus at 100 K. Data collection and unit cell refinement for the data sets were done using the Bruker APPEX-II suite, data reduction and integration were performed using SAINTV 7.685A (Bruker AXS, 2009) and absorption corrections and scaling were done using SADABSV2008/1 (Bruker AXS, 2009). Single crystal X-ray diffraction data of **3, 5** and **8** were collected using a Rigaku XtaLAB mini diffractometer equipped with Mercury375M CCD detector. The data were collected with graphite monochromatic MoKα radiation (λ = 0.71073 Å) at 100.0(2) K using scans. During the data collection the detector distance was 50 mm (constant) and the detector was placed at 2θ = 29.85° (fixed) for all the data sets. The data collection and data reduction were done using Crystal Clear suite.[35a] The crystal structures were solved by using either OLEX2[35b] or WINGX package using SHELXS-97 and the structure were refined using SHELXL-97 2008.[35c] All non hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed at geometrically calculated positions and were refined using riding. Half molecule of disordered toluene that was found in the asymmetric unit of **2** and **8** could not be treated using standard commands available in SHELXL. The squeeze method was used to remove the contribution of these disordered molecules from the original *hkl* file. The resulting squeezed *hkl* file was used for further refinement. Diamond version 2.1d was used to generate graphics for the X-ray structures.

Synthesis of [(2,6-*i*Pr$_2$C$_6$H$_3$N)P(Ph$_2$)(N*t*Bu)]GeCl (1)

A solution of [(2,6-*i*Pr$_2$C$_6$H$_3$N)P(Ph$_2$)(N*t*Bu)]H (**LH**) (0.86 g, 2.0 mmol) in Et$_2$O (20 mL) was cooled to −78 °C. To it was added *n*BuLi (1.25 mL, 2.0 mmol, 1.6 M in hexane) and was allowed to warm to room temperature and stirred for 3 h. The resultant solution was added to a solution of GeCl$_2$·dioxane (0.46 g, 2.0 mmol) in Et$_2$O at −78 °C. The mixture was slowly warmed to room temperature and stirred for further 12 h. The precipitate formed was filtered, and the solvent was partially reduced (ca. 15 mL). Keeping the solution at −30 °C for overnight afforded colourless crystals of **1**, which were suitable for X-ray diffraction analysis, 0.38 g (63 %); m. p. 137 °C; ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 0.22 (d, $^3J_{H\text{-}H}$ = 5.7 Hz, 3 H, CH*Me*$_2$), 0.63 (d, $^3J_{H\text{-}H}$ = 6.5 Hz, 3 H, CH*Me*$_2$), 1.05 (d, $^3J_{H\text{-}H}$ = 6.3 Hz, 3 H, CH*Me*$_2$), 1.24 (s, 9 H, *t*Bu), 1.46 (d, $^3J_{H\text{-}H}$ = 6.5 Hz, 3 H, CH*Me*$_2$), 2.99 (broad, 1 H, *CH*Me$_2$), 4.36 (broad, 1 H, *CH*Me$_2$), 6.89−6.94 (m, 3 H, Ar), 6.99−7.06 (m, 6 H, Ar), 7.44−7.49 (m, 2 H, Ar), 8.40−8.45 (m, 2 H, Ar); ^{13}C NMR (100 MHz, C$_6$D$_6$): δ = 22.7, 24.3, 25.7, 28.6 (d, $J_{C\text{-}P}$ = 8.7 Hz), 29.4, 32.0, 33.1 (d, $J_{C\text{-}P}$ = 6.4 Hz), 53.6, 124.3 (d, $J_{C\text{-}P}$ = 21.4 Hz), 125.9 (d, $J_{C\text{-}P}$ = 3.4 Hz), 128.6 (dd, $J_{C\text{-}P}$ = 12.0 & 6.0 Hz), 128.7, 129.7, 131.9 (d, $J_{C\text{-}P}$ = 9.8 Hz), 132.2 (d, $J_{C\text{-}P}$ = 2.6 Hz), 132.4, 133.0 (d, $J_{C\text{-}P}$ = 2.9 Hz), 133.3, 134.8 (d, $J_{C\text{-}P}$ = 12.0 Hz), 135.6 (d, $J_{C\text{-}P}$ = 2.6 Hz), 147.4, 148.9; ^{31}P{^{1}H}NMR (162 MHz, C$_6$D$_6$): δ = 47.2; Mass spectrum (+ve ion, EI), *m/z* = 539.1488 [M]$^+$, 505.1878 [M−Cl]$^+$; IR (nujol, cm^{-1}): 2923, 2854, 2722, 1586, 1459, 1378, 1366, 1323, 1222, 1202, 1139, 1106, 987, 840, 790, 721, 696.

Synthesis of [(2,6-*i*Pr$_2$C$_6$H$_3$N)P(Ph$_2$)(N*t*Bu)]Ge(Cl)Fe(CO)$_4$ (2)

THF (50 mL) was added to a mixture of **1** (0.59 g, 1.0 mmol) and diironnonacarbonyl (0.38 g, 1.1 mmol) at room temperature under N$_2$. After stirring for overnight, the initial light orange solution became darker to ultimately give a garnet brown solution. The solvent was then removed under vacuum, and the residue was washed with *n*hexane (50 mL) that afforded brown solid. This solid gave X-ray quality crystals from toluene at −30 °C, 0.64 g (90 %); m. p. 219 °C; ^{1}H NMR (400 MHz, C$_6$D$_6$ & THF-d_8; 1:0.3): δ = 0.05 (d, $^3J_{H\text{-}H}$ = 6.5 Hz, 3 H, CH*Me*$_2$), 0.49 (d, $^3J_{H\text{-}H}$ = 6.6 Hz, 3 H, CH*Me*$_2$), 1.12 (d, $^3J_{H\text{-}H}$ = 6.7 Hz, 3 H, CH*Me*$_2$), 1.25 (d, $^3J_{H\text{-}H}$ = 6.7 Hz, 3 H, CH*Me*$_2$), 1.29 (s, 9 H, *t*Bu), 3.16 (broad, 1 H, *CH*Me$_2$), 4.16 (broad, 1 H, *CH*Me$_2$), 6.84−6.89 (m, 1 H, Ar), 6.92−6.99 (m, 2

H, Ar), 7.03−7.07 (m, 5 H, Ar), 7.55−7.59 (m, 2 H, Ar), 7.97 (broad, 1 H, Ar), 8.12−8.16 (m, 2 H, Ar); ^{13}C NMR (100 MHz, C_6D_6 & THF-d_8; 1:0.3): δ = 22.6, 23.4 (d, $J_{C\text{-}P}$ = 16.5 Hz), 27.1, 28.7 (d, $J_{C\text{-}P}$ = 12.0 Hz), 28.9, 29.5, 32.3 (d, $J_{C\text{-}P}$ = 5.5 Hz), 56.2, 123.7, 124.9 (dd, $J_{C\text{-}P}$ = 12.0 & 1.7 Hz), 125.4 (d, $J_{C\text{-}P}$ = 20.9 Hz), 126.3, 128.7, 129.2 (dd, $J_{C\text{-}P}$ = 13.0 & 6.6 Hz), 129.6, 131.3 (d, $J_{C\text{-}P}$ = 1.6 Hz), 133.5 (d, $J_{C\text{-}P}$ = 10.7 Hz), 133.9, 135.1 (d, $J_{C\text{-}P}$ = 12.0 Hz), 143.0 (d, $J_{C\text{-}P}$ = 2.8 Hz), 149.4 (d, $J_{C\text{-}P}$ = 4.4 Hz), 149.9 (d, $J_{C\text{-}P}$ = 4.2 Hz), 214.7 (s, CO); ^{31}P{^{1}H} NMR (162 MHz, C_6D_6 & THF-d_8; 1:0.3): δ = 52.2; Mass spectrum (+ve ion, EI), *m/z* = 709.0754 $[M+H]^+$, 539.1456 $[M-Fe(CO)_4]^+$, 505.1847 $[M-Fe(CO)_4\text{-}Cl]^+$; IR (nujol, cm^{-1}): 2953, 2923, 2853, 2172, 2040 (st, CO), 1968 (m, CO), 1926 (st, CO), 1462, 1376, 1260, 1191, 1129, 1093, 1020, 974, 853, 801, 747, 722, 699.

Synthesis of [(2,6-*i*Pr$_2$C$_6$H$_3$N)P(Ph$_2$)(N*t*Bu)]GeO*t*Bu (3)

A solution of **1** (1.07 g, 2.0 mmol) in THF (10 mL) was added to a solution of KO*t*Bu (0.24 g, 2.1 mmol) in THF (10 mL) at room temperature and stirred for 8 h. The solvent was removed under vacuum and the residue obtained was extracted with Et_2O (10 mL) to afford an off-white solid. X-ray quality crystals of **3** were grown from its toluene solution at 4 ºC; 0.75 g (64 %); m. p. 138 °C; ^{1}H NMR (400 MHz, C_6D_6): δ = 0.11 (d, $^3J_{H\text{-}H}$ = 6.4 Hz, 3 H, CH*Me$_2$*), 0.41 (d, $^3J_{H\text{-}H}$ = 6.4 Hz, 3 H, CH*Me$_2$*), 1.31 (d, $^3J_{H\text{-}H}$ = 6.8 Hz, 3 H, CH*Me$_2$*), 1.36 (s, 9 H, *t*Bu), 1.64 (d, $^3J_{H\text{-}H}$ = 6.8 Hz, 3 H, CH*Me$_2$*), 1.83 (s, 9 H, O*t*Bu), 3.64 (sept, $^3J_{H\text{-}H}$ = 6.8 Hz, 1 H, *CH*Me$_2$), 4.07 (sept, $^3J_{H\text{-}H}$ = 6.8 Hz, 1 H, *CH*Me$_2$), 6.85−6.92 (m, 1 H, Ar), 6.93-7.08 (m, 8 H, Ar), 7.52−7.58 (m, 2 H, Ar), 8.22−8.29 (m, 2 H, Ar); ^{13}C NMR (100 MHz, C_6D_6): δ = 23.4, 25.3, 26.4, 28.5, 29.5, 30.3, 32.8, 33.3 (d, $J_{C\text{-}P}$ = 5.6 Hz), 55.3, 75.9, 123.7, 124.4 (d, $J_{C\text{-}P}$ = 2.4 Hz), 125.5, 125.7 (d, $J_{C\text{-}P}$ = 2.4 Hz), 126.5, 127.3 (d, $J_{C\text{-}P}$ = 2.7 Hz), 129.15 (d, $J_{C\text{-}P}$ = 12.9 Hz), 129.7, 132.4, 132.5 (multiplet), 133.4 (broad), 135.3 (d, $J_{C\text{-}P}$ = 11.6 Hz), 149.2 (d, $J_{C\text{-}P}$ = 4.4 Hz), 151.0 (d, $J_{C\text{-}P}$ = 4.6 Hz); ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ = 39.0; Mass spectrum (+ve ion, EI), *m/z* = 503.1851 $[M-OtBu]^+$; IR (nujol, cm^{-1}): 2923, 2853, 1587, 1462, 1378, 1326, 1261, 1180, 1157, 1075, 1048, 1015, 932, 1260, 1177, 1113, 1048, 1017, 933, 890, 794, 769, 692.

Synthesis of [(2,6-*i*Pr$_2$C$_6$H$_3$N)P(Ph$_2$)(N*t*Bu)]GeOTf (4)

A solution of **1** (0.54 g, 1.0 mmol) in toluene (20 mL) was added to a stirred suspension of $AgSO_3CF_3$ (0.26 g, 1.0 mmol) in toluene (10 mL) at room temperature and was stirred for 12 h. The precipitate formed was filtered off, and the solvent was partially removed (*ca.* 15 mL) under vacuum. Storage of the remaining solution at −10 °C gave colourless solid **4**, 0.48 g (74 %); m. p. 162 °C (decomp); ^{1}H NMR (400 MHz, C_6D_6): δ = 0.37 (broad, 6 H, CH*Me$_2$*), 1.23 (s, 9 H, *t*Bu), 1.35 (broad, 6 H, CH*Me$_2$*), 3.40 (broad sept, 2 H, *CH*Me$_2$), 6.86−6.98 (m, 9 H, Ar), 7.72−7.77 (m, 4 H, Ar); ^{13}C NMR (100 MHz, C_6D_6): δ = 23.3, 27.5, 29.1, 32.6 (d, $J_{C\text{-}P}$ = 5.4 Hz), 55.0, 124.5, 127.2, 129.0 (d, $J_{C\text{-}P}$ = 12.6 Hz), 129.3, 133.5 (d, $J_{C\text{-}P}$ = 3.8 Hz), 133.9, 148.1;* ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ = 62.1. ^{19}F NMR (376 MHz, C_6D_6): δ = −77.4. Mass spectrum (+ve ion, EI), *m/z* = 653.1266 $[M]^+$; IR (nujol, cm^{-1}): 2923, 2853, 1725, 1589, 1462, 1377, 1338, 1288, 1258, 1187, 1112, 1054, 1030, 976, 846, 794, 745, 722, 695, 634, 593, 519.

* One signal in ^{13}C NMR of **4** could not be detected and is believed to be masked by the residual solvent signal in the aromatic region.

Synthesis of [(2,6-*i*Pr$_2$C$_6$H$_3$N)P(Ph$_2$)(N*t*Bu)]Ge(S)Cl (5)

A solution of **1** (0.54 g, 1.0 mmol) in toluene (20 mL) was added to a stirred suspension of sulfur (0.03 g, 1.1 mmol) in toluene (20 mL). The reaction mixture was stirred at room temperature for 12 h to afford a colourless solution. Storage of the reaction mixture at -30 °C for 2 days afforded colorless crystals of the title compound **5**, 0.37 g (65 %); m. p. 162 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (d, $^3J_{H\text{-}H}$ = 6.8 Hz, 12 H, CH*Me$_2$*), 1.25 (s, 9 H, *t*Bu), 3.09 (sept, $^3J_{H\text{-}H}$ = 6.8 Hz, 2 H, CH*Me$_2$*), 6.82−6.87 (m, 2 H, Ar), 7.00−7.07 (m, 1 H, Ar), 7.48−7.55 (m, 4 H, Ar), 7.63−7.69 (m, 2 H, Ar), 7.76−7.85 (m, 4 H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.0, 28.6, 32.1 (broad), 52.4, 118.4, 122.8, 128.2 (d, $J_{C\text{-}P}$ = 12.6 Hz), 130.6, 131.9 (d, $J_{C\text{-}P}$ = 9.3 Hz), 136.1 (d, $J_{C\text{-}P}$ = 131.6 Hz), 141.97 (d, $J_{C\text{-}P}$ = 7.0 Hz), 144.5; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 37.5; Mass spectrum (+ve ion, EI), *m/z* = 569.1334 $[M+H]^+$, 537.1467 $[M-S]^+$; IR (nujol, cm^{-1}): 2922, 2853, 2723, 2368, 1583, 1458, 1375, 1312, 1260, 1169, 1105, 1053, 1023, 968, 723.

Synthesis of [(2,6-*i*Pr$_2$C$_6$H$_3$N)P(Ph$_2$)(N*t*Bu)]Ge(Se)Cl (6)

Synthesis of compound **6** was similar to that of **5**. Quantity of reagents used were **1** (0.54 g, 1.0 mmol) and selenium (0.08 g, 1.1 mmol), 0.40 g (65 %); m. p. 168 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.92 (d, $^3J_{H\text{-}H}$ = 6.7 Hz, 12 H, CH*Me$_2$*), 1.26 (s, 9 H, *t*Bu), 3.05 (sept, $^3J_{H\text{-}H}$ = 6.7 Hz, 2 H, C*H*Me$_2$), 6.88 (d, $^3J_{H\text{-}H}$ = 7.7 Hz, 2 H, Ar), 7.51−7.54 (m, 5 H, Ar), 7.65−7.75 (m, 6 H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.4, 28.9, 31.4 (d, $J_{C\text{-}P}$ = 4.1 Hz), 54.5, 123.4, 123.5 (d, $J_{C\text{-}P}$ = 1.5 Hz), 124.6, 128.9 (d, $J_{C\text{-}P}$ = 4.1 Hz), 129.1 (dd, $J_{C\text{-}P}$ = 154.0 & 2.3 Hz), 133.4 (d, $J_{C\text{-}P}$ = 11.0 Hz), 134.3 (d, $J_{C\text{-}P}$ = 2.8 Hz), 148.3 (d, $J_{C\text{-}P}$ = 3.4 Hz); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 36.2; Mass spectrum (+ve ion, EI), *m/z* = 619.2278 $[M+H]^+$, 583.2417 $[M-Cl]^+$, 539.2768 $[M-Se]^+$, 505.3071 $[M-SeCl]^+$; IR (nujol, cm^{-1}): 2949, 2874, 1588, 1461, 1377, 1282, 1255, 1227, 1154, 1053, 1032, 975, 845, 794, 722, 693, 637, 513.

Synthesis of [(2,6-*i*Pr$_2$C$_6$H$_3$N)P(Ph$_2$)(N*t*Bu)]Ge(S)O*t*Bu (7)

Synthesis of compound **7** was similar to that of **5**. Quantity of reagents used were **3** (0.58 g, 1.0 mmol) and sulfur (0.032 g, 1.1 mmol), 0.46 g (73 %); m. p. 151 °C (decomp). ^{1}H NMR (400 MHz, $CDCl_3$): δ = −0.12 (d, $^3J_{H\text{-}H}$ = 6.8 Hz, 3 H, CH*Me$_2$*), 0.22 (d, $^3J_{H\text{-}H}$ = 6.8 Hz, 3 H, CH*Me$_2$*), 1.17 (overlapped doublets, $^3J_{H\text{-}H}$ = 6.4 & 5.1 Hz), 1.35 (s, 9 H, *t*Bu), 1.60 (s, 9 H, O*t*Bu), 3.12 (sept, $^3J_{H\text{-}H}$ = 6.8 Hz, 1 H, *CH*Me$_2$), 3.84 (sept, $^3J_{H\text{-}H}$ = 6.8 Hz, 1 H, *CH*Me$_2$), 6.84−7.07 (m, 3 H, Ar), 7.43−7.55 (m, 4 H, Ar), 7.55−7.64 (m, 4 H, Ar), 8.29−8.37 (m, 2 H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.3, 24.6, 25.6, 27.8, 28.6, 29.3, 32.2, 32.8 (d, $J_{C\text{-}P}$ = 5.6 Hz), 55.0, 75.3, 123.6 (d, $J_{C\text{-}P}$ = 2.5 Hz), 124.4 (d, $J_{C\text{-}P}$ = 2.6 Hz), 124.6 (d, $J_{C\text{-}P}$ = 102 Hz), 126.3 (d, $J_{C\text{-}P}$ = 2.8 Hz), 128.4, (d, $J_{C\text{-}P}$ = 13.0 Hz), 128.7 (d, $J_{C\text{-}}$

$_P$ = 12.9 Hz), 131.0 (d, J_{C-P} = 99.2 Hz), 131.3 (d, J_{C-P} = 1.5 Hz), 132.6 (d, J_{C-P} = 10.4 Hz), 133.2 (vtr, J_{C-P} = 6.9 & 3.4 Hz), 134.8 (d, J_{C-P} = 11.6 Hz), 148.4 (d, J_{C-P} = 4.2 Hz), 150.1 (d, J_{C-P} = 4.5 Hz); $^{31}P\{^1H\}$NMR (162 MHz, $CDCl_3$): δ = 42.3; Mass spectrum (+ve ion, EI), *m/z* = 610.2121 $[M+H]^+$, 577.2296 $[M-S]^+$; IR (Nujol, cm^{-1}): 2954, 2924, 2854, 2722, 1589, 1462, 1378, 1364, 1312, 1248, 1198, 1119, 986, 931, 906, 800, 754, 710, 666, 644, 609, 585, 521.

Synthesis of [(2,6-*i*Pr$_2$C$_6$H$_3$N)P(Ph$_2$)(N*t*Bu)]Ge(Se)O*t*Bu (8)

Synthesis of compound **8** was similar to that of **5**. Quantity of reagents used were **3** (0.58 g, 1.0 mmol) and selenium (0.08 g, 1.1 mmol), X-ray quality crystals of **8** were grown from its toluene solution at 4 ºC; 0.45 g (69 %); m. p. 167 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = −0.13 (d, $^3J_{H-H}$ = 6.8 Hz, 3 H, CH*Me*$_2$), 0.23 (d, $^3J_{H-H}$ = 6.8 Hz, 3 H, CH*Me*$_2$), 1.18 (overlapped doublets, 6 H, CH*Me*$_2$), 1.36 (s, 9 H, *t*Bu), 1.63 (s, 9 H, O*t*Bu), 3.13 (sept, $^3J_{H-H}$ = 6.8 Hz, 1 H, *CH*Me$_2$), 3.85 (sept, $^3J_{H-H}$ = 6.8 Hz, 1 H, *CH*Me$_2$), 6.85−7.05 (m, 3 H, Ar), 7.45−7.50 (m, 4 H, Ar), 7.57−7.62 (m, 4 H, Ar), 8.32−8.36 (m, 2 H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.3, 24.6, 25.7, 27.8, 28.5, 30.2, 32.4, 32.9 (d, J_{C-P} = 5.4 Hz), 55.2, 75.7, 123.6 (d, J_{C-P} = 2.3 Hz), 124.7 (d, J_{C-P} = 2.4 Hz), 124.8 (d, J_{C-P} = 101 Hz), 126.3 (d, J_{C-P} = 2.9 Hz), 128.4, (d, J_{C-P} = 13.1 Hz), 128.8 (d, J_{C-P} = 13.1 Hz), 131.4 (d, J_{C-P} = 98.6 Hz), 131.4 (d, J_{C-P} = 1.8 Hz), 132.6 (d, J_{C-P} = 10.4 Hz), 133.2 (vtr, J_{C-P} = 6.3 & 3.2 Hz), 134.8 (d, J_{C-P} = 11.7 Hz), 148.5 (d, J_{C-P} = 4.4 Hz), 150.0 (d, J_{C-P} = 4.4 Hz); $^{31}P\{^1H\}$NMR (162 MHz, $CDCl_3$): δ = 43.6; Mass spectrum (+ve ion, EI), *m/z* = 656.1664 $[M]^+$, 577.2399 $[M-Se]^+$; IR (nujol, cm^{-1}): 2958, 2924, 2854, 2724, 1587, 1461, 1377, 1324, 1244, 1197, 1133, 1098, 1037, 995, 962, 901, 821, 799, 754, 702, 626, 607, 583, 545, 520, 502.

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