

Supplementary data

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

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Contents

- (1) **Fig. S1-S3** Heteronuclear NMR Spectra of compound **1**
- (2) **Fig. S4-S6** Heteronuclear NMR Spectra of compound **2**
- (3) **Fig. S7-S9** Heteronuclear NMR Spectra of compound **3**
- (4) **Fig. S10-S12** Heteronuclear NMR Spectra of compound **4**
- (5) **Fig. S13-S15** Heteronuclear NMR Spectra of compound **5**
- (6) **Fig. S16-S18** Heteronuclear NMR Spectra of compound **6**
- (7) **Fig. S19-S21** Heteronuclear NMR Spectra of compound **7**
- (8) **Fig. S22-S24** ^1H - ^{13}C HSQC NMR spectrum of compound **7**
- (9) **Fig. S25-S27** ^1H - ^{13}C HMBC NMR spectrum of compound **7**
- (10) **Fig. S28-S30** Heteronuclear NMR Spectra of compound **8**

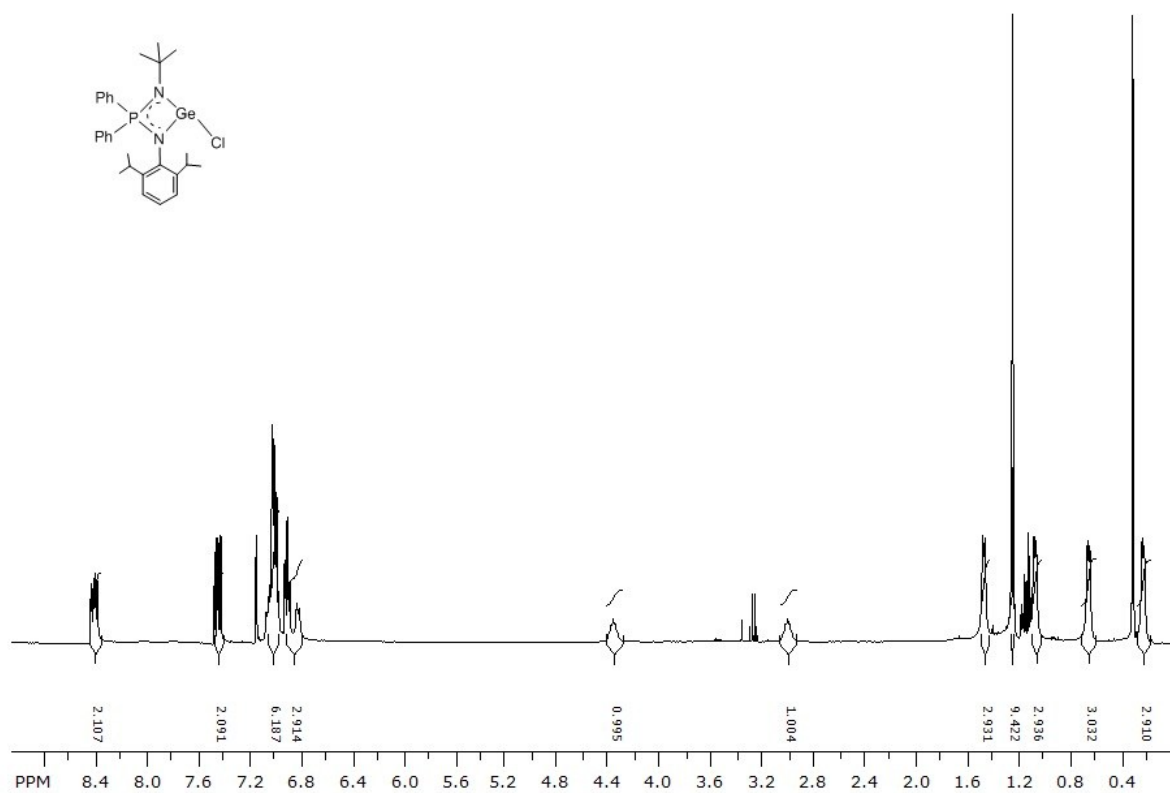


Fig. S1 ^1H NMR (400MHz, C_6D_6) spectrum of $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N})\text{P}(\text{Ph})_2(\text{N}t\text{Bu})]\text{GeCl}$ (1).

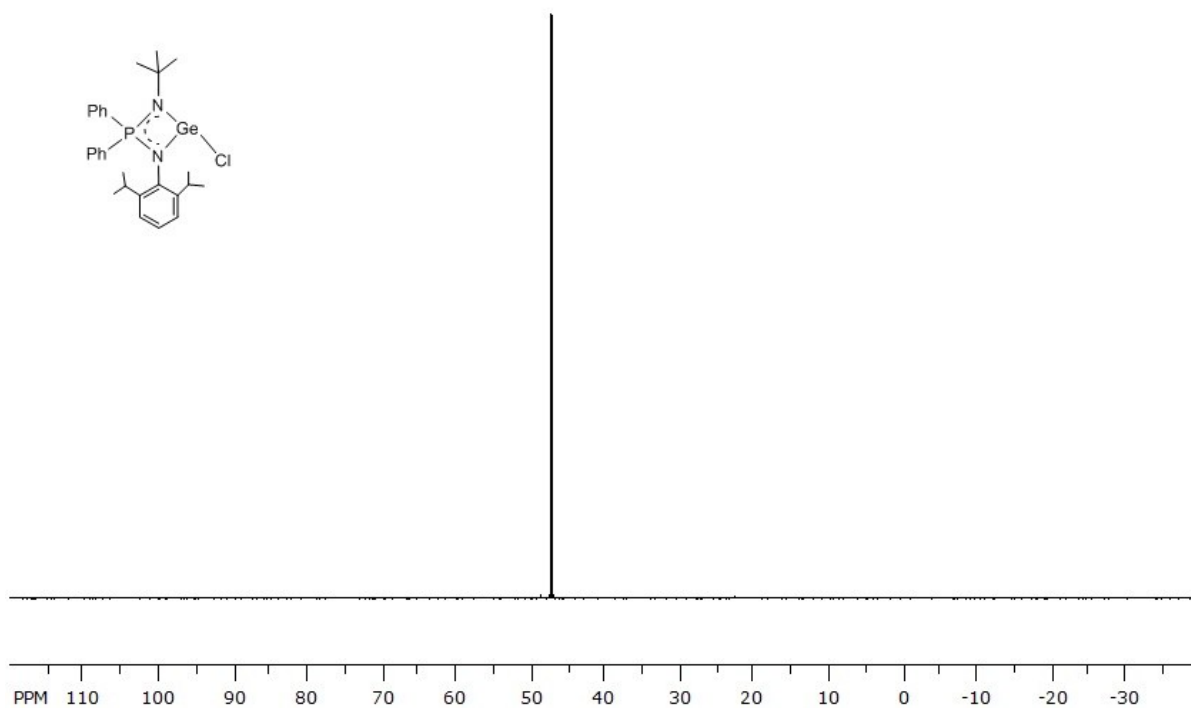


Fig. S2 $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6) spectrum of $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N})\text{P}(\text{Ph})_2(\text{N}t\text{Bu})]\text{GeCl}$ (1).

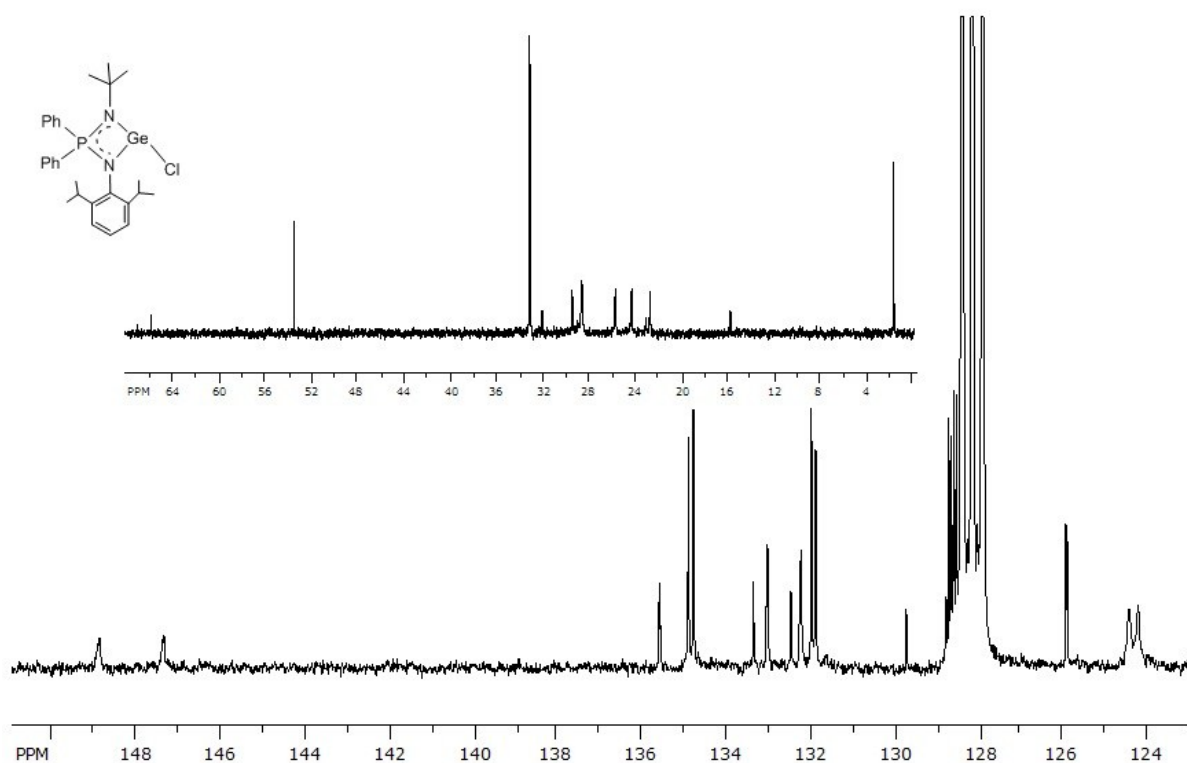


Fig. S3 ¹³C NMR (100 MHz, C₆D₆) spectrum of $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N})\text{P}(\text{Ph}_2)(\text{NtBu})]\text{GeCl}$ (**1**). Inset shows expansion of the aliphatic region.

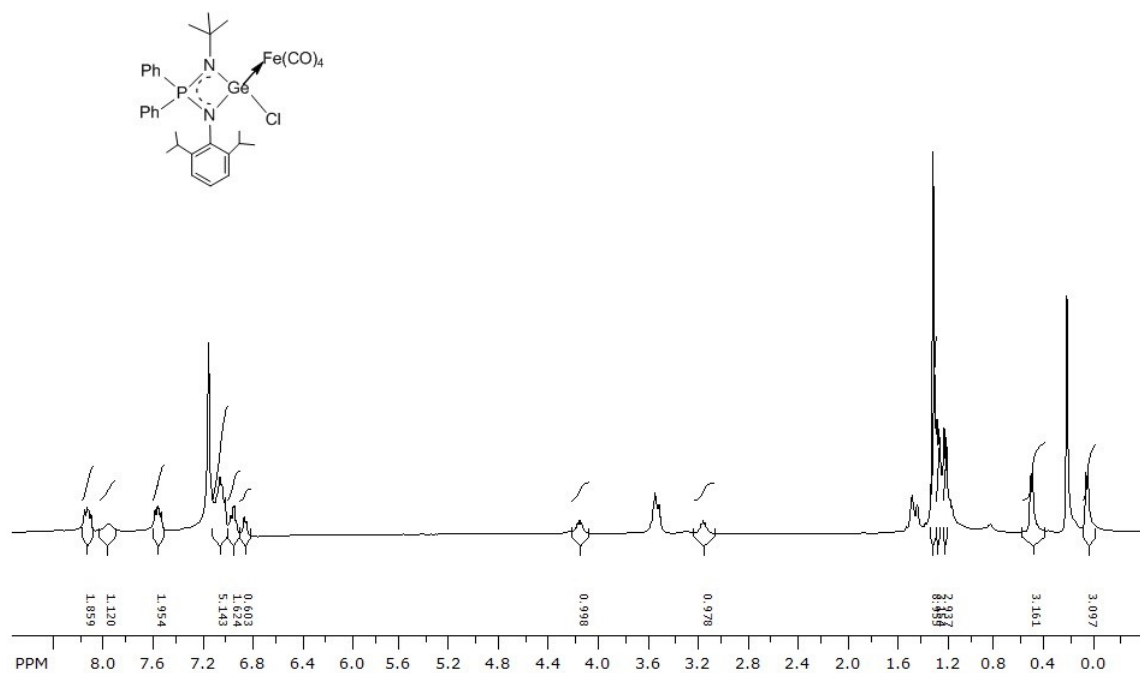


Fig. S4 ¹H NMR (400 MHz, C₆D₆ + THF-*d*₈ (1:0.3)) spectrum of $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N})\text{P}(\text{Ph}_2)(\text{NtBu})]\text{Ge}(\text{Cl})\text{Fe}(\text{CO})_4$ (**2**).

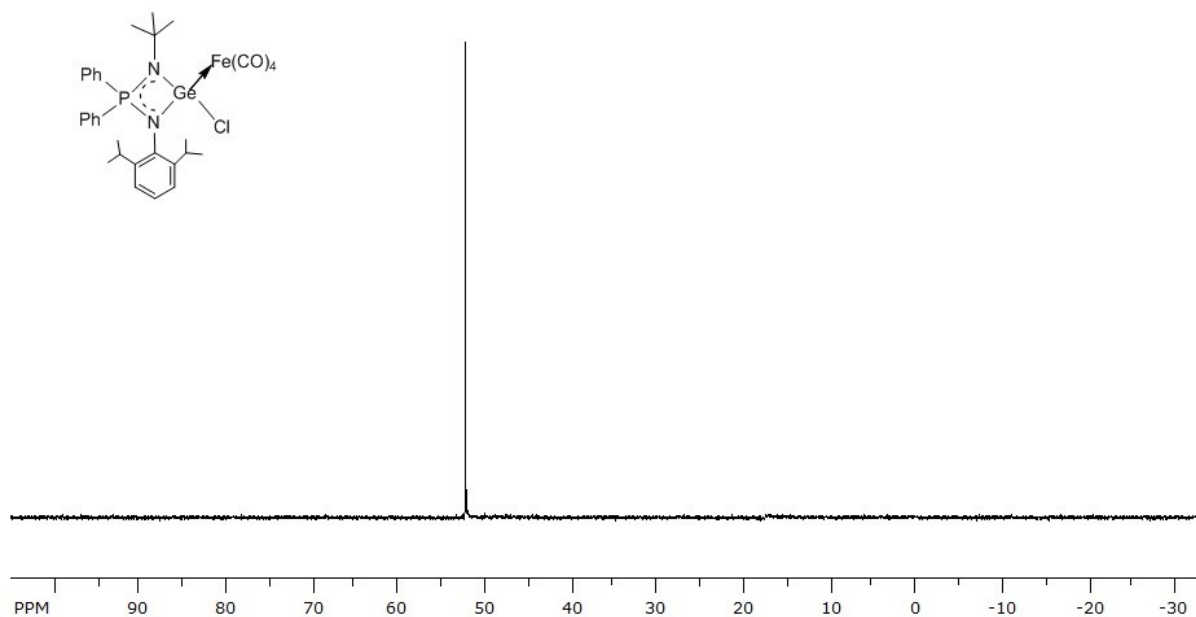


Fig. S5 $^{31}\text{P}\{^1\text{H}\}$ NMR (162MHz, $\text{C}_6\text{D}_6 + \text{THF-}d_8$ (1:0.3)) spectrum of $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N})\text{P}(\text{Ph}_2)(\text{N}t\text{Bu})]\text{Ge}(\text{Cl})\text{Fe}(\text{CO})_4$ (**2**).

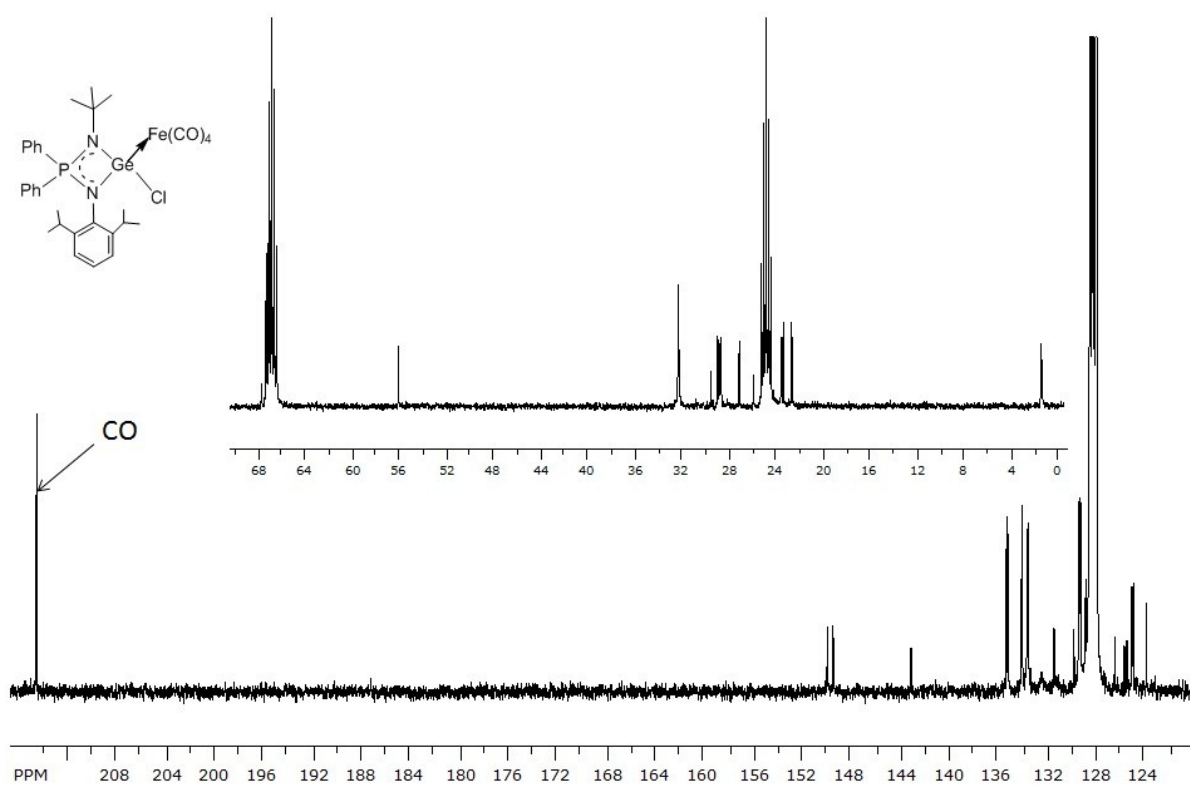


Fig. S6 ^{13}C NMR (100 MHz, $\text{C}_6\text{D}_6 + \text{THF-}d_8$ (1:0.3)) spectrum of $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N})\text{P}(\text{Ph}_2)(\text{N}t\text{Bu})]\text{Ge}(\text{Cl})\text{Fe}(\text{CO})_4$ (**2**). Inset shows expansion of the aliphatic region.

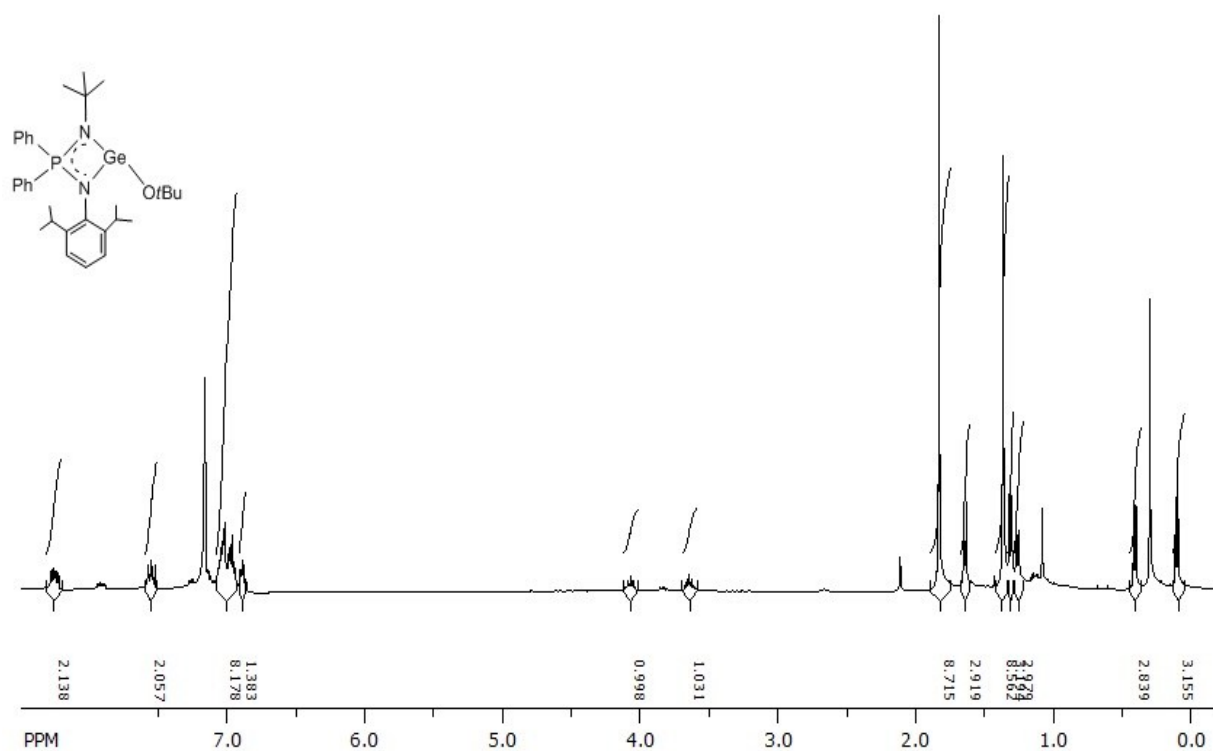


Fig. S7 ^1H NMR (400 MHz, C_6D_6) spectrum of $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N})\text{P}(\text{Ph})_2(\text{N}t\text{Bu})]\text{GeO}t\text{Bu}$ (**3**).

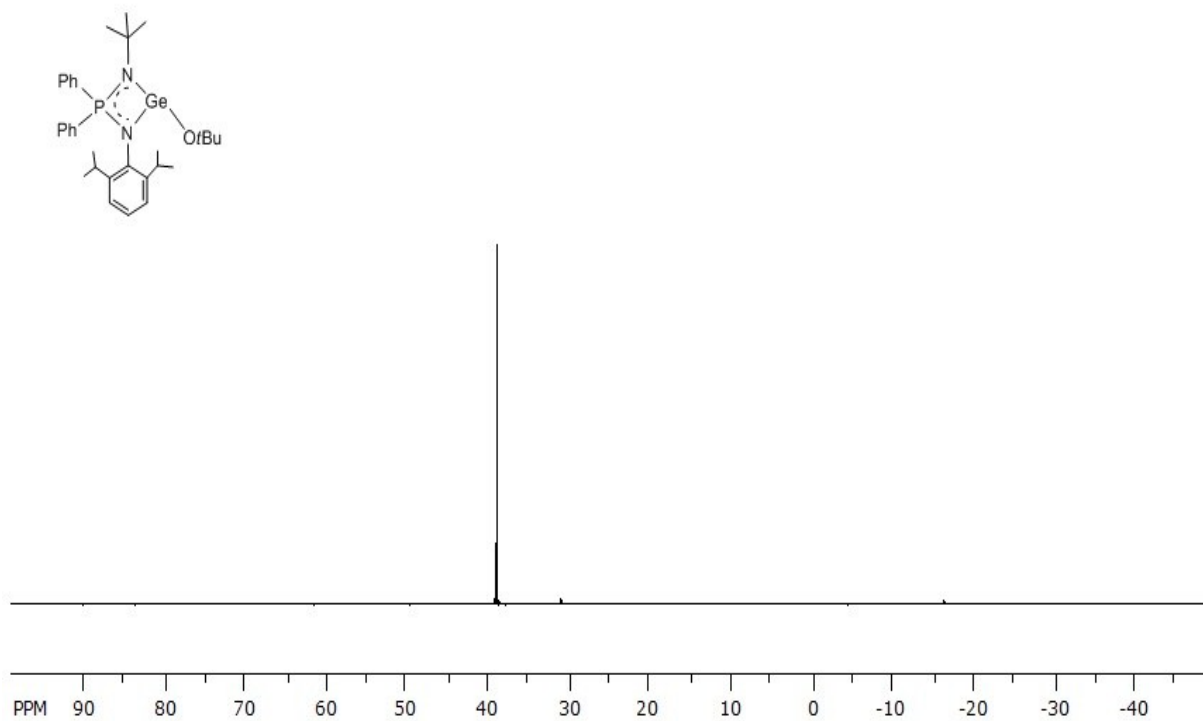


Fig. S8 $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6) spectrum of $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N})\text{P}(\text{Ph})_2(\text{N}t\text{Bu})]\text{GeO}t\text{Bu}$ (**3**).

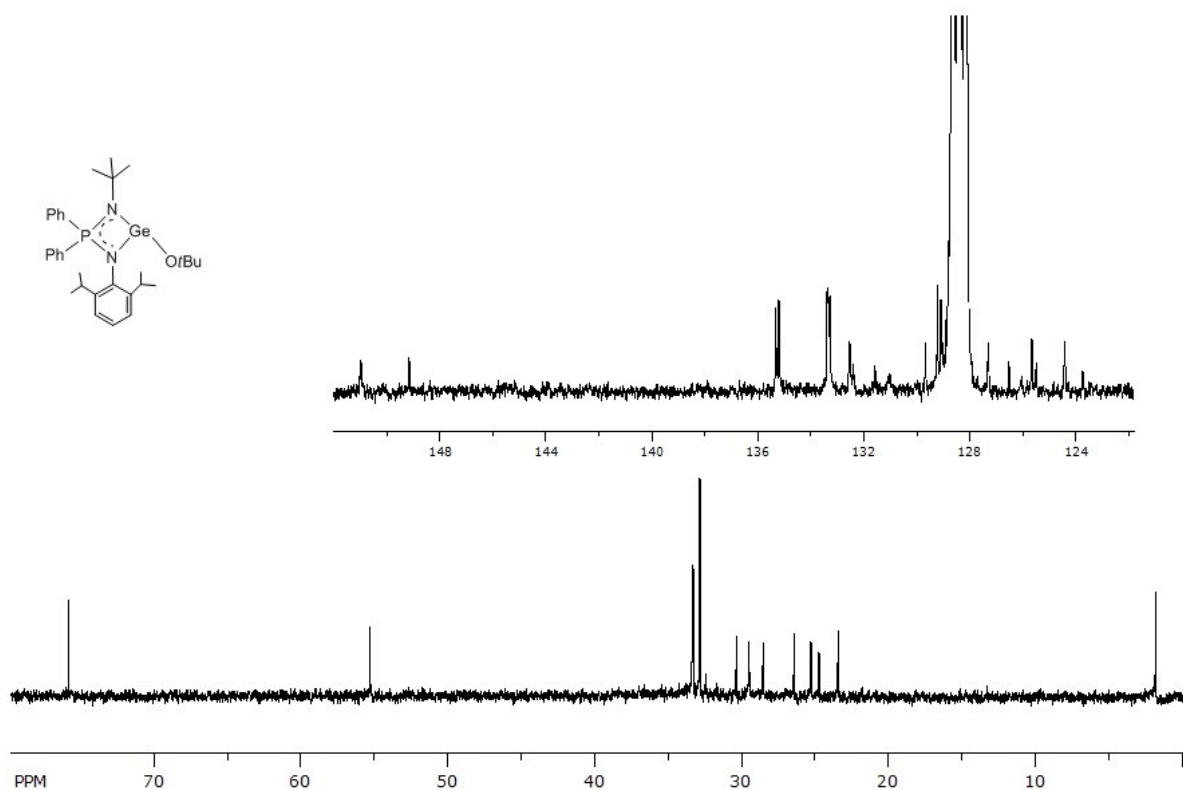


Fig. S9 ^{13}C NMR (100MHz, C_6D_6) spectrum of $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N})\text{P}(\text{Ph})_2(\text{N}t\text{Bu})]\text{GeO}t\text{Bu}$ (**3**). Inset shows expansion of the aromatic region.

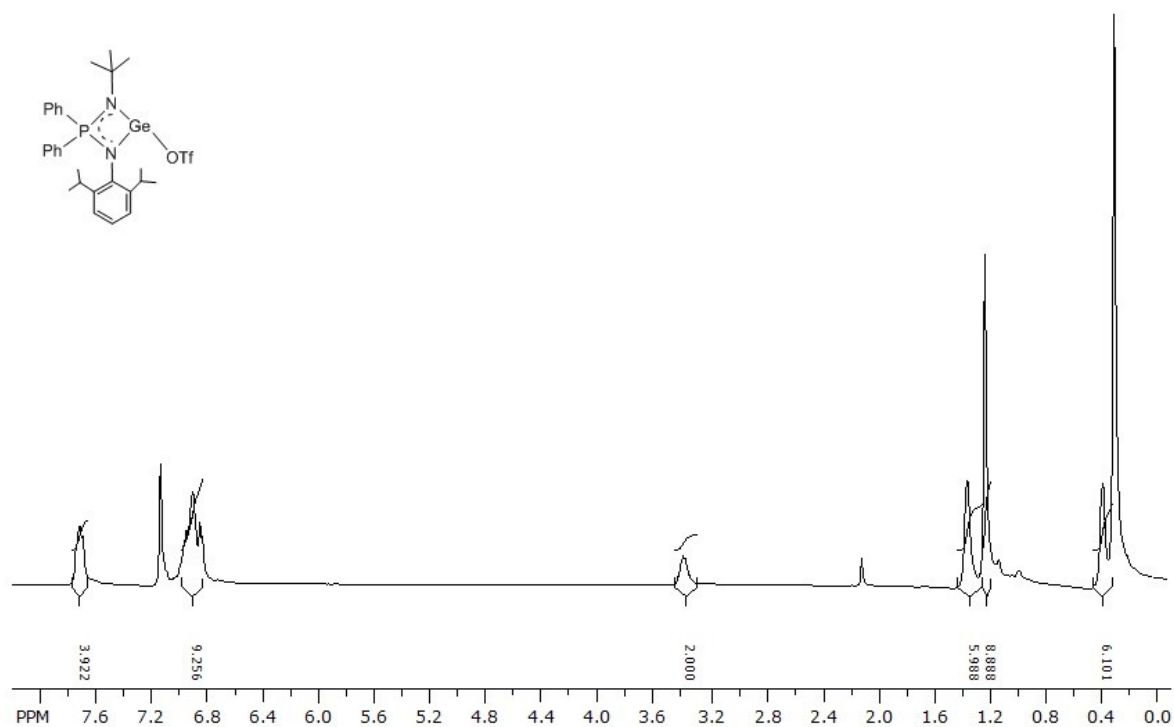


Fig. S10 ^1H NMR (400 MHz, C_6D_6) spectrum of $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N})\text{P}(\text{Ph})_2(\text{N}t\text{Bu})]\text{GeOTf}$ (**4**).

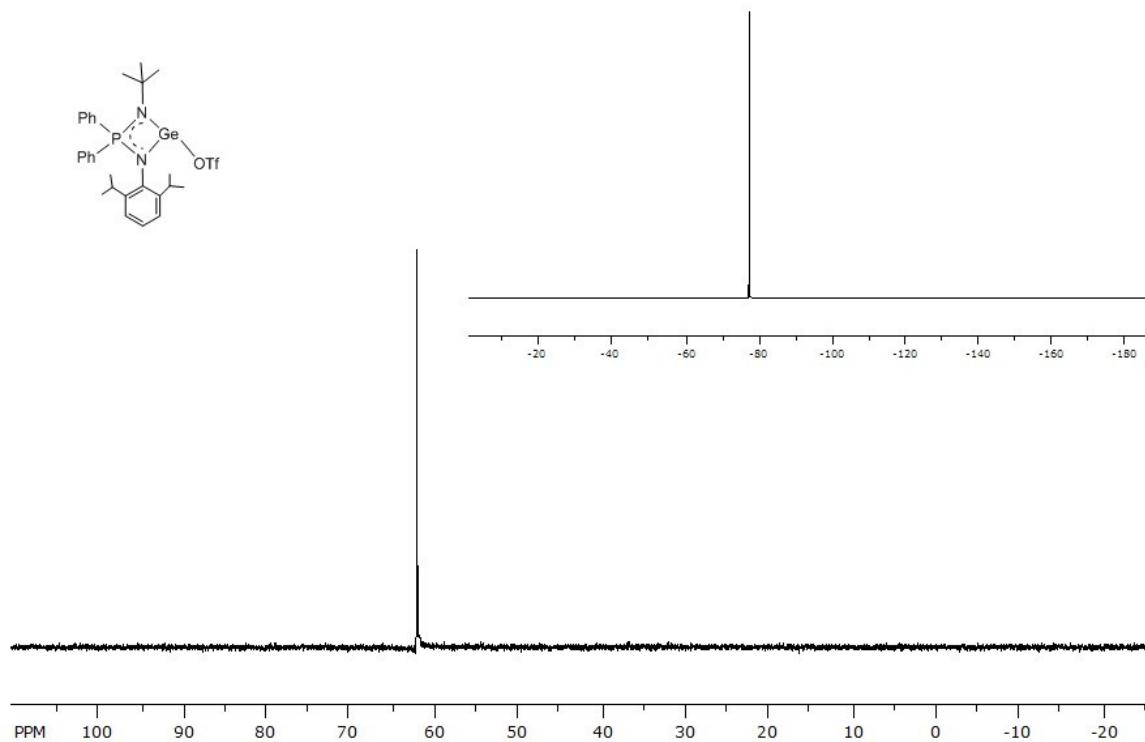


Fig. S11 $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6) spectrum of $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N})\text{P}(\text{Ph})_2(\text{N}t\text{Bu})]\text{GeOTf}$ (**4**). Inset shows its ^{19}F NMR (376 MHz, C_6D_6) spectrum.

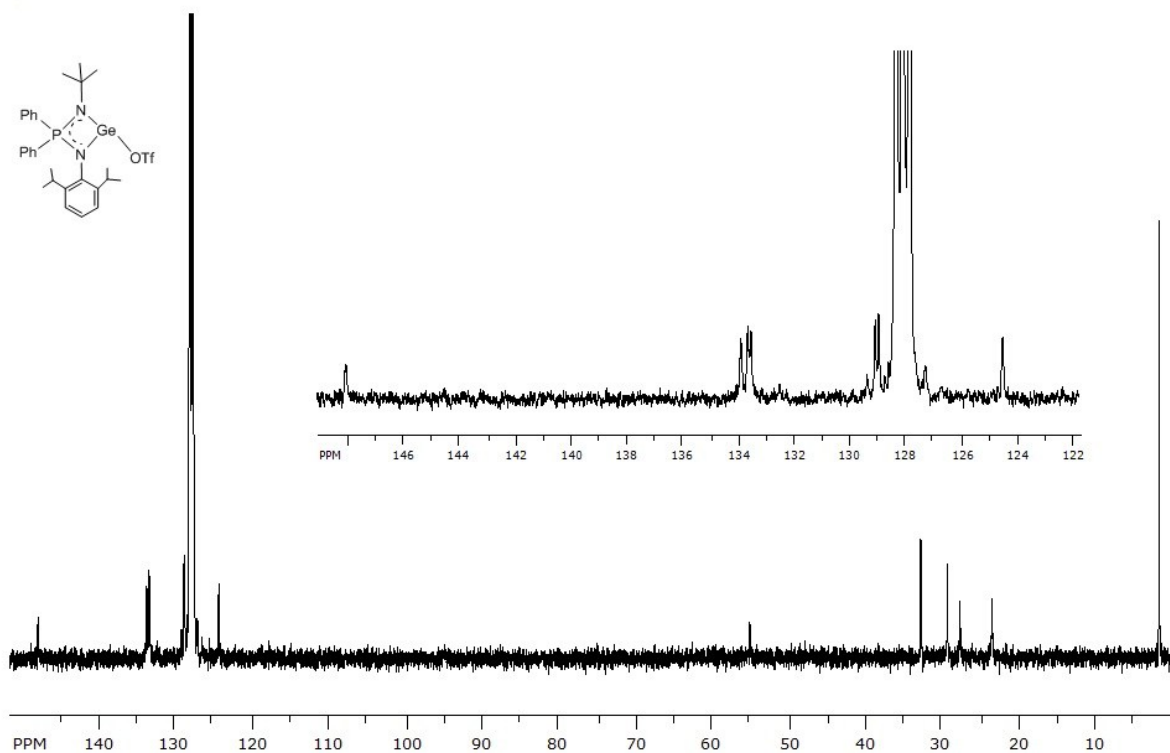


Fig. S12 ^{13}C NMR (100 MHz, C_6D_6) spectrum of $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N})\text{P}(\text{Ph})_2(\text{N}t\text{Bu})]\text{GeOTf}$ (**4**). Inset shows expansion of the aromatic region.

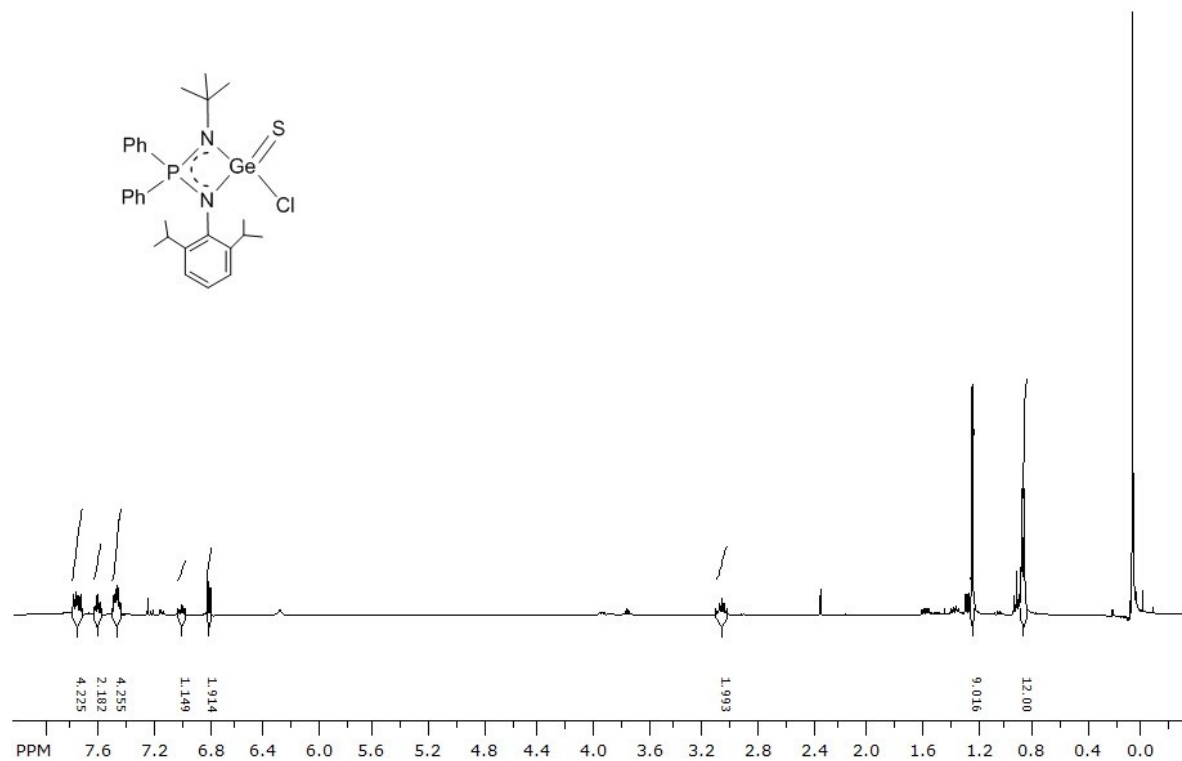


Fig. S13 ^1H NMR (400 MHz, CDCl_3) spectrum of $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N})\text{P}(\text{Ph})_2(\text{N}t\text{Bu})]\text{Ge}(\text{S})\text{Cl}$ (**5**).

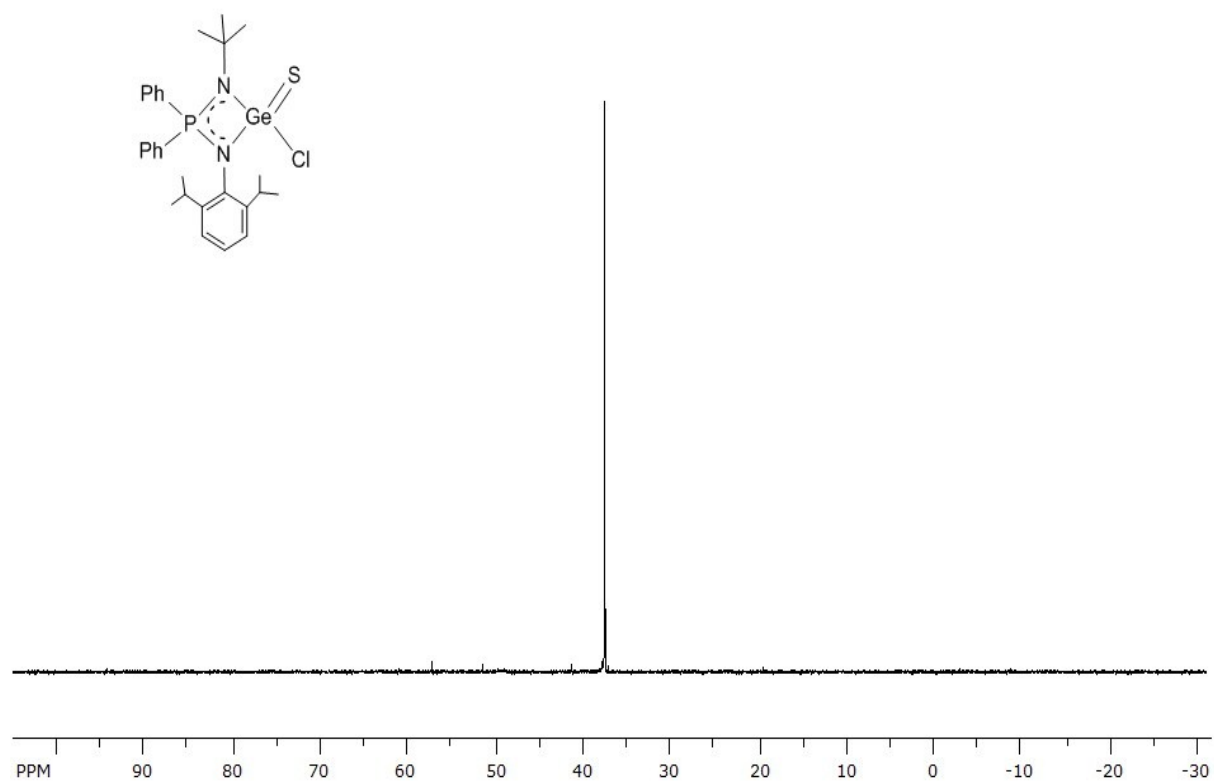


Fig. S14 $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) spectrum of $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N})\text{P}(\text{Ph})_2(\text{N}t\text{Bu})]\text{Ge}(\text{S})\text{Cl}$ (**5**).

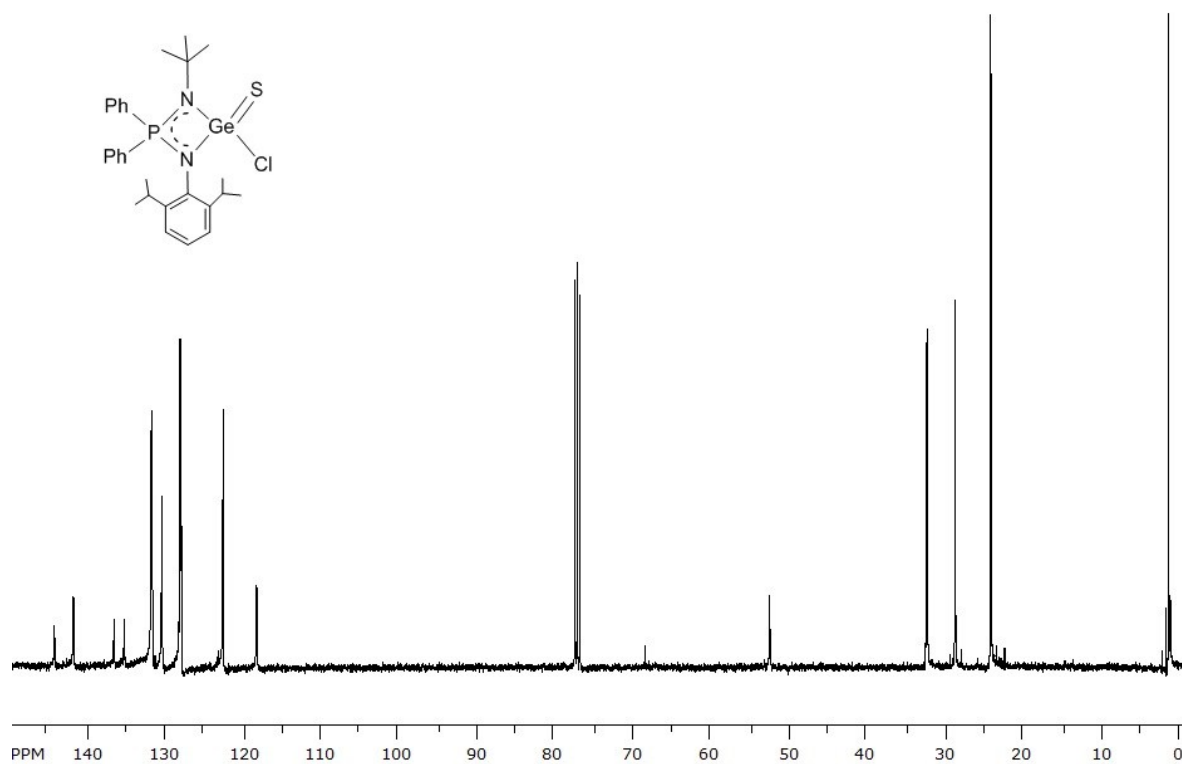


Fig. S15 ^{13}C NMR (100 MHz, CDCl_3) spectrum of $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N})\text{P}(\text{Ph}_2)(\text{N}t\text{Bu})]\text{Ge}(\text{S})\text{Cl}$ (**5**).

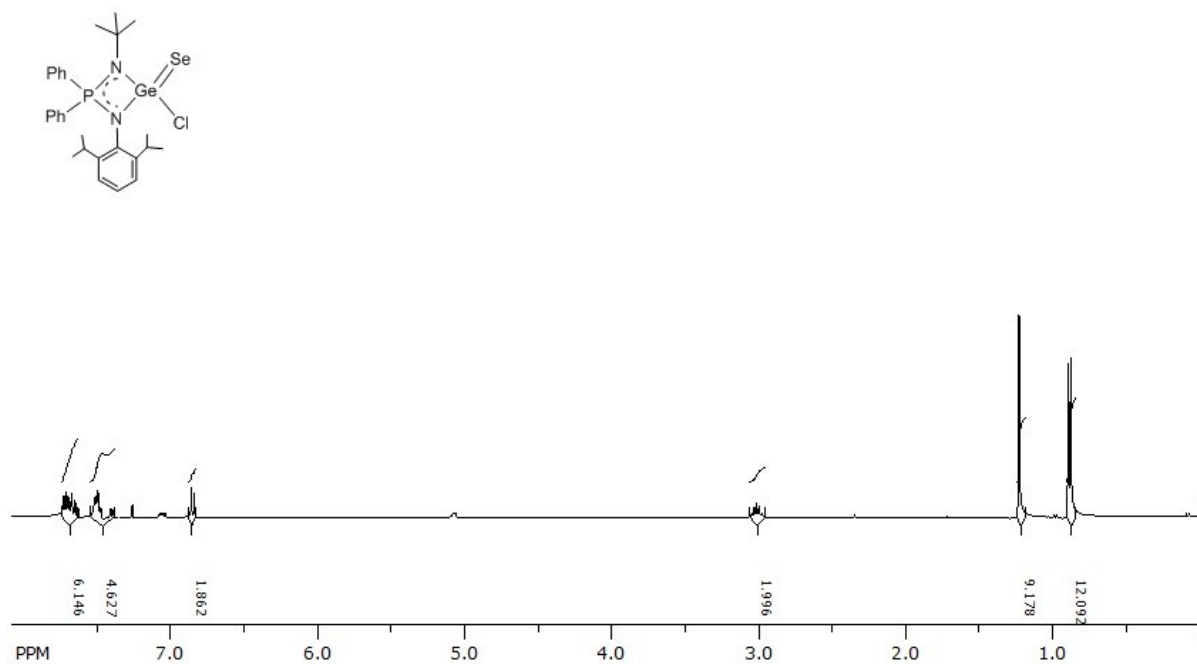


Fig. S16 ^1H NMR (400 MHz, CDCl_3) spectrum of $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N})\text{P}(\text{Ph}_2)(\text{N}t\text{Bu})]\text{Ge}(\text{Se})\text{Cl}$ (**6**).

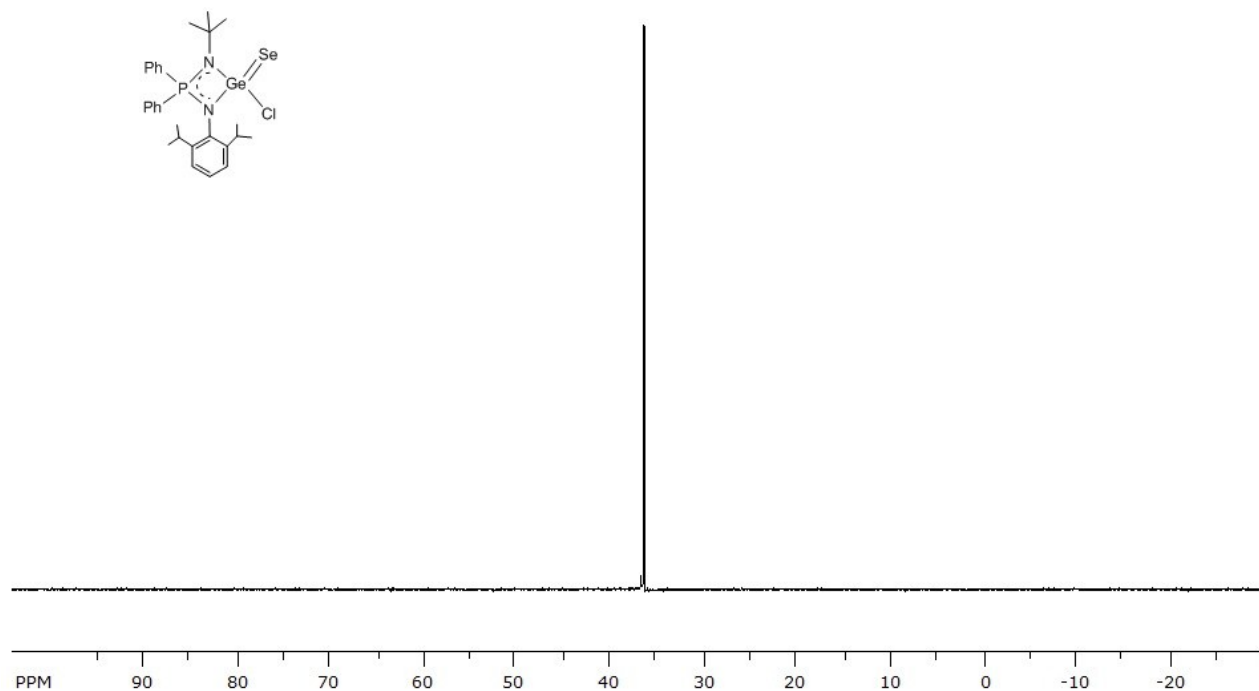


Fig. S17 $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) spectrum of $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N})\text{P}(\text{Ph})_2(\text{N}t\text{Bu})]\text{Ge}(\text{Se})\text{Cl}$ (6).

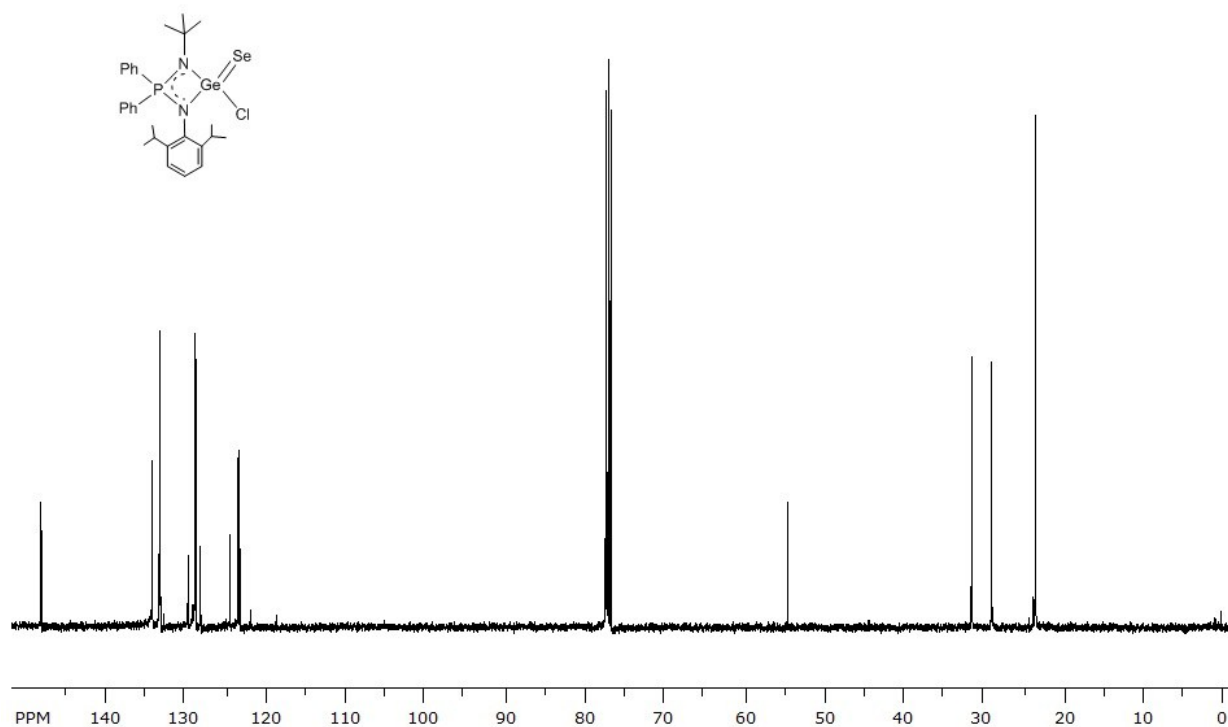


Fig. S18 ^{13}C NMR (100 MHz, CDCl_3) spectrum of $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N})\text{P}(\text{Ph})_2(\text{N}t\text{Bu})]\text{Ge}(\text{Se})\text{Cl}$ (6).

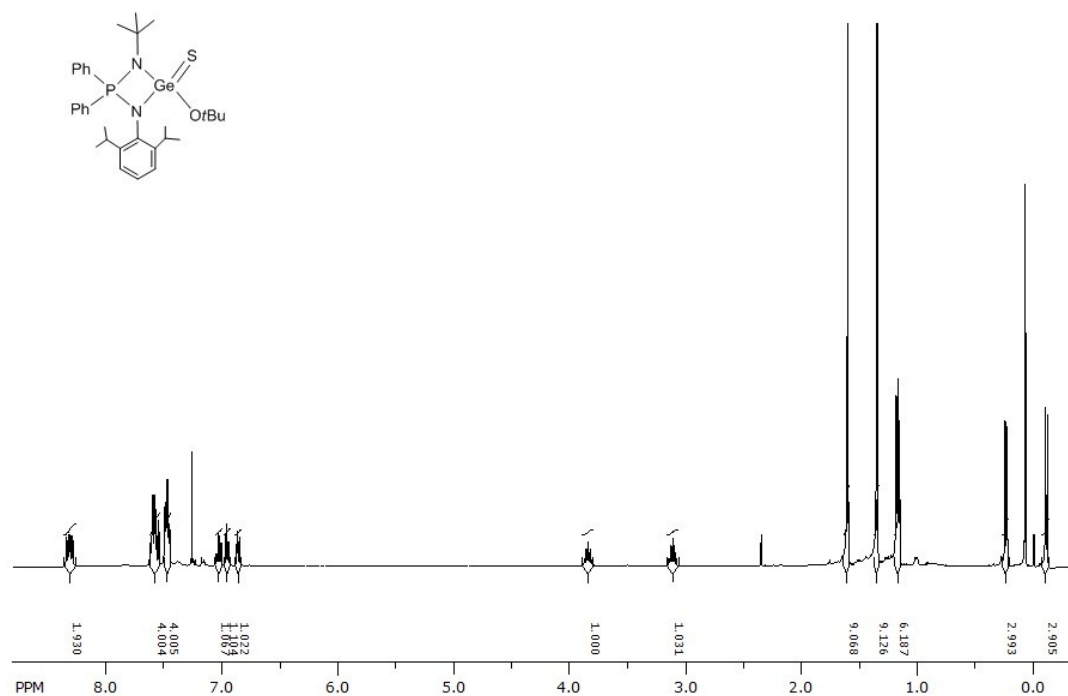


Fig. S19 ^1H NMR (400MHz, CDCl_3) spectrum of $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N})\text{P}(\text{Ph})_2(\text{N}t\text{Bu})]\text{Ge}(\text{S})\text{O}t\text{Bu}$ (7).

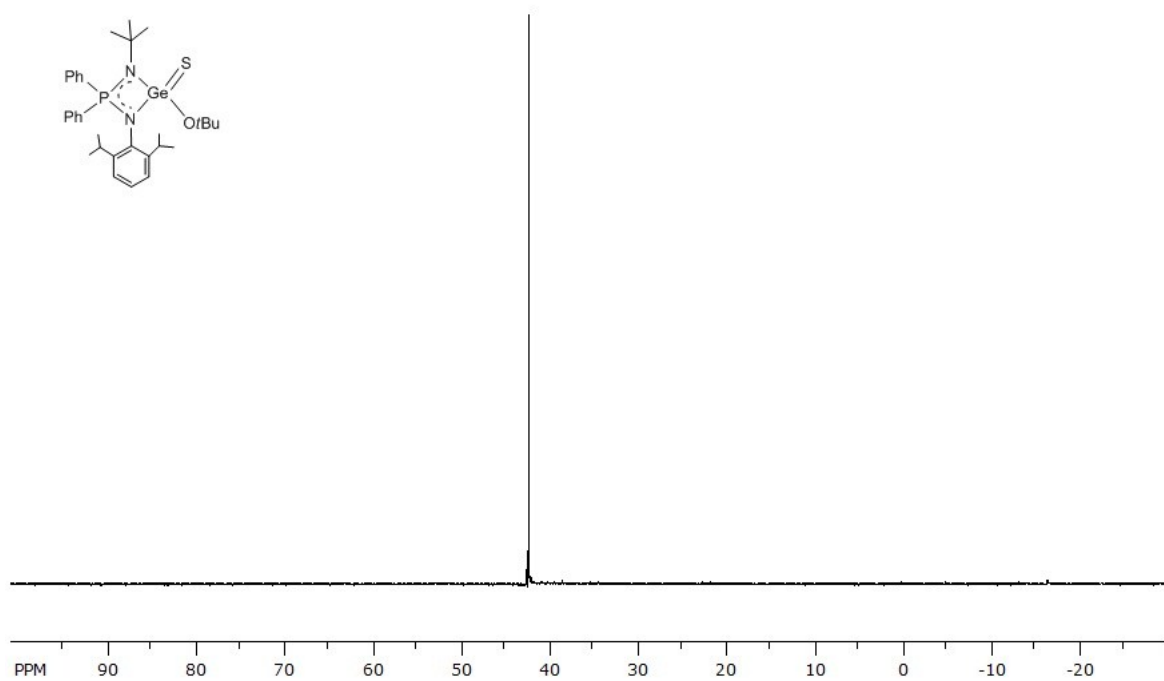


Fig. S20 $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) spectrum of $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N})\text{P}(\text{Ph})_2(\text{N}t\text{Bu})]\text{Ge}(\text{S})\text{O}t\text{Bu}$ (7).

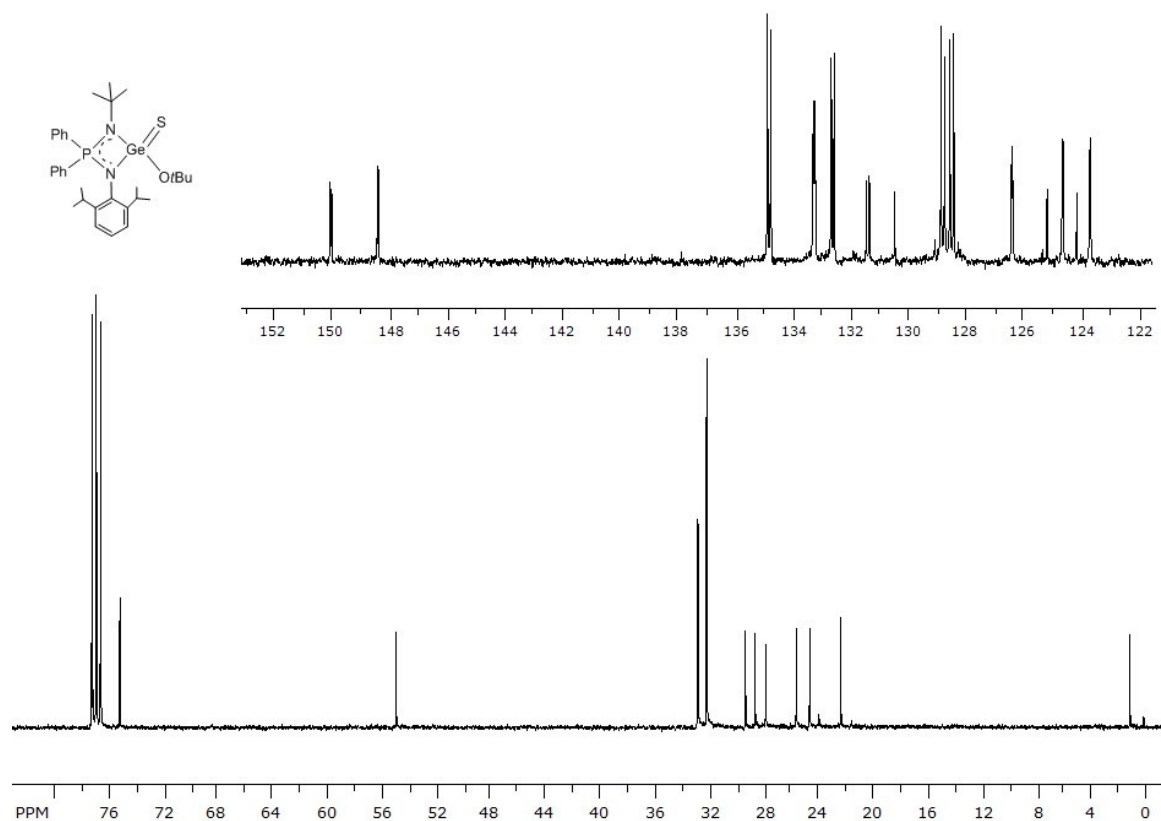


Fig. S21 ^{13}C NMR (100MHz, CDCl_3) spectrum of $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N})\text{P}(\text{Ph}_2)(\text{N}t\text{Bu})]\text{Ge}(\text{S})\text{O}t\text{Bu} (**7**). Inset shows expansion of the aromatic region.$

^1H - ^{13}C HSQC NMR spectrum of compound **7**

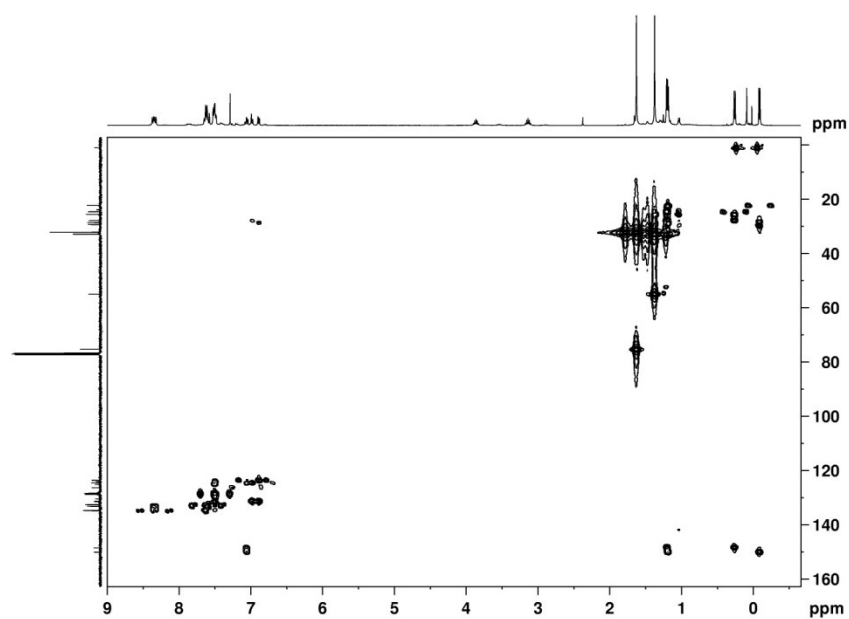


Fig. S22 ^1H - ^{13}C HSQC NMR spectrum of $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N})\text{P}(\text{Ph}_2)(\text{N}t\text{Bu})]\text{Ge}(\text{S})\text{O}t\text{Bu} (**7**).$

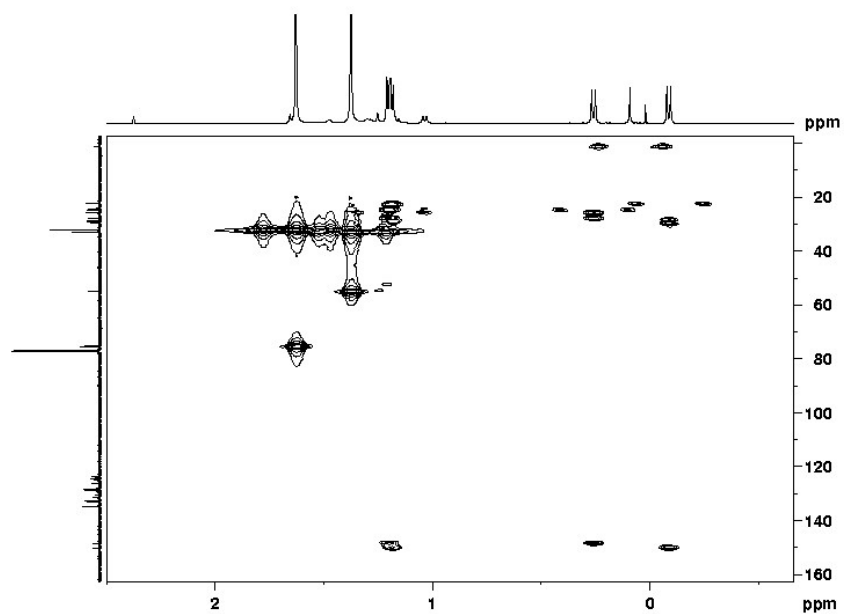


Fig. S23 Expansion of the aliphatic region of ^1H - ^{13}C HSQC NMR spectrum of [(2,6-*i*Pr₂C₆H₃N)P(Ph₂)(N*t*Bu)]Ge(S)O*t*Bu (**7**).

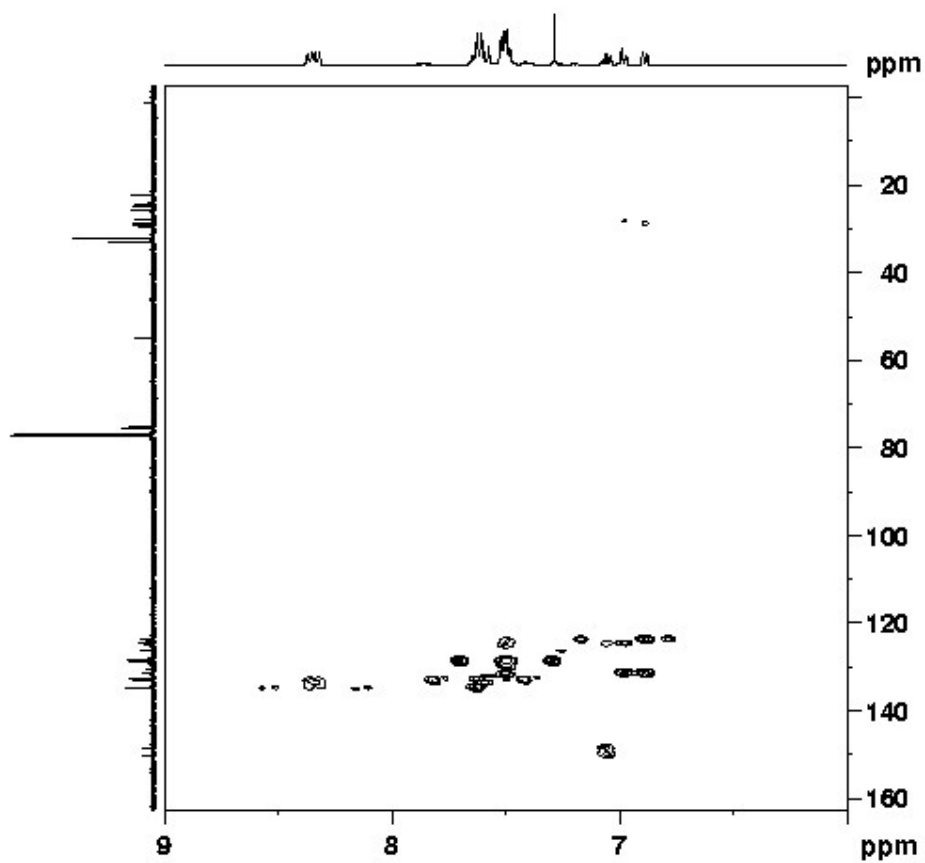


Fig. S24 Expansion of the aromatic region of ^1H - ^{13}C HSQC NMR spectrum of [(2,6-*i*Pr₂C₆H₃N)P(Ph₂)(N*t*Bu)]Ge(S)O*t*Bu (**7**).

^1H - ^{13}C HMBC NMR spectrum of compound 7

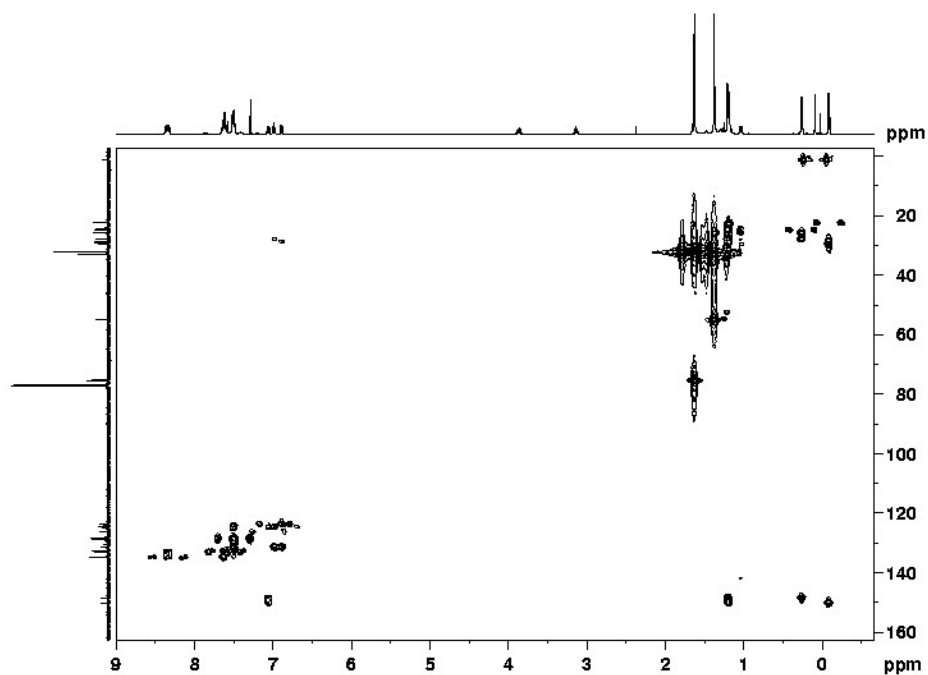


Fig. S25 ^1H - ^{13}C HMBC NMR spectrum of $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N})\text{P}(\text{Ph}_2)(\text{N}t\text{Bu})]\text{Ge}(\text{S})\text{O}t\text{Bu}$ (**7**).

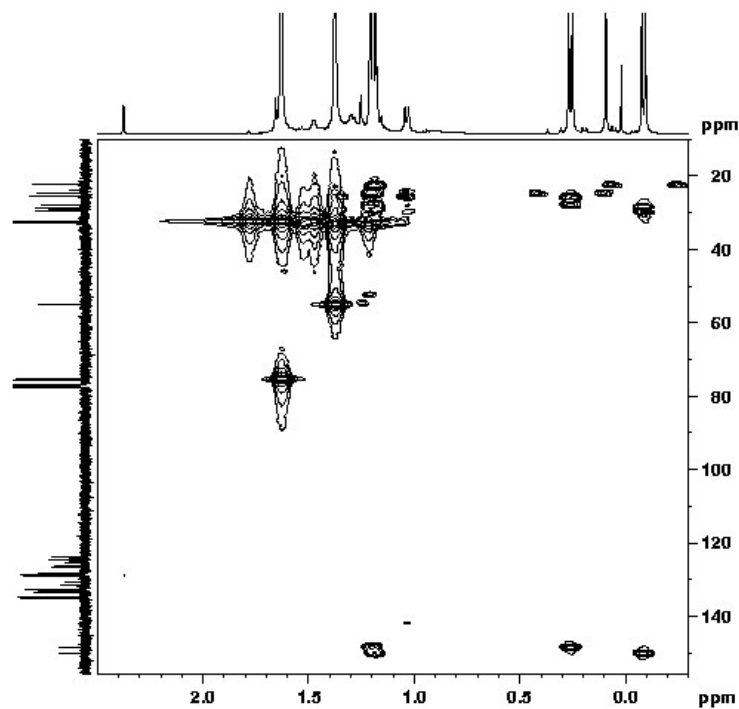


Fig. S26 Expansion of the aliphatic region of ^1H - ^{13}C HMBC NMR spectrum of $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N})\text{P}(\text{Ph}_2)(\text{N}t\text{Bu})]\text{Ge}(\text{S})\text{O}t\text{Bu}$ (**7**).

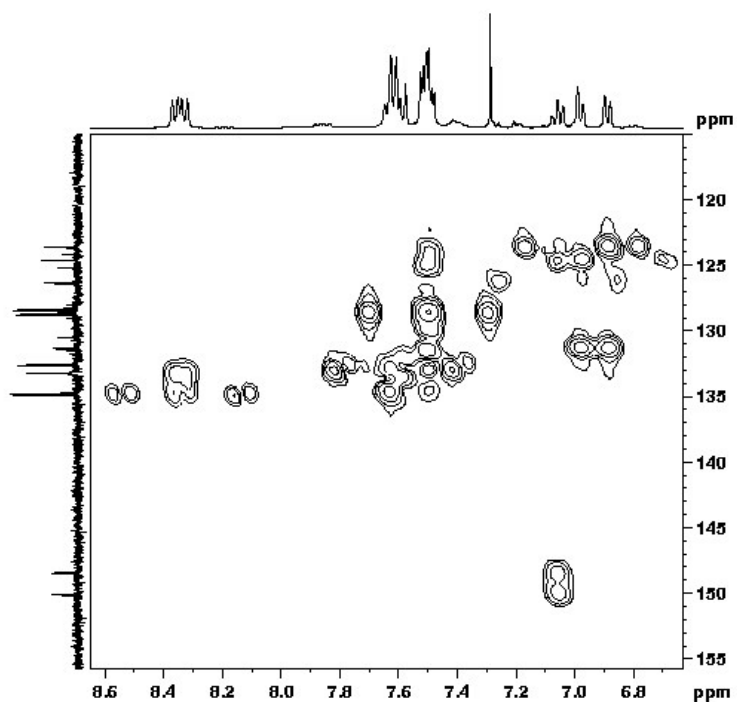
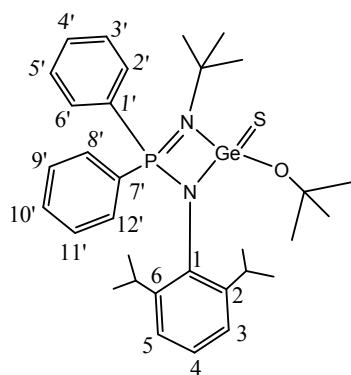


Fig. S27 Expansion of the aromatic region of ^1H - ^{13}C HMBC NMR spectrum of [(2,6-*i*Pr₂C₆H₃N)P(Ph₂)(N*t*Bu)]Ge(S)O*t*Bu (**7**).

Assignment of ^1H and ^{13}C NMR signals of [(2,6-*i*Pr₂C₆H₃N)P(Ph₂)(N*t*Bu)]Ge(S)O*t*Bu (7**)**



Compound **7**

^1H NMR (400 MHz, CDCl_3): δ = -0.12 (d, $^3J_{\text{H-H}}$ = 6.8 Hz, 3 H, C^{2or6}(CH)(CH₃)(CH₃)), 0.22 (d, $^3J_{\text{H-H}}$ = 6.8 Hz, 3 H, C^{2or6}(CH)(CH₃)(CH₃)), 1.17 (overlapped doublets, $^3J_{\text{H-H}}$ = 6.4 & 5.1 Hz, 6 H, 2x C^{2&6}(CH)(CH₃)(CH₃)), 1.35 (s, 9 H, NC(CH₃)₃), 1.60 (s, 9 H, OC(CH₃)₃), 3.12 (sept, $^3J_{\text{H-H}}$ = 6.8 Hz, 1 H, C^{2or6}(CH)(CH₃)(CH₃)), 3.84 (sept, $^3J_{\text{H-H}}$ = 6.8 Hz, 1 H, C^{2or6}(CH)(CH₃)(CH₃)), 6.84–6.88

(m, 1 H, C^{3or5}-H, Dipp), 6.94–6.97 (m, 1 H, C^{3or5}-H, Dipp), 7.00–7.07 (m, 1 H, C⁴-H, Dipp), 7.43–7.55 (m, 4 H, 2xC^{(3'&5')or(9'&11')}-H, Ph), 7.55–7.64 (m, 4 H, 2xC^{(2'&6')or(8'&12')}-H, Ph), 8.29–8.37 (m, 2 H, C^{4'&10'}-H, Ph).

¹³C NMR (100 MHz, CDCl₃): δ = 22.3 (s, 1 C, C^{2or6}CH(CH₃)(CH₃)), 24.6 (s, 1 C, C^{2or6}CH(CH₃)(CH₃)), 25.6 (s, 1 C, C^{2or6}CH(CH₃)(CH₃)), 27.8 (s, 1 C, C^{2or6}CH(CH₃)(CH₃)), 28.6 (s, 1 C, C^{2or6}CH(CH₃)₂), 29.3 (s, 1 C, C^{2or6}CH(CH₃)₂), 32.2 (s, 3 C, 1xOC(CH₃)₃), 32.8 (d, J_{C-P} = 5.6 Hz, 3 C, 1xNC(CH₃)₃), 55.0 (s, 1 C, NC(CH₃)₃), 75.3 (s, 1 C, OC(CH₃)₃), 123.6 (d, J_{C-P} = 2.5 Hz, 1 C, C^{2or6}, Dipp), 124.1 (d, J_{C-P} = 2.6 Hz, 1 C, C^{2or6}, Dipp), 124.6 (d, J_{C-P} = 102.0 Hz, C_{ipso}^{1'or7'}, Ph), 126.3 (d, J_{C-P} = 2.8 Hz, C⁴, Dipp), 128.4 (d, J_{C-P} = 13.0 Hz, 2 C, 1xC^{(3'&5')or(9'&11')}, Ph), 128.7 (d, J_{C-P} = 12.9 Hz, 2 C, 1xC^{(3'&5')or(9'&11')}, Ph), 131.0 (d, J_{C-P} = 99.2 Hz, 1 C, C_{ipso}^{1'or7'}, Ph), 131.3 (d, J_{C-P} = 1.5 Hz, C_{ipso}¹, Dipp), 132.6 (d, J_{C-P} = 10.4 Hz, 2 C, 1xC^{(2'&6')or(8'&12')}, Ph), 133.2 (vtr, J_{C-P} = 6.9 & 3.4 Hz, 2 C, C^{4'&10'}, Ph), 134.8 (d, J_{C-P} = 11.6 Hz, 2 C, 1xC^{(2'&6')or(8'&12')}, Ph), 148.4 (d, J_{C-P} = 4.2 Hz, 1 C, C³, Dipp), 150.1 (d, J_{C-P} = 4.5 Hz, 1 C, C⁵, Dipp).

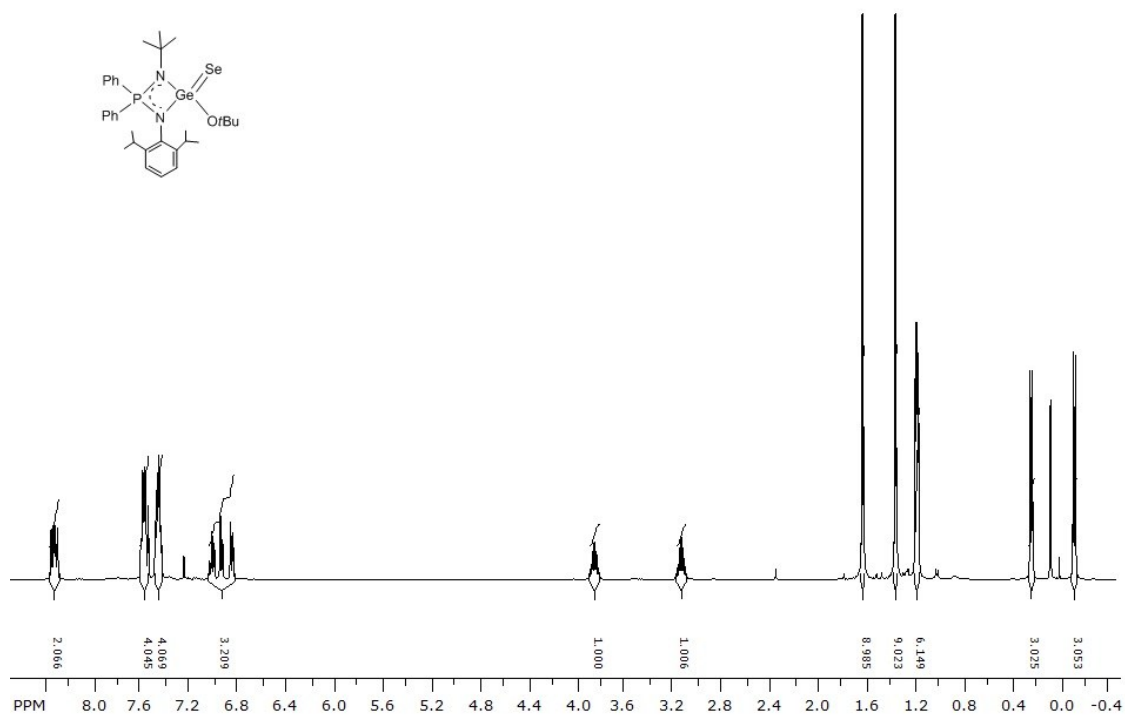


Fig. S28 ^1H NMR (400MHz, CDCl_3) spectrum of $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N})\text{P}(\text{Ph}_2)(\text{N}t\text{Bu})]\text{Ge}(\text{Se})\text{O}t\text{Bu}$ (**8**).

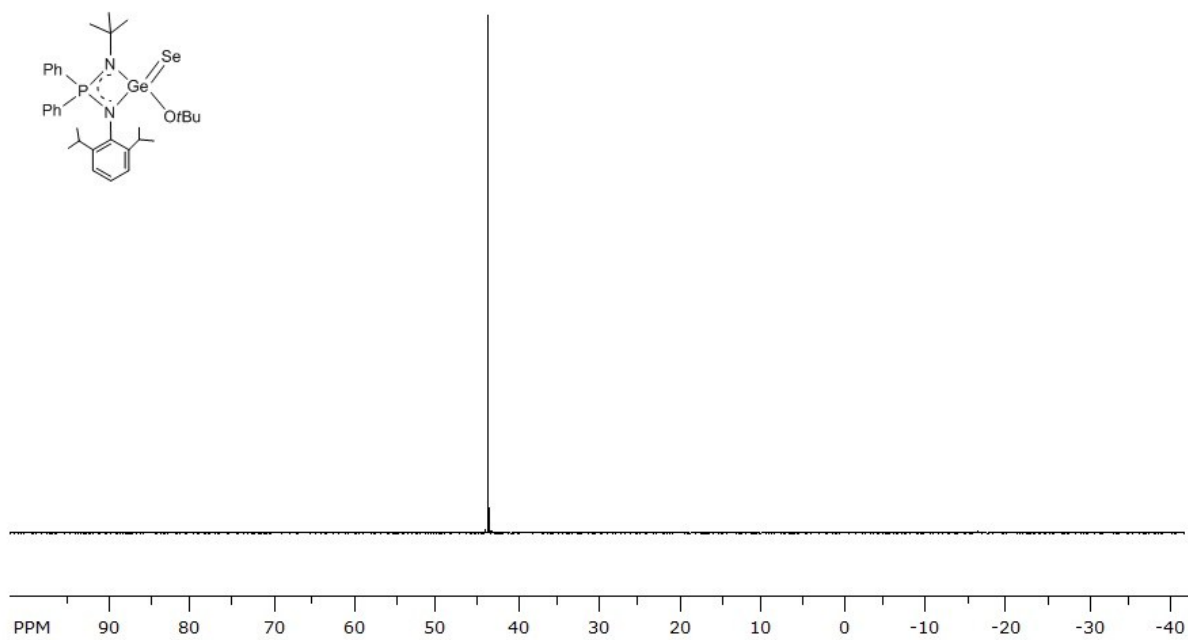


Fig. S29 $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) spectrum of $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N})\text{P}(\text{Ph}_2)(\text{N}t\text{Bu})]\text{Ge}(\text{Se})\text{O}t\text{Bu}$ (**8**).

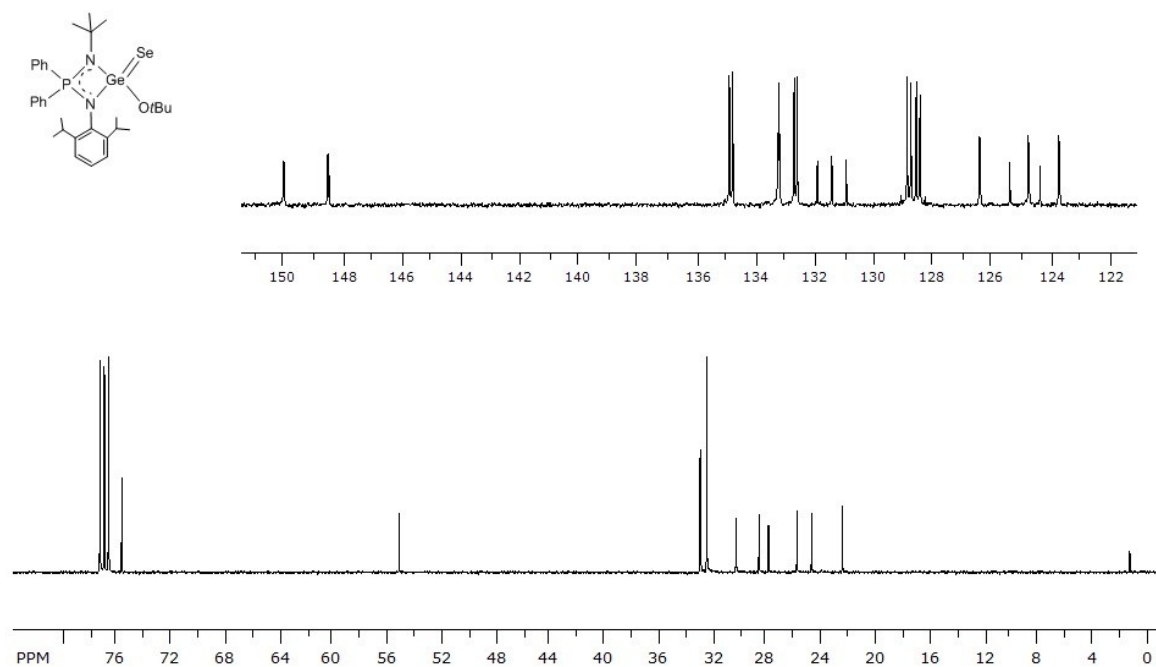


Fig. S30 ¹³C NMR (100MHz, CDCl₃) spectrum of [(2,6-*i*Pr₂C₆H₃N)P(Ph₂)(N*t*Bu)]Ge(Se)O*t*Bu (**8**). Inset shows expansion of the aromatic region.