Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

An Iron Germylene Complex Having Fe-H and Ge-H Bonds: Synthesis, Structure and Reactivity

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1. **NMR and IR spectra**
2. **X-ray crystallographic analysis (additional comments) and crystal data**

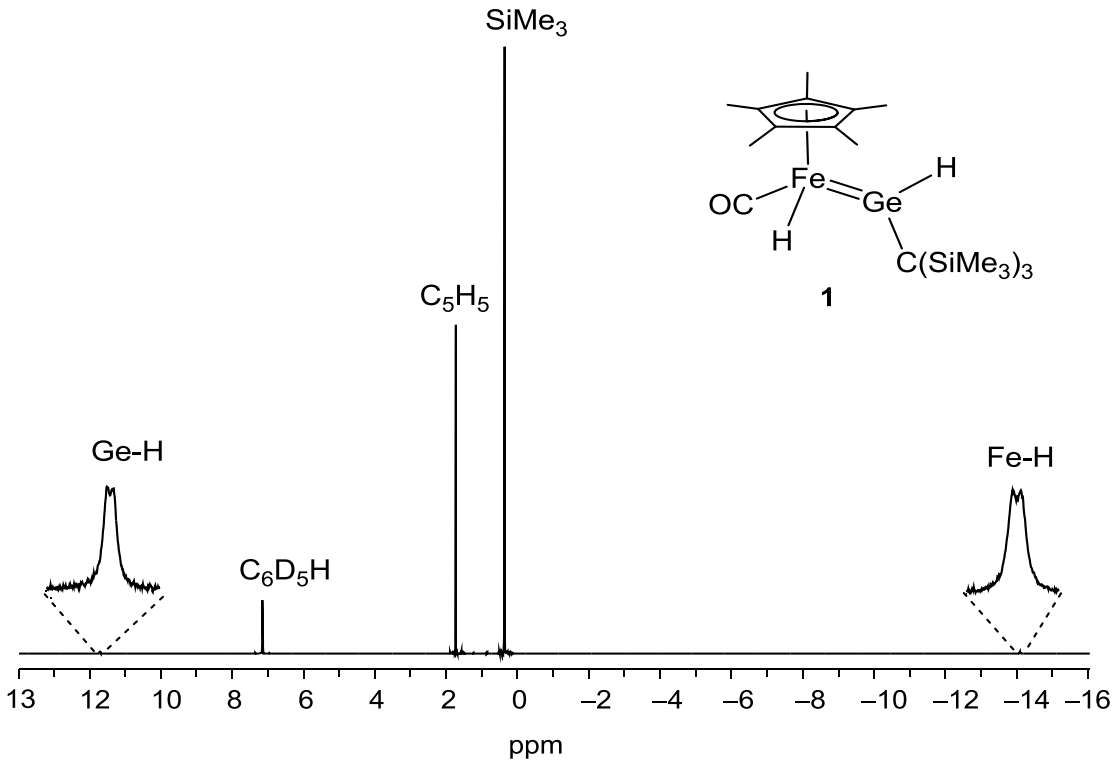

Figure S1. ^{1}H NMR spectrum of Cp*(CO)(H)Fe=Ge(H){C(SiMe$_3$)$_3$} (**1**) (400 MHz, C_6D_6).

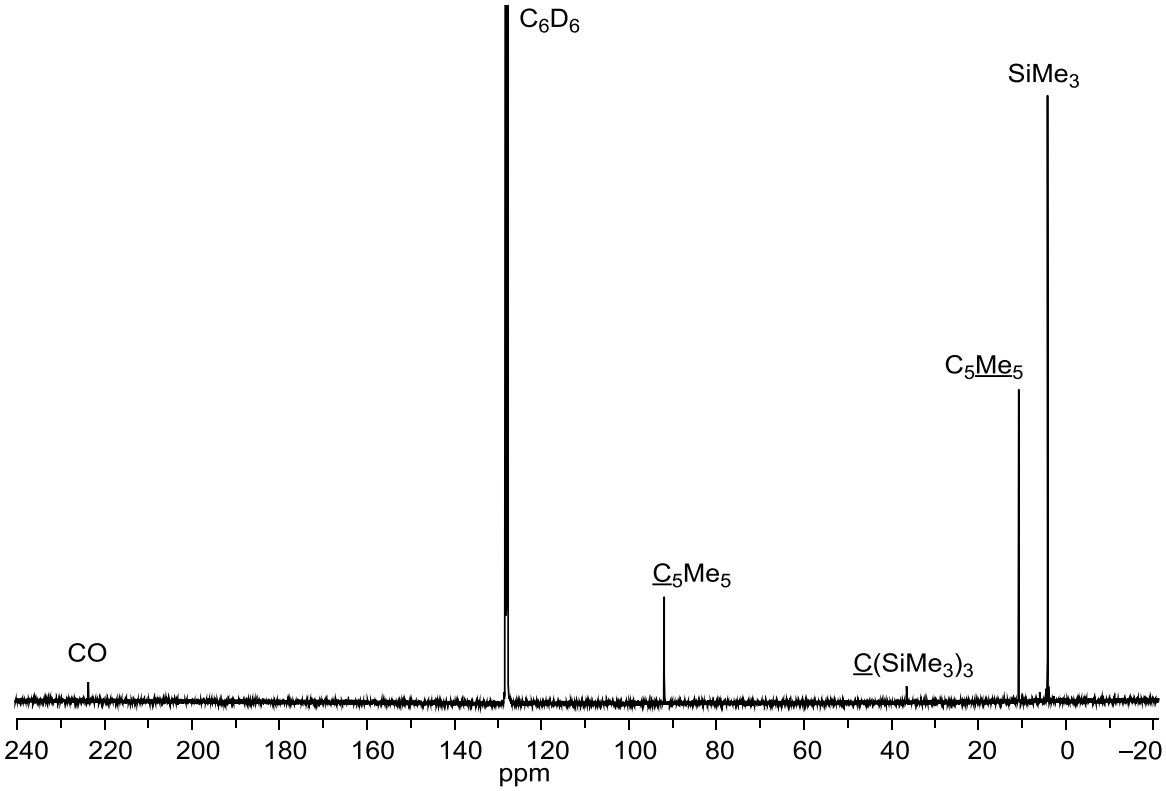

Figure S2. ^{13}C{^{1}H} NMR spectrum of Cp*(CO)(H)Fe=Ge(H){C(SiMe$_3$)$_3$ (**1**) (100 MHz, C_6D_6).

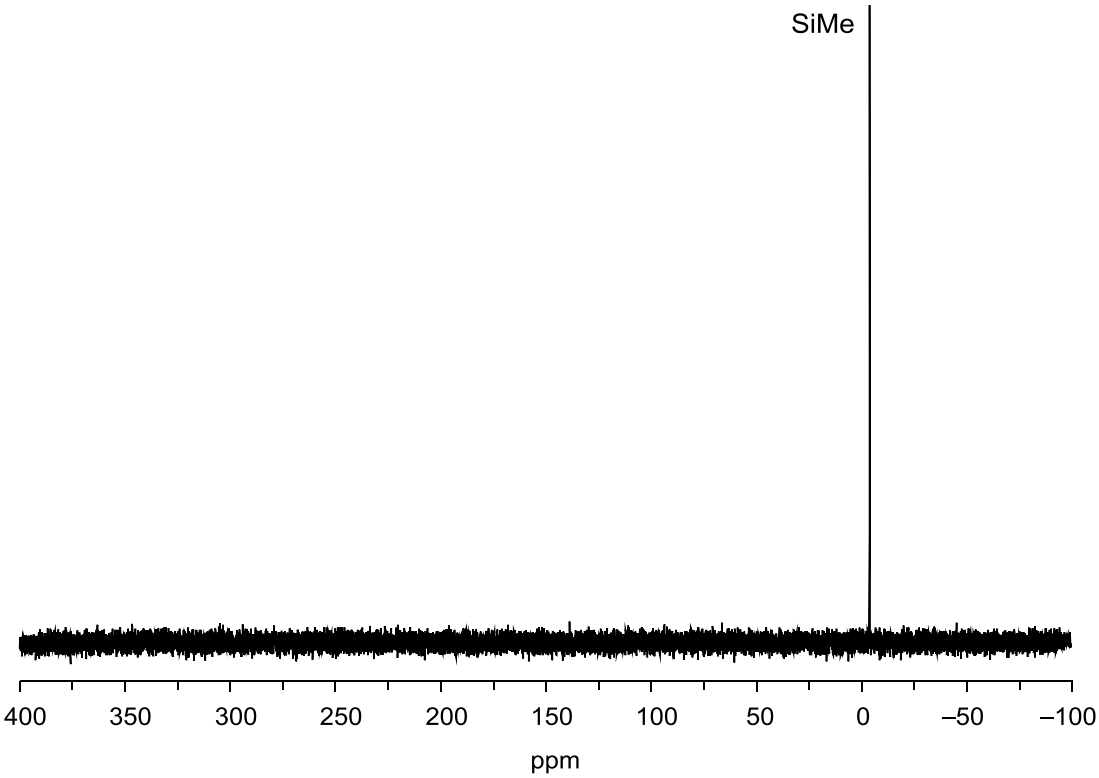

Figure S3. $^{29}Si\{^{1}H\}$ NMR spectrum of Cp*(CO)(H)Fe=Ge(H){C(SiMe$_3$)$_3$ (**1**) (79.5 MHz, C_6D_6).

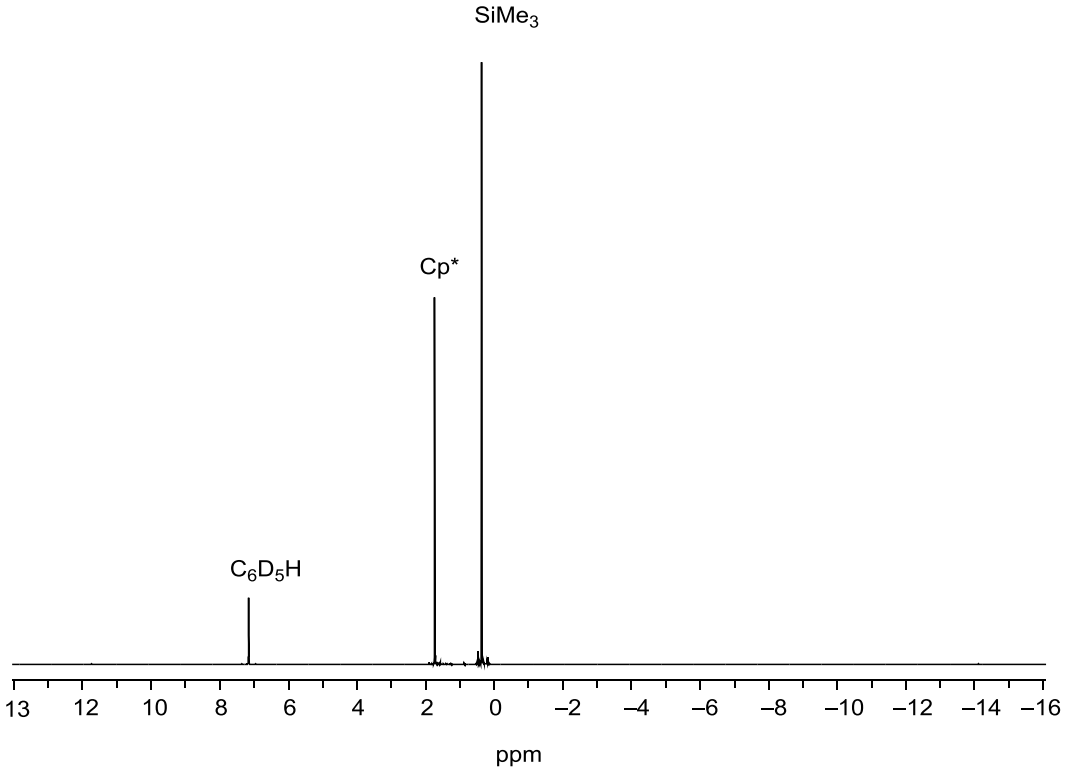

Figure S4. ^{1}H NMR spectrum of Cp*(CO)(D)Fe=Ge(D){C(SiMe$_3$)$_3$} (**1**-d_2) (400 MHz, C_6D_6).

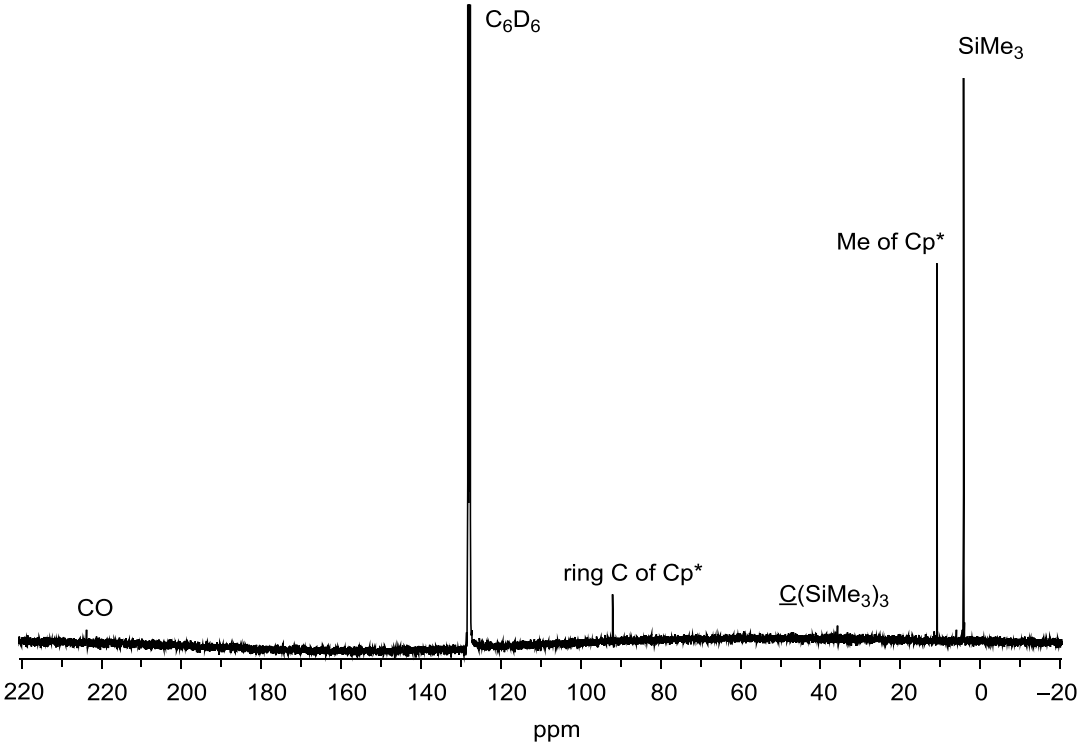

Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of Cp*(CO)(D)Fe=Ge(D){C(SiMe$_3$)$_3$} (**1**-d_2) (100 MHz, C_6D_6).

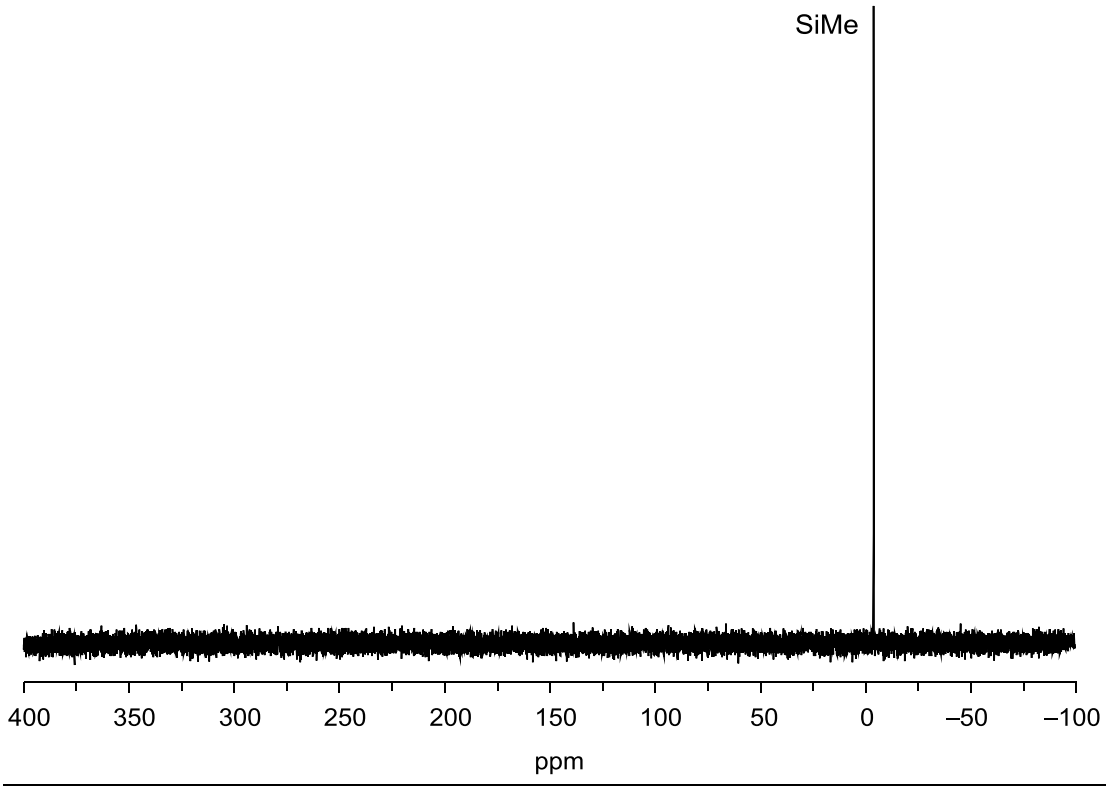

Figure S6. $^{29}Si\{^{1}H\}$ NMR spectrum of Cp*(CO)(D)Fe=Ge(D){C(SiMe$_3$)$_3$} (**1**-d_2) (79.5 MHz, C_6D_6).

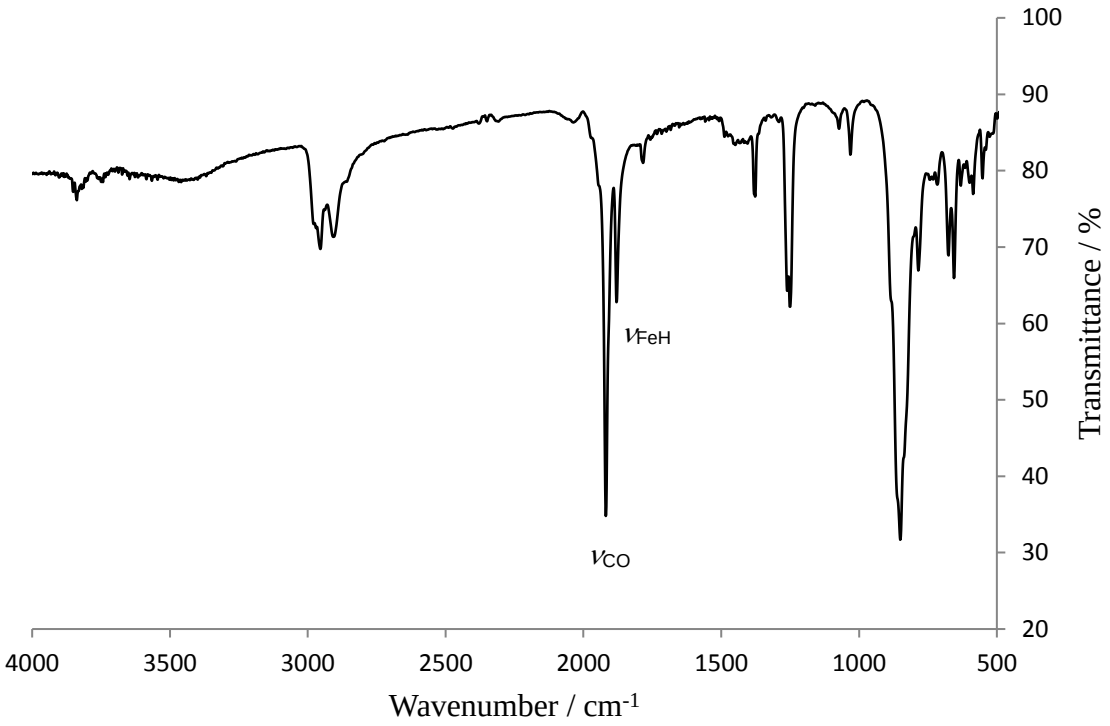

Figure S7. IR spectrum of Cp*(CO)(H)Fe=Ge(H){C(SiMe$_3$)$_3$} (**1**) (KBr).

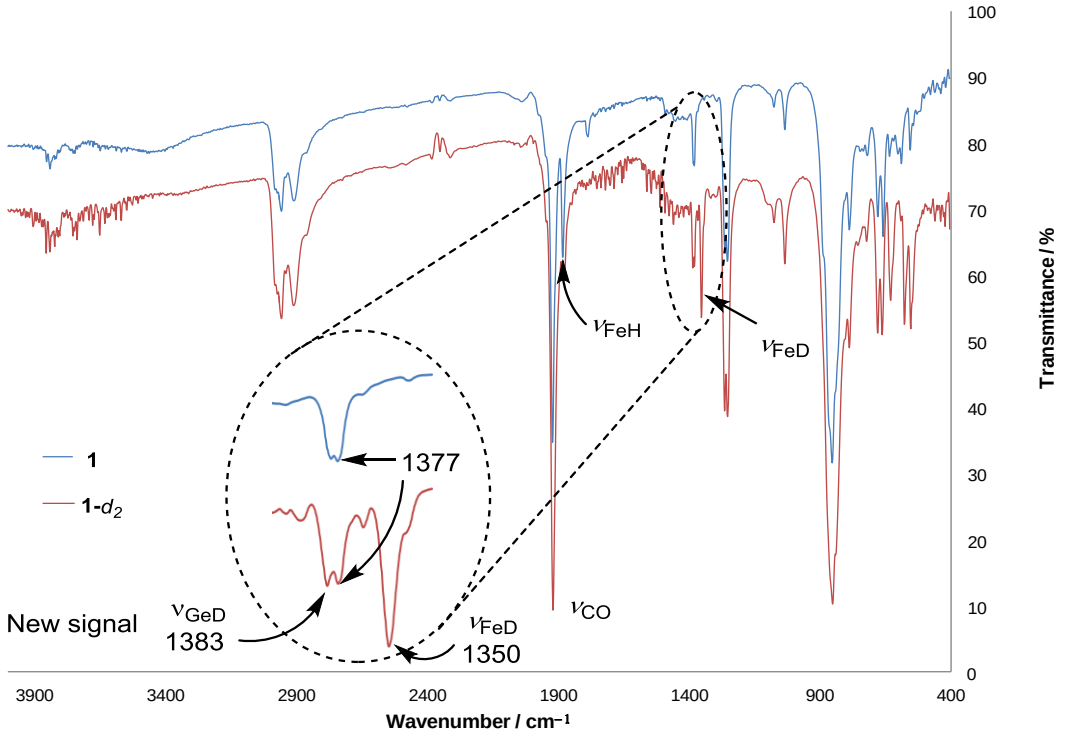

Figure S8. Comparison of IR spectra of complexes **1** and **1**-d_2 (KBr).

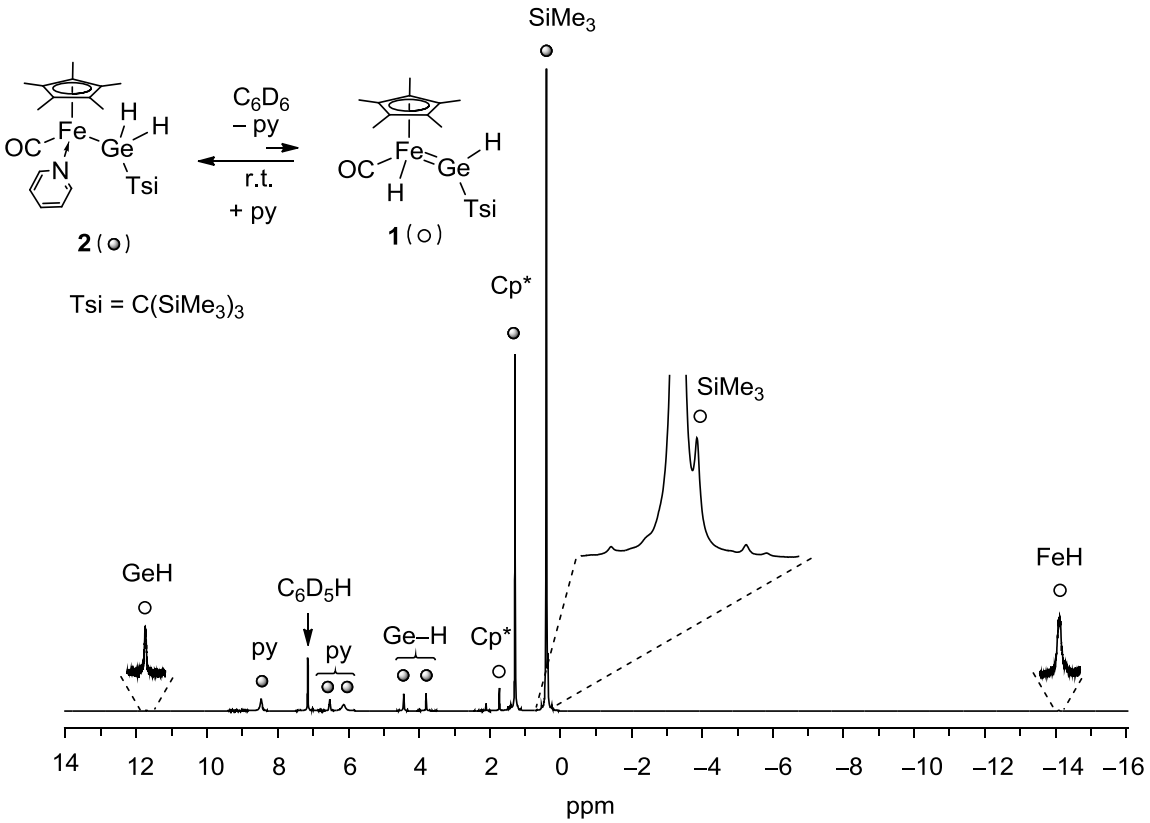

Figure S9. ^{1}H NMR spectrum of Cp*(CO)(py)FeGeH$_2${C(SiMe$_3$)$_3$} (**2**) (400 MHz, C_6D_6).

Table S1 The ratio of **2** : **1** vs. the concentration of **2** in C_6D_6

The ratio of **2** : **1**		Initial concentration of **2**
2	**1**	(mol/L) in C_6D_6
94	6	3.3×10^{-2}
93	7	2.5×10^{-2}
89	11	1.2×10^{-2}
86	14	8.3×10^{-3}
84	16	6.2×10^{-3}

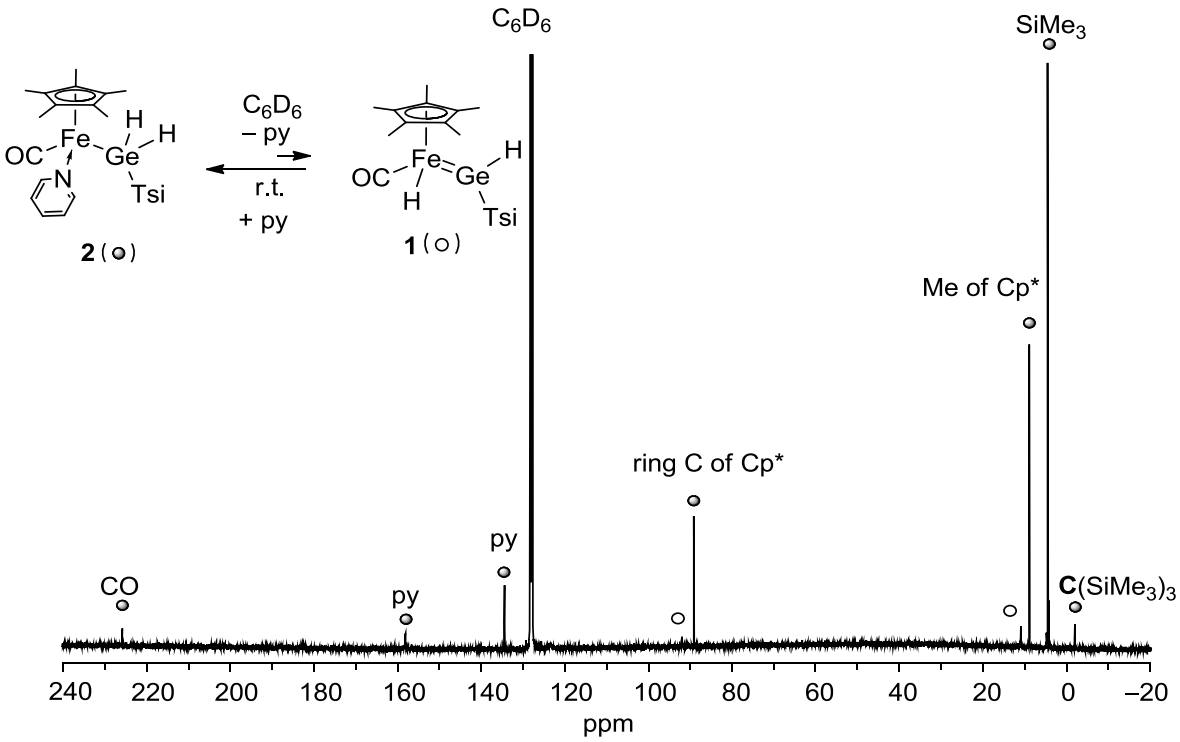

Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of Cp*(CO)(py)FeGeH$_2${C(SiMe$_3$)$_3$} (**2**) (100 MHz, C_6D_6).

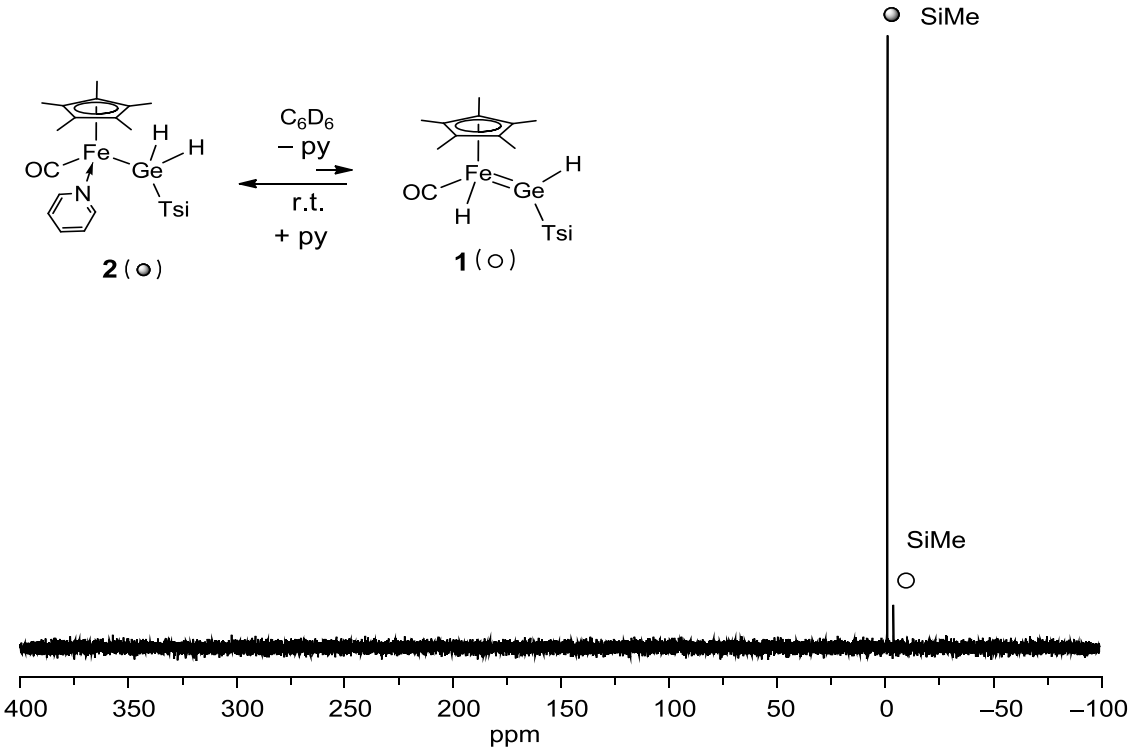

Figure S11. $^{29}Si\{^{1}H\}$ NMR spectrum of Cp*(CO)(py)FeGeH$_2${C(SiMe$_3$)$_3$} (**2**) (79.5 MHz, C_6D_6).

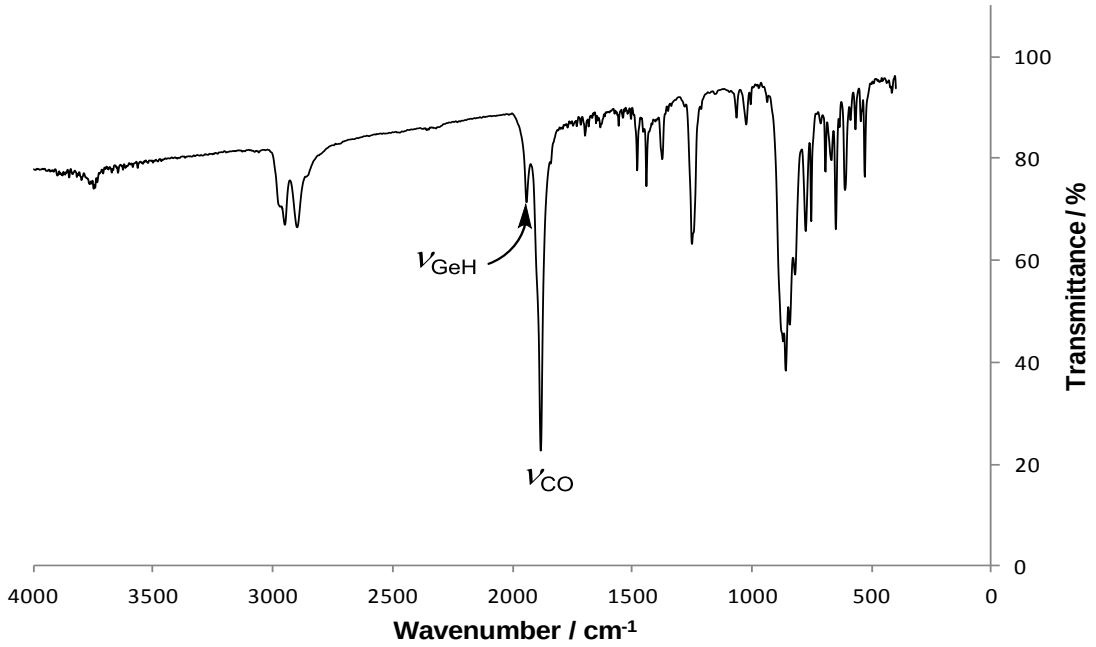

Figure S12. IR spectrum of Cp*(CO)(py)FeGeH$_2${C(SiMe$_3$)$_3$} (**2**) (KBr).

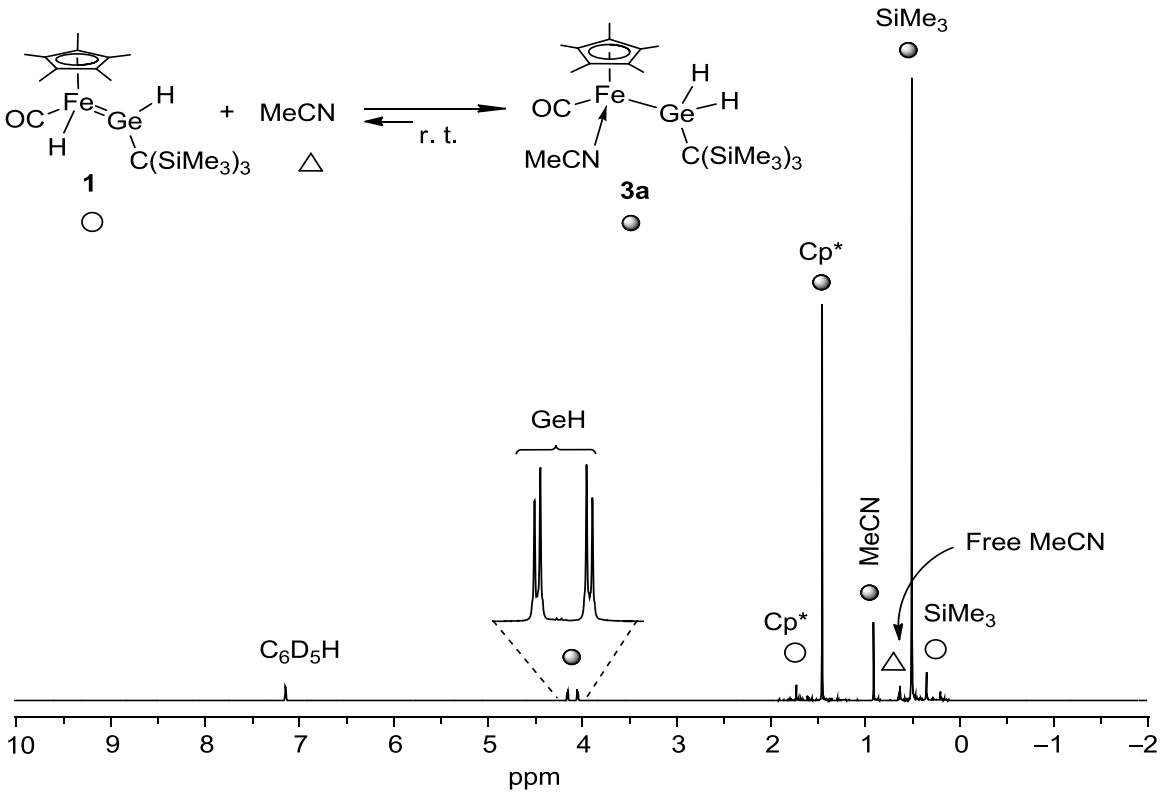

Figure S13. ^{1}H NMR spectrum of Cp*(CO)(MeCN)FeGeH$_2${C(SiMe$_3$)$_3$} (**3a**) (400 MHz, C_6D_6)

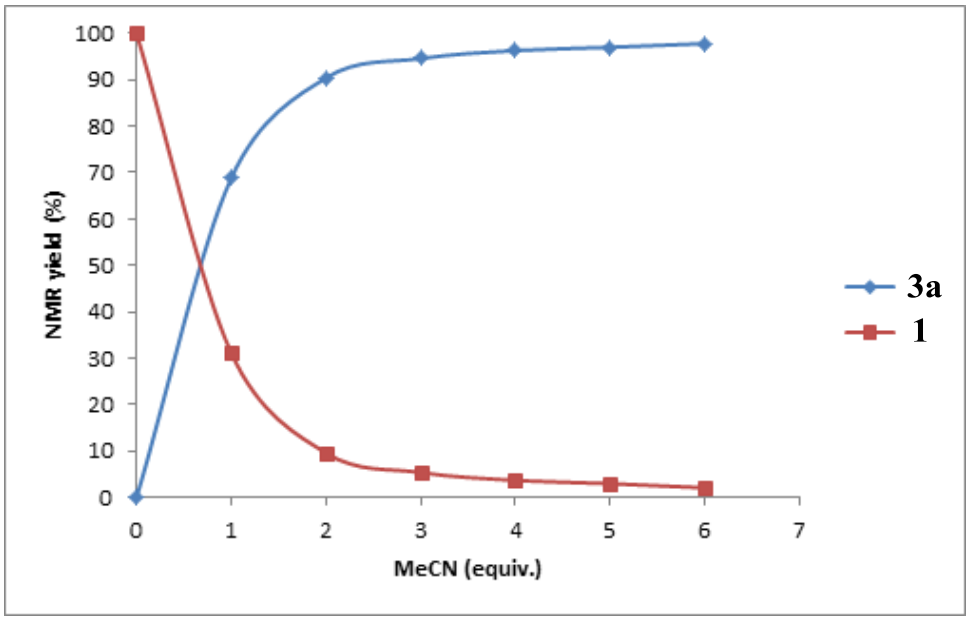

Figure S14. NMR yield (%) of **3a** vs. equivalent of MeCN added to **1** (5 mg) in C_6D_6.

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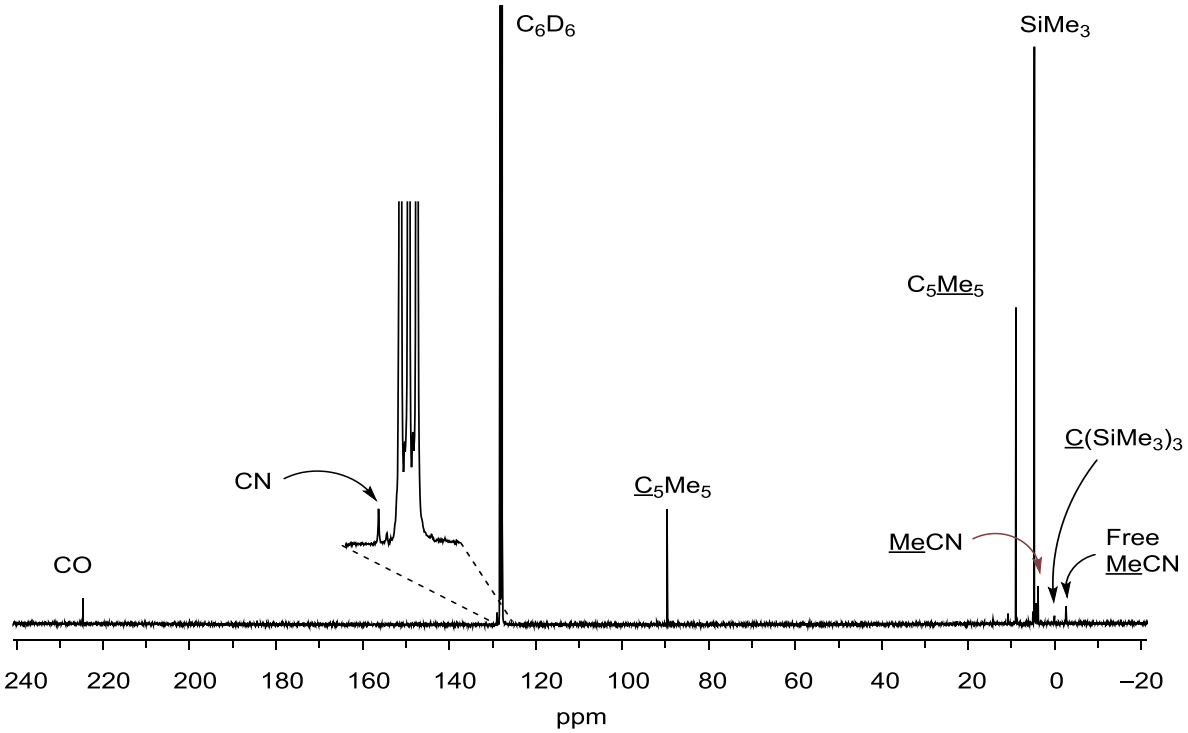

Figure S15 $^{13}C\{^1H\}$NMR spectrum of Cp*(CO)(MeCN)Fe-GeH_2{$C(SiMe_3)_3$} (**3a**) (100 MHz, C_6D_6).

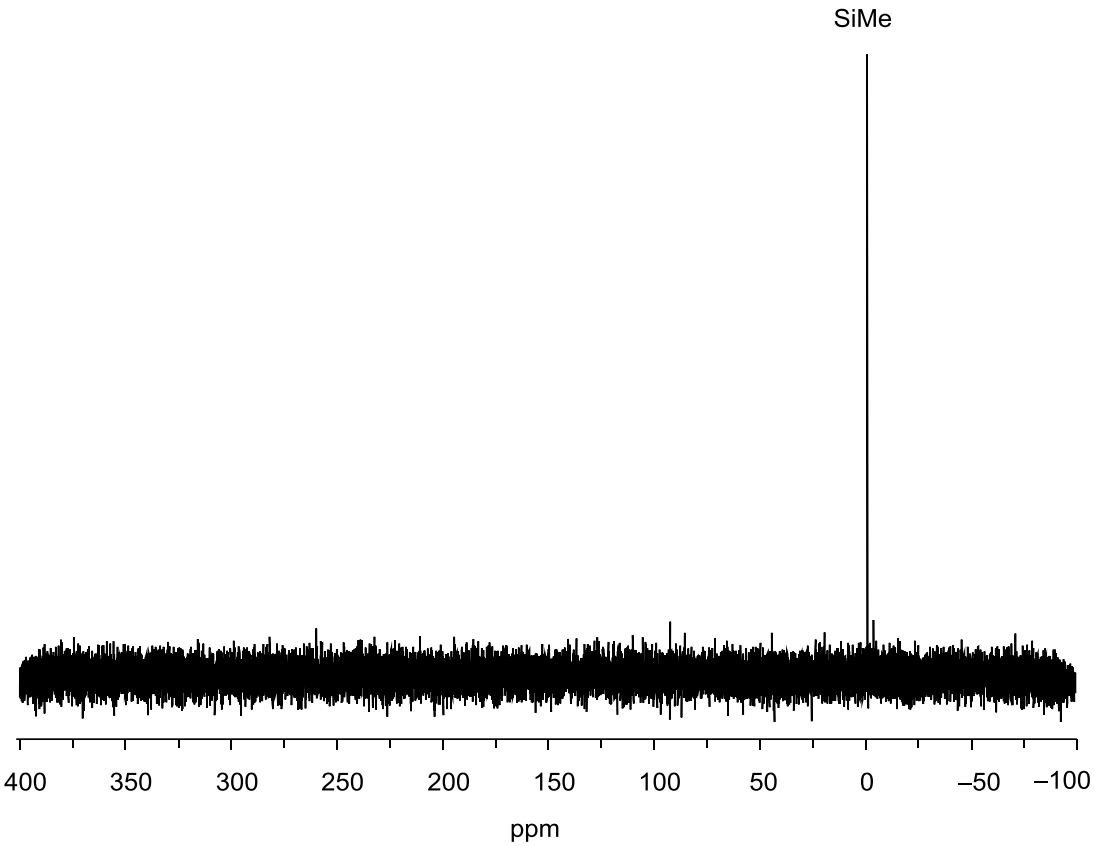

Figure S16. $^{29}Si\{^{1}H\}$ NMR spectrum of Cp*(CO)(MeCN)FeGeH$_2${C(SiMe$_3$)$_3$} (**3a**) (79.5 MHz, C_6D_6).

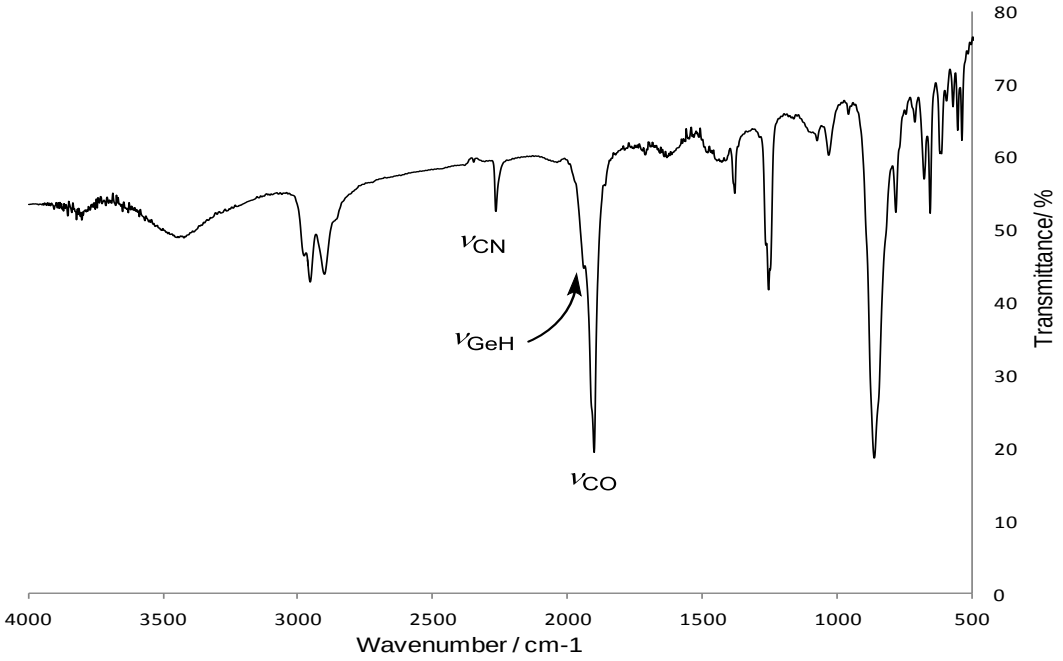

Figure S17. IR spectrum of Cp*(CO)(MeCN)FeGeH$_2${C(SiMe$_3$)$_3$} (**3a**) (KBr).

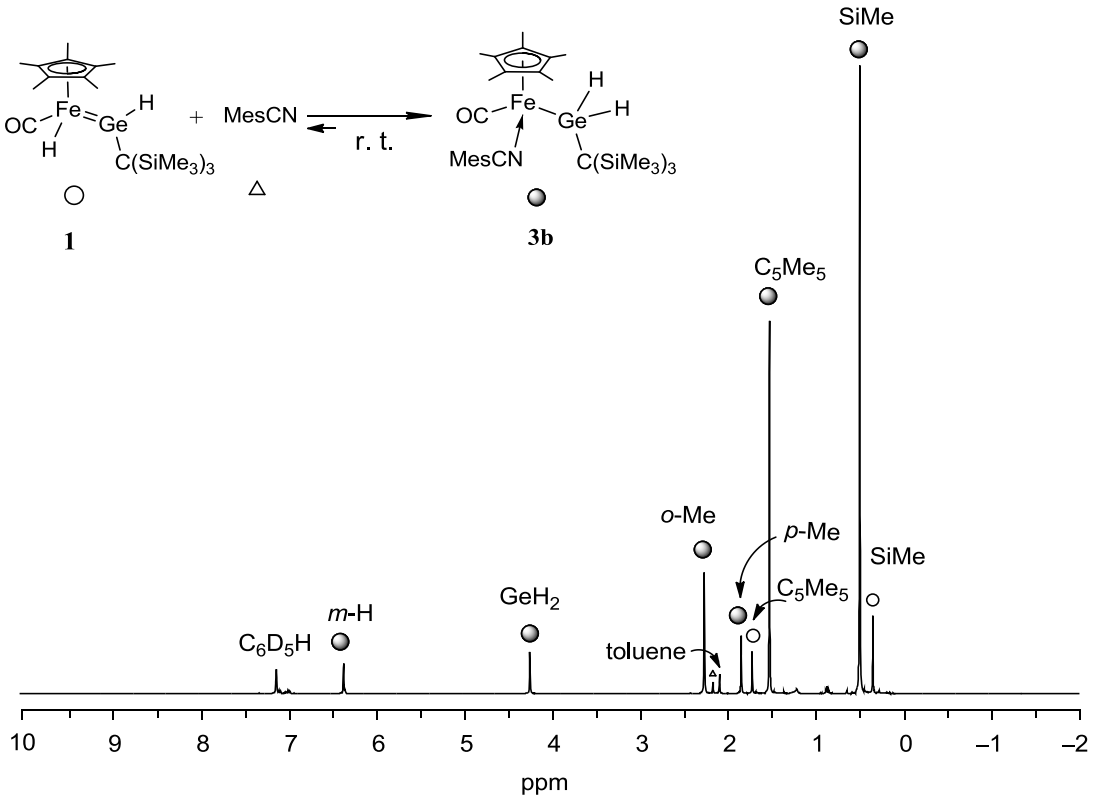

Figure S18. ^{1}H NMR spectrum of Cp*(CO)(MesCN)FeGeH$_2${C(SiMe$_3$)$_3$} (**3b**) (400 MHz, C_6D_6).

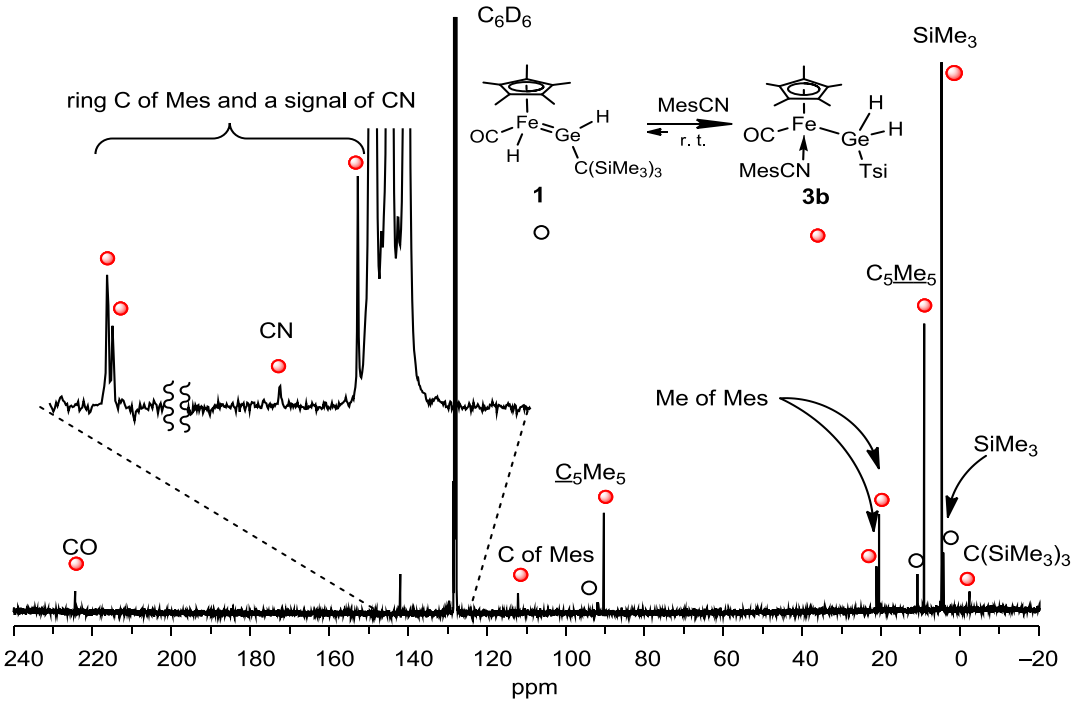

Figure S19. ^{13}C{^{1}H} NMR spectrum of Cp*(CO)(MesCN)FeGeH$_2${C(SiMe$_3$)$_3$} (**3b**) (100 MHz, C_6D_6).

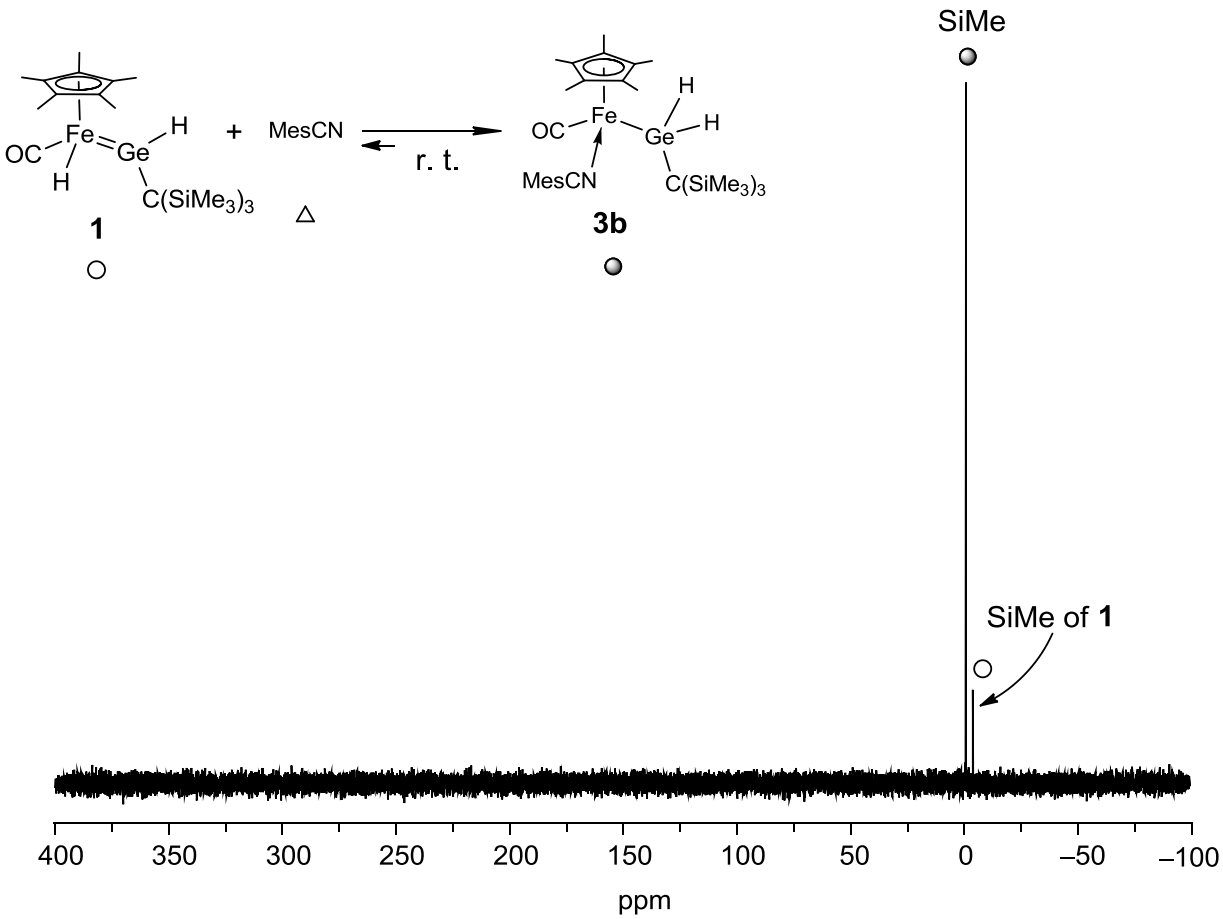

Figure S20. $^{29}Si\{^{1}H\}$ NMR spectrum of Cp*(CO)(MesCN)FeGeH$_2${C(SiMe$_3$)$_3$} (**3b**) (79.5 MHz, C_6D_6).

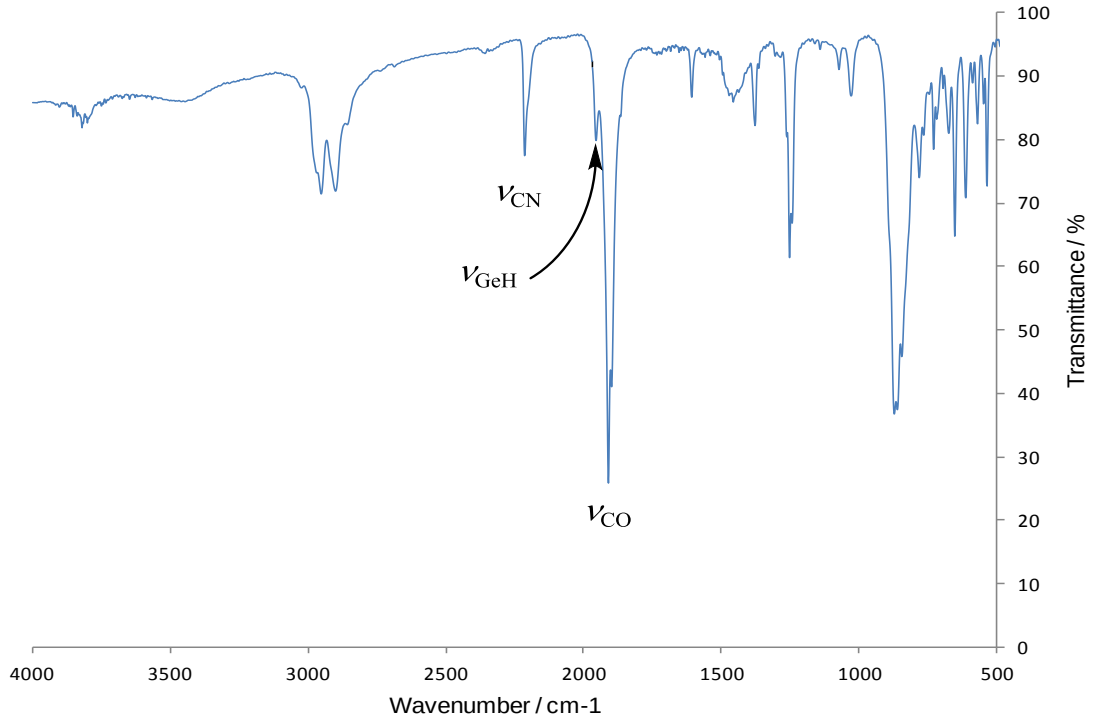

Figure S21. IR spectrum of Cp*(CO)(MesCN)FeGeH$_2${C(SiMe$_3$)$_3$} (**3b**) (KBr).

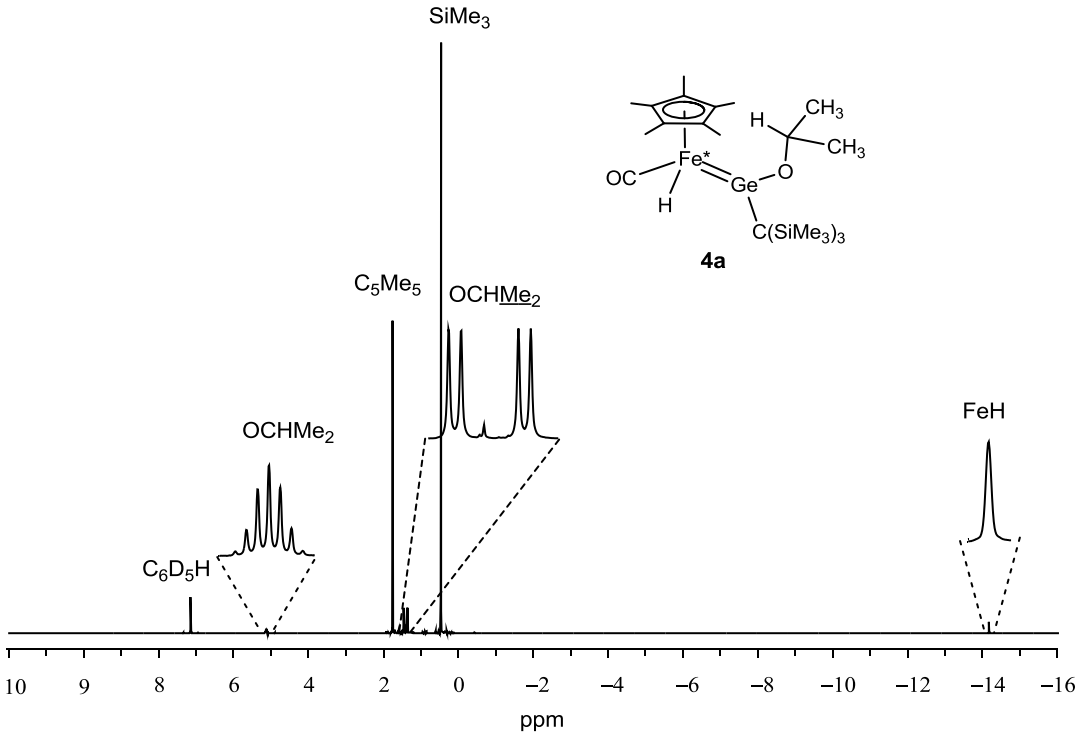

Figure S22. ^{1}H NMR spectrum of Cp*(CO)(H)Fe=Ge(OCHMe$_2$){C(SiMe$_3$)$_3$} (**4a**) (400 MHz, C_6D_6).

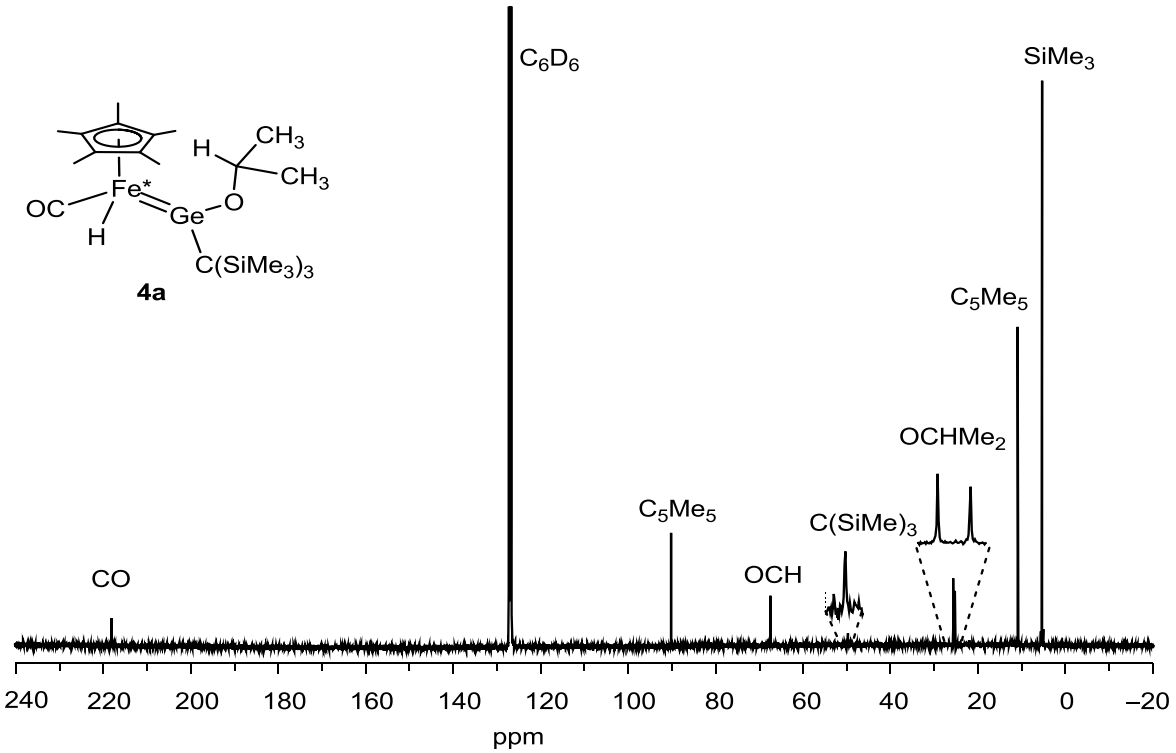

Figure 23. ^{13}C{^{1}H} NMR spectrum of Cp*(CO)(H)Fe=Ge(OCHMe$_2$){C(SiMe$_3$)$_3$} (**4a**) (100 MHz, C_6D_6).

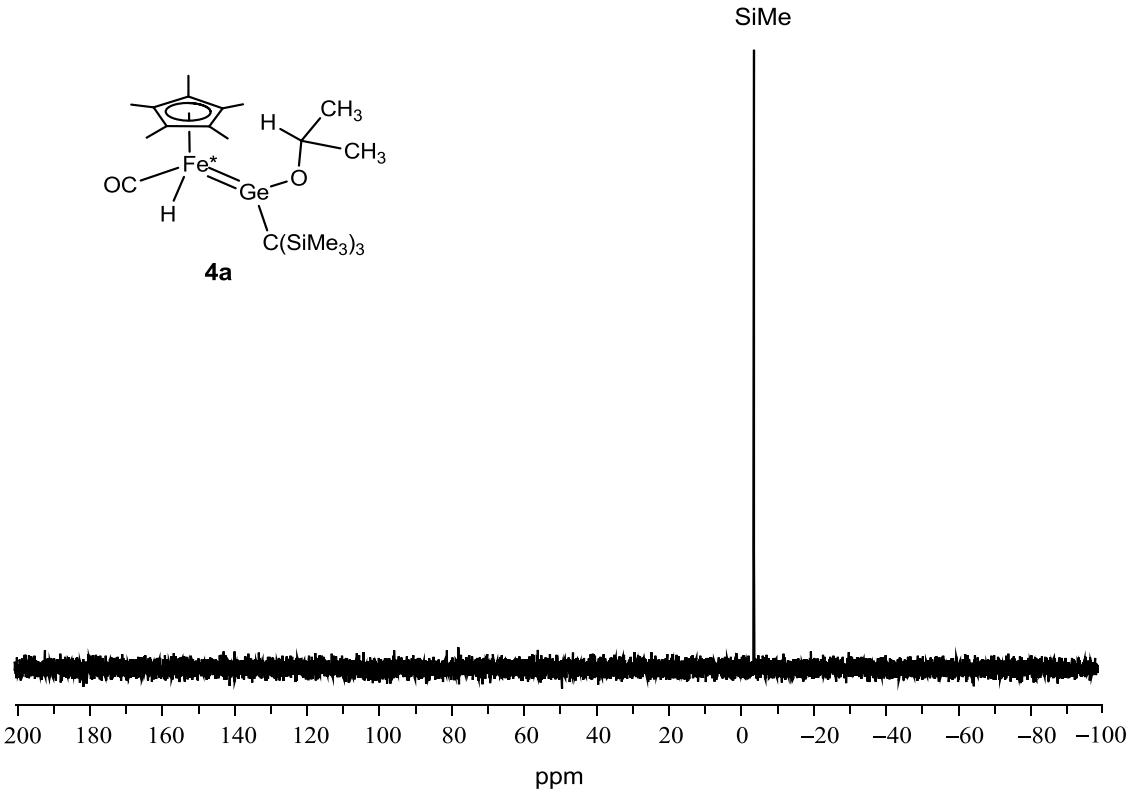

Figure S24. $^{29}Si\{^{1}H\}$ NMR spectrum of Cp*(CO)(H)Fe=Ge(OCHMe$_2$){C(SiMe$_3$)$_3$} (**4a**) (79.5 MHz, C_6D_6).

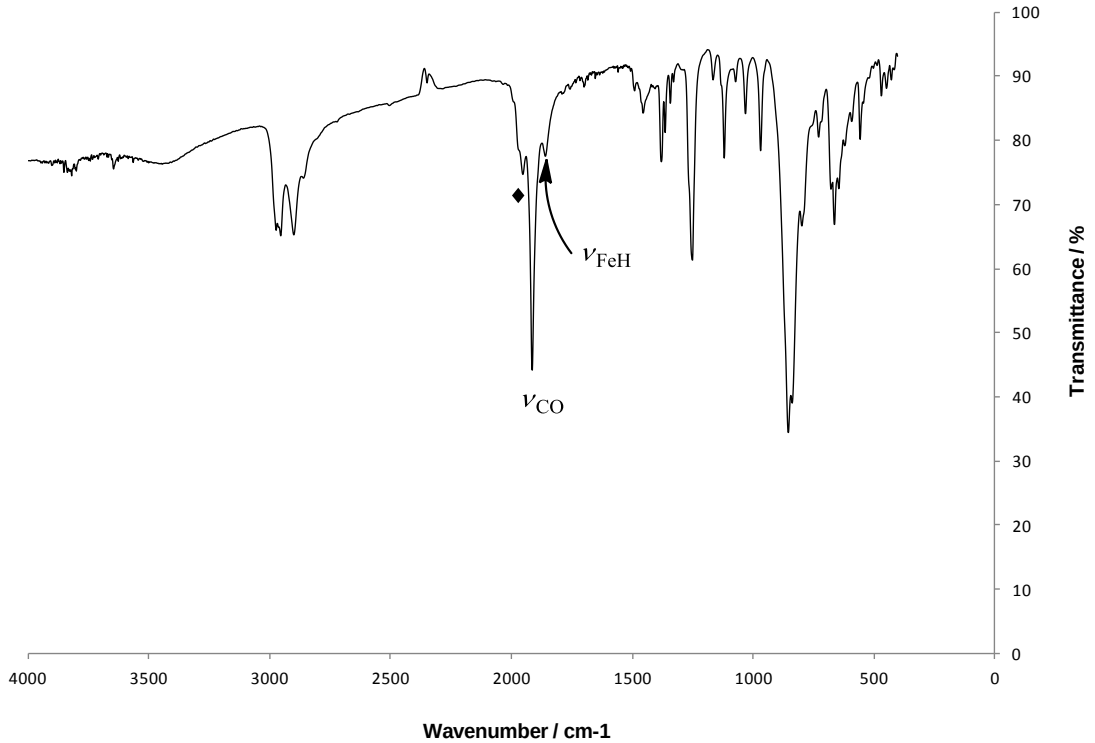

Figure S25. IR spectrum of Cp*(CO)(H)Fe=Ge(OCHMe$_2$){C(SiMe$_3$)$_3$} (**4a**) (KBr).
(The peak denoted by ♦ is attributable to a product of the decomposition of **4a** during the IR measurement: The ν_{CO} for **4a** changed into this peak after the KBr sample was exposed to air.)

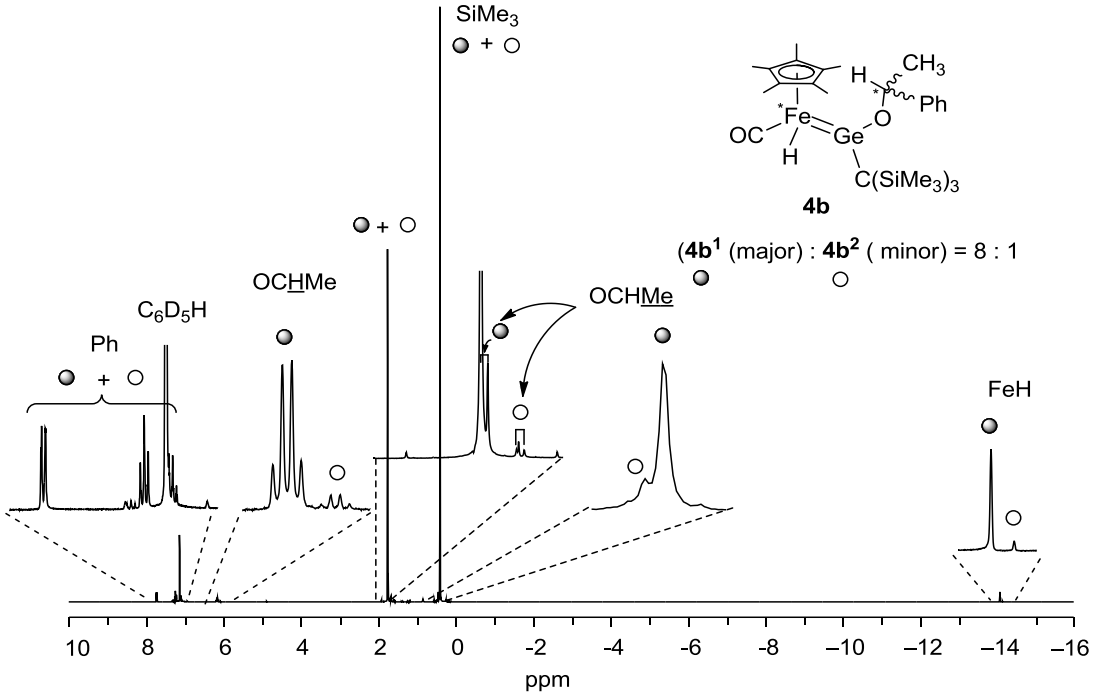

Figure S26. ^{1}H NMR Spectrum of Cp*(CO)(H)Fe=Ge(OCHMePh){C(SiMe$_3$)$_3$}(**4b**) (dr. 8:1) (400 MHz, C_6D_6).

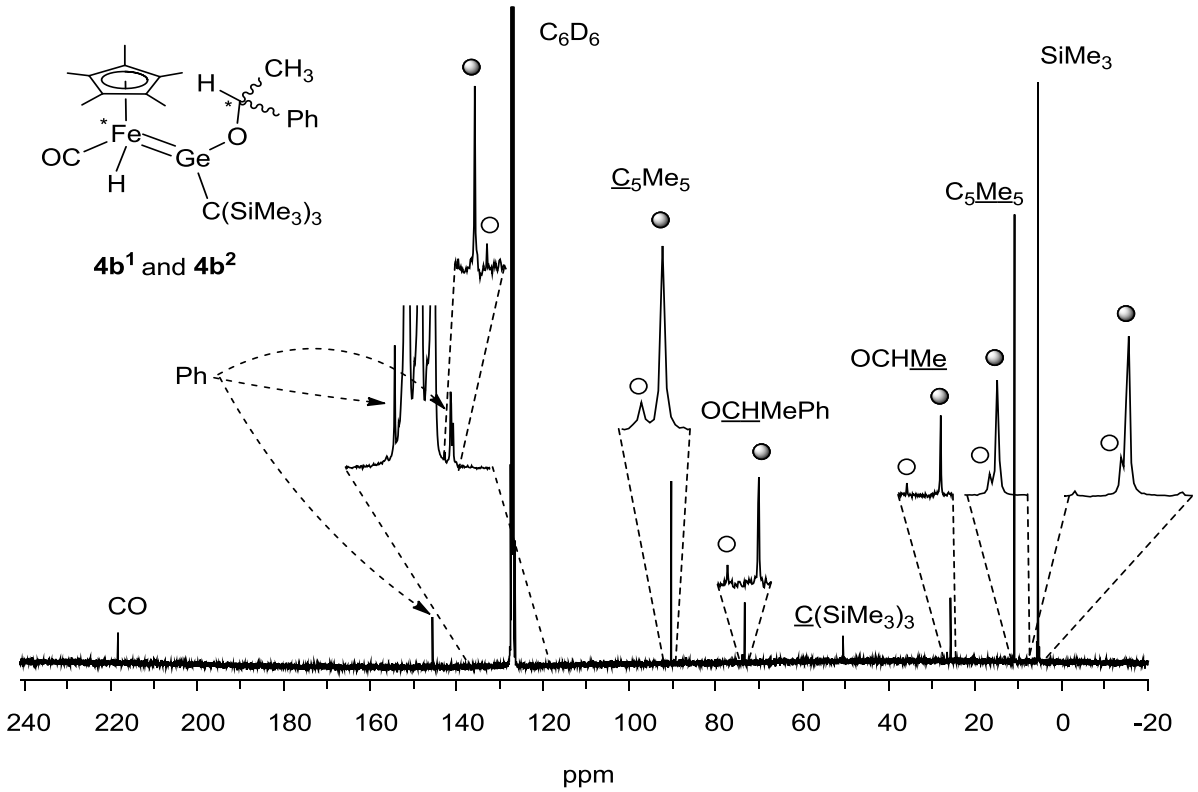

Figure S27. ^{13}C{^{1}H} NMR Spectrum of Cp*(CO)(H)Fe=Ge{OCHMePh}{C(SiMe$_3$)$_3$} (**4b**) (100 MHz, C_6D_6).

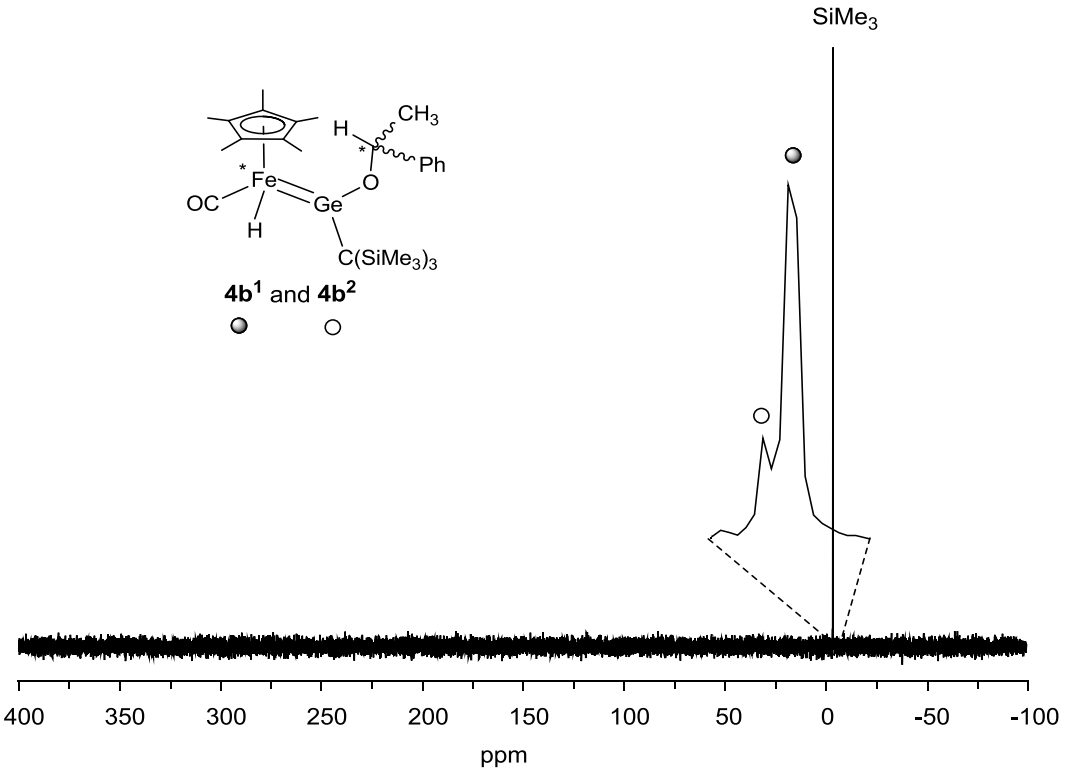

Figure S28. $^{29}Si\{^{1}H\}$ NMR Spectrum of Cp*(CO)(H)Fe=Ge(OCHMePh){$C(SiMe_3)_3$} (**4b**) (79.5 MHz, C_6D_6).

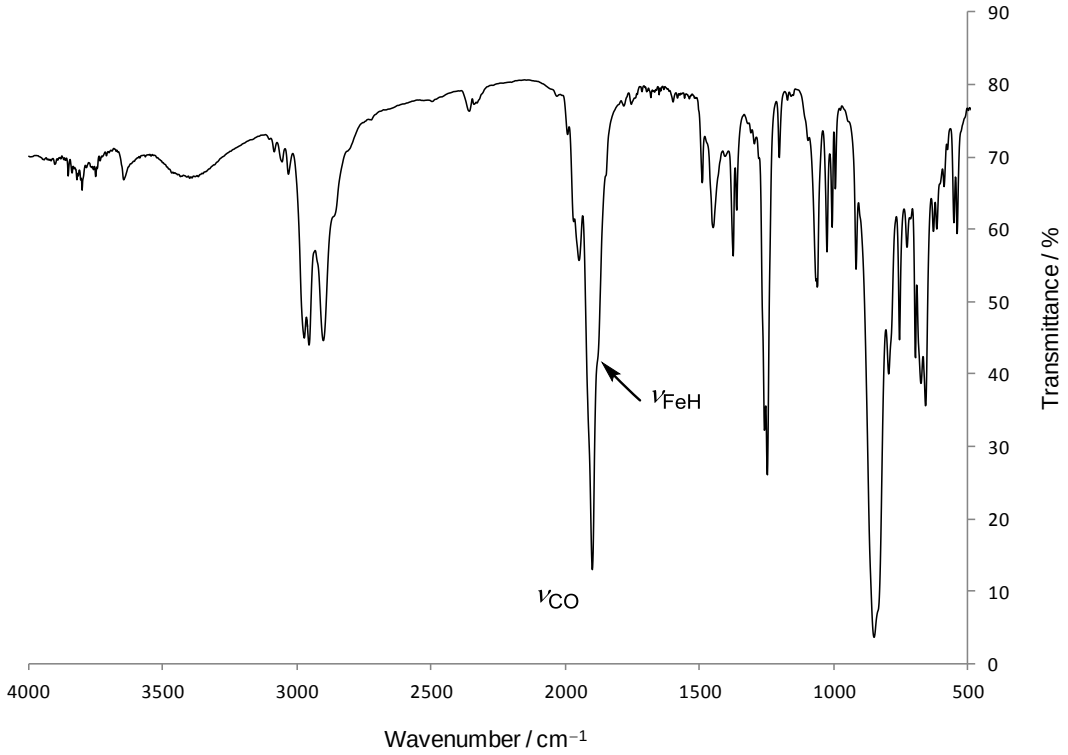

Figure S29. IR Spectrum of Cp*(CO)(H)FeGe(OCHMePh){$C(SiMe_3)_3$} (**4b**) (KBr).

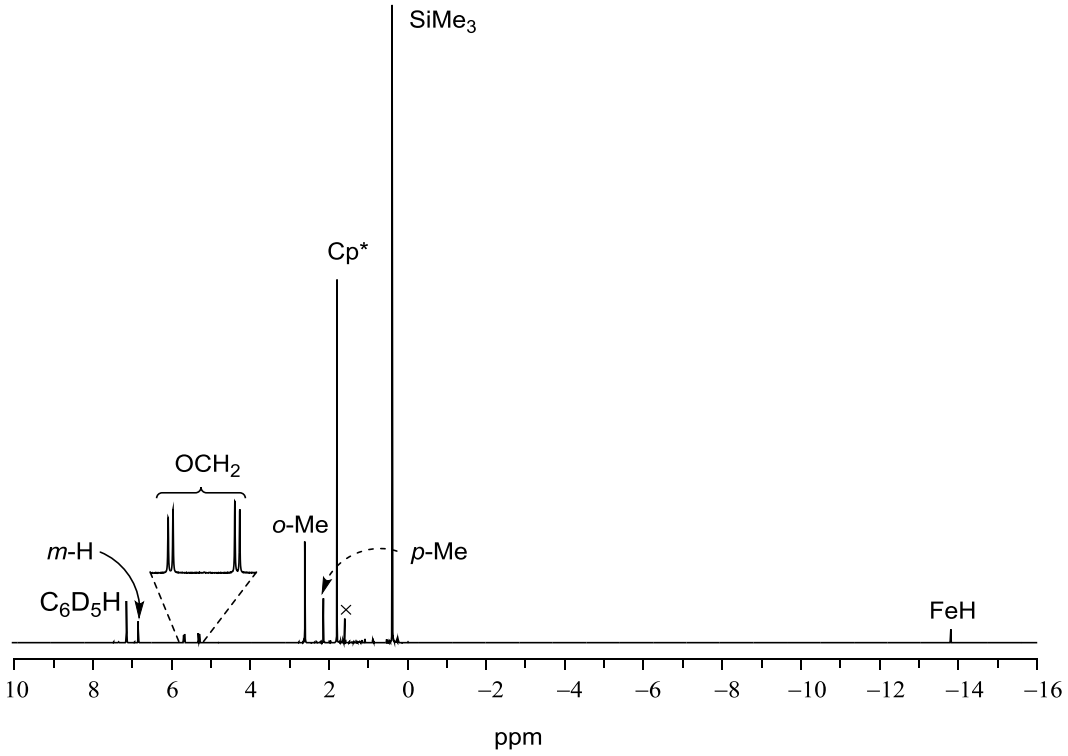

Figure S30. ^{1}H NMR Spectrum of Cp*(CO)(H)Fe=Ge(OCH$_2$Mes){C(SiMe$_3$)$_3$} (**5a**) (400 MHz, C_6D_6)

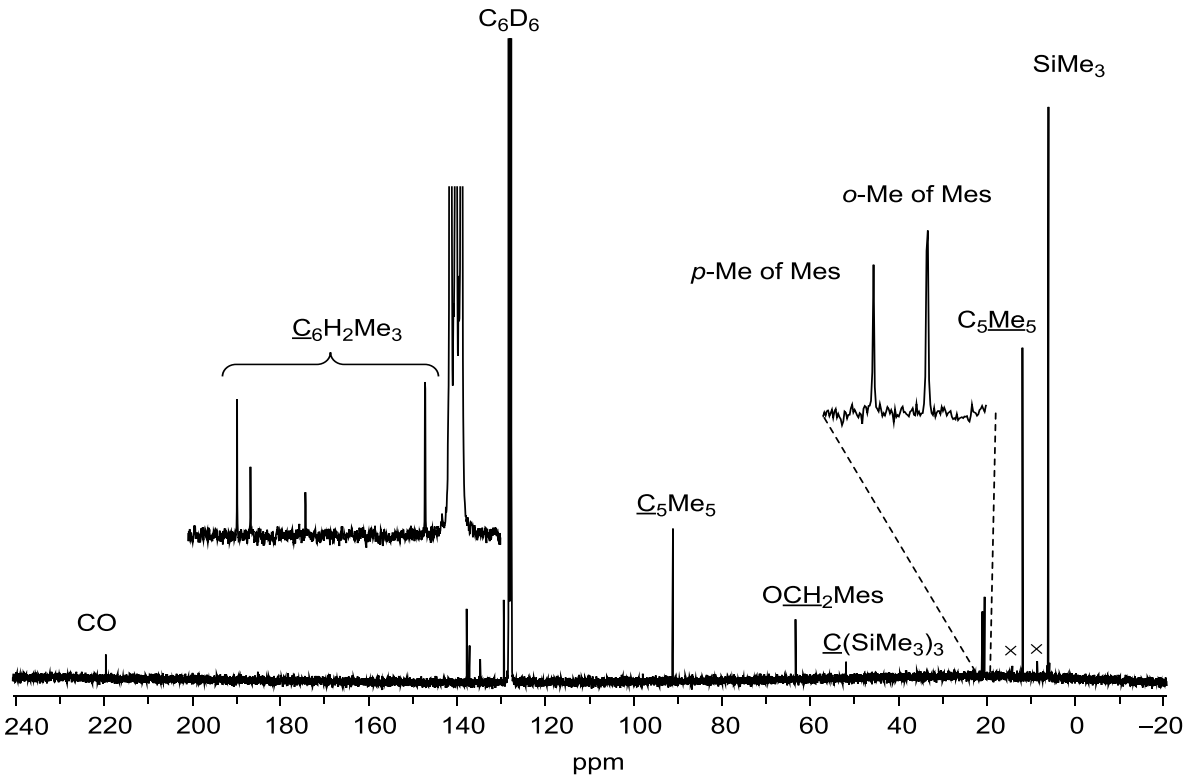

Figure S31. ^{13}C{^{1}H} NMR Spectrum of Cp*(CO)(H)Fe=Ge(OCH$_2$Mes){C(SiMe$_3$)$_3$} (**5a**) (100 MHz, C_6D_6).

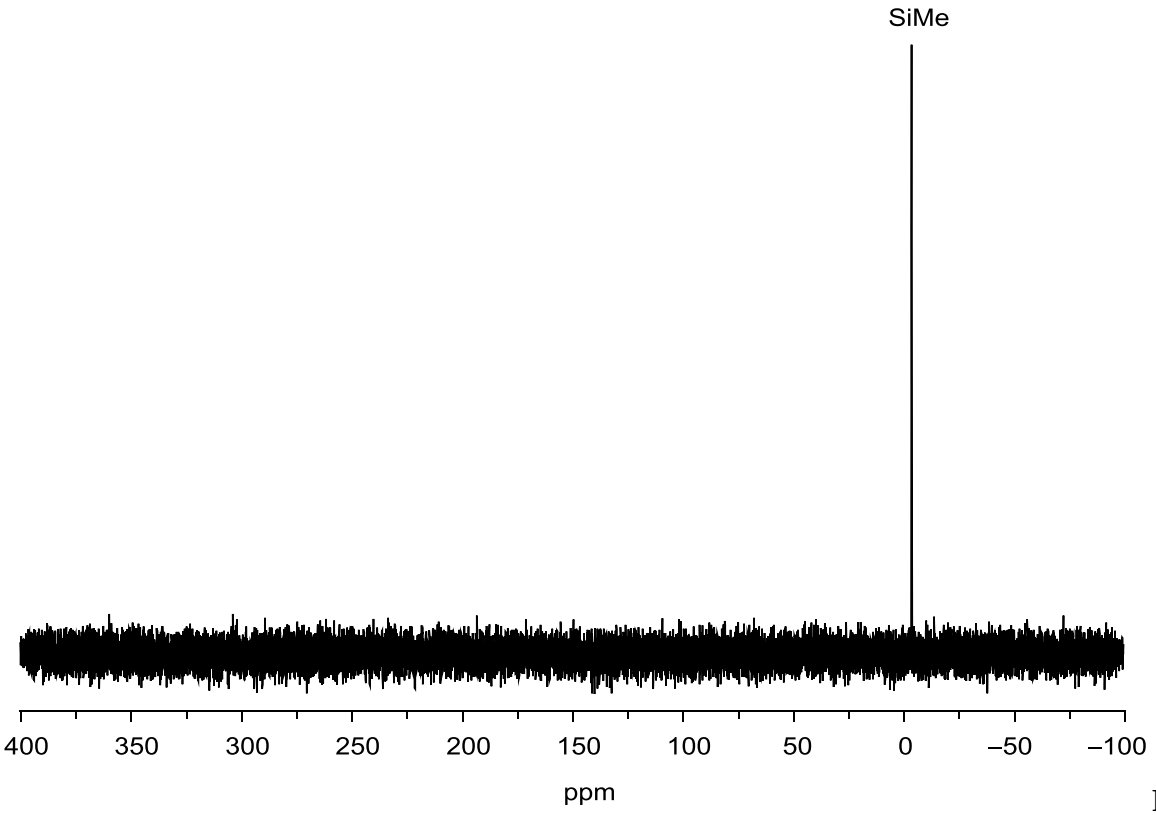

Figure S32. $^{29}Si\{^{1}H\}$ NMR Spectrum of Cp*(CO)(H)Fe=Ge(OCH_2Mes){$C(SiMe_3)_3$} (**5a**) (79.5 MHz, C_6D_6).

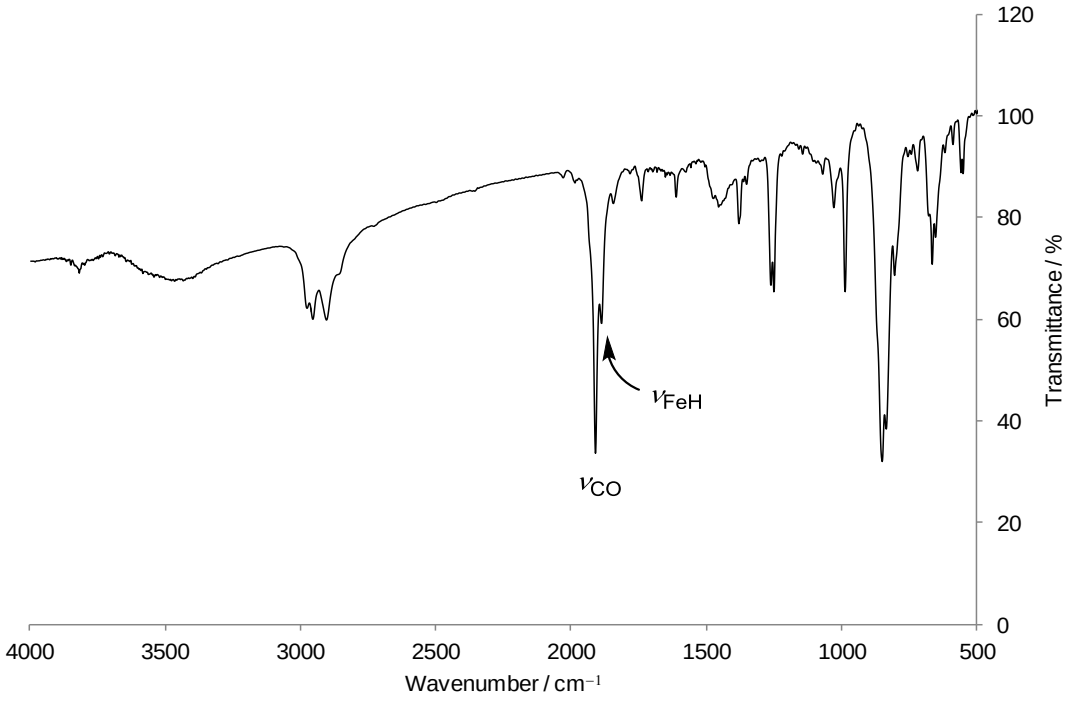

Figure S33. IR Spectrum of Cp*(CO)(H)Fe=Ge(OCH_2Mes){$C(SiMe_3)_3$} (**5a**) (KBr).

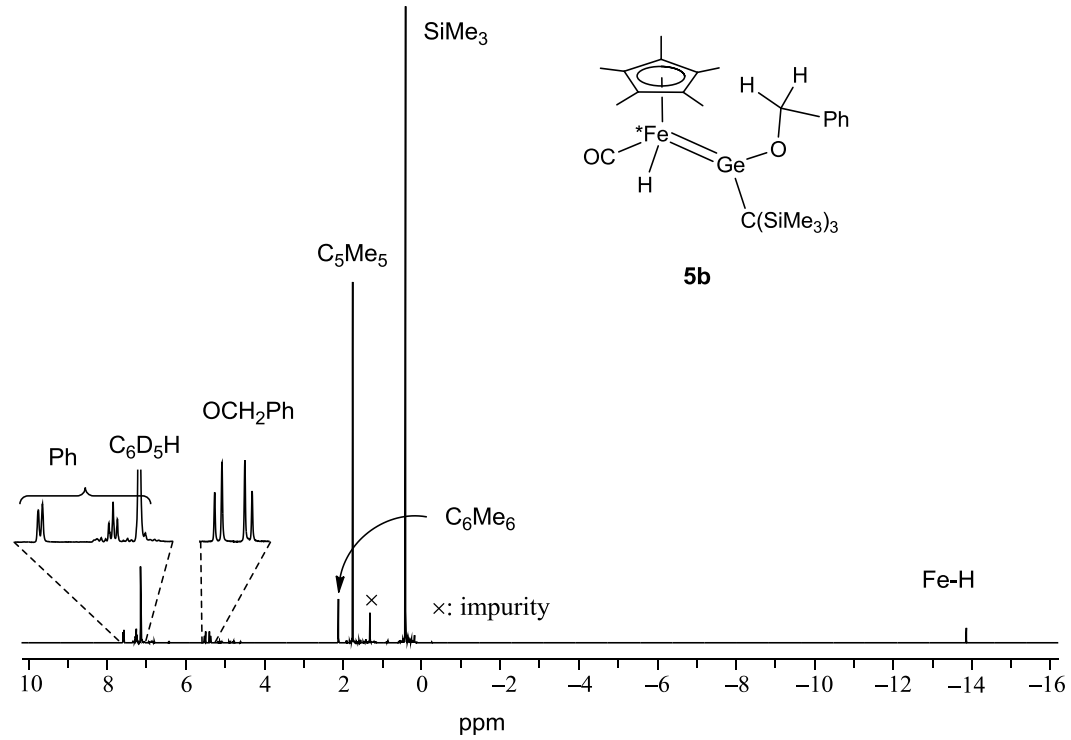

Figure S34. ^{1}H NMR Spectrum of Cp*(CO)(H)Fe=Ge(OCH$_2$Ph){C(SiMe$_3$)$_3$} (**5b**) (400 MHz, C$_6$D$_6$).

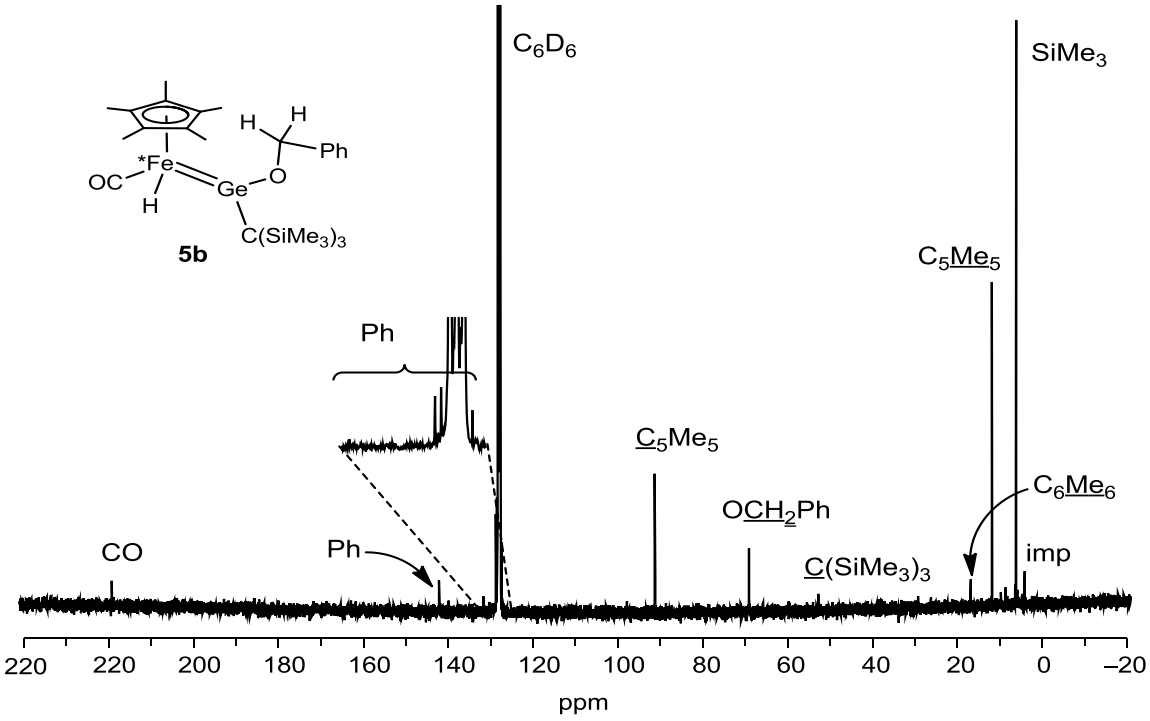

Figure S35. ^{13}C{^{1}H} NMR Spectrum of Cp*(CO)(H)Fe=Ge(OCH$_2$Ph){C(SiMe$_3$)$_3$} (**5b**) (100 MHz, C$_6$D$_6$).

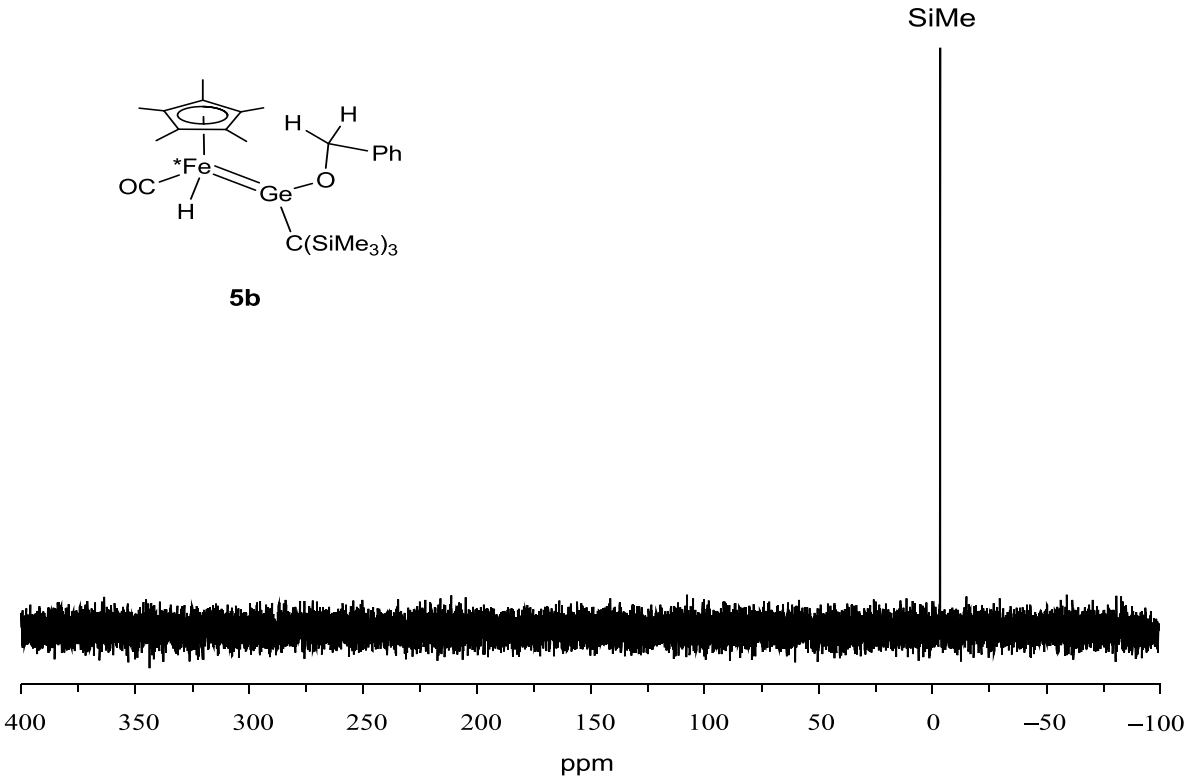

Figure S36. $^{29}Si\{^{1}H\}$ NMR Spectrum of Cp*(CO)(H)Fe=Ge(OCH$_2$Ph){C(SiMe$_3$)$_3$} (**5b**) (79.5 MHz, C_6D_6).

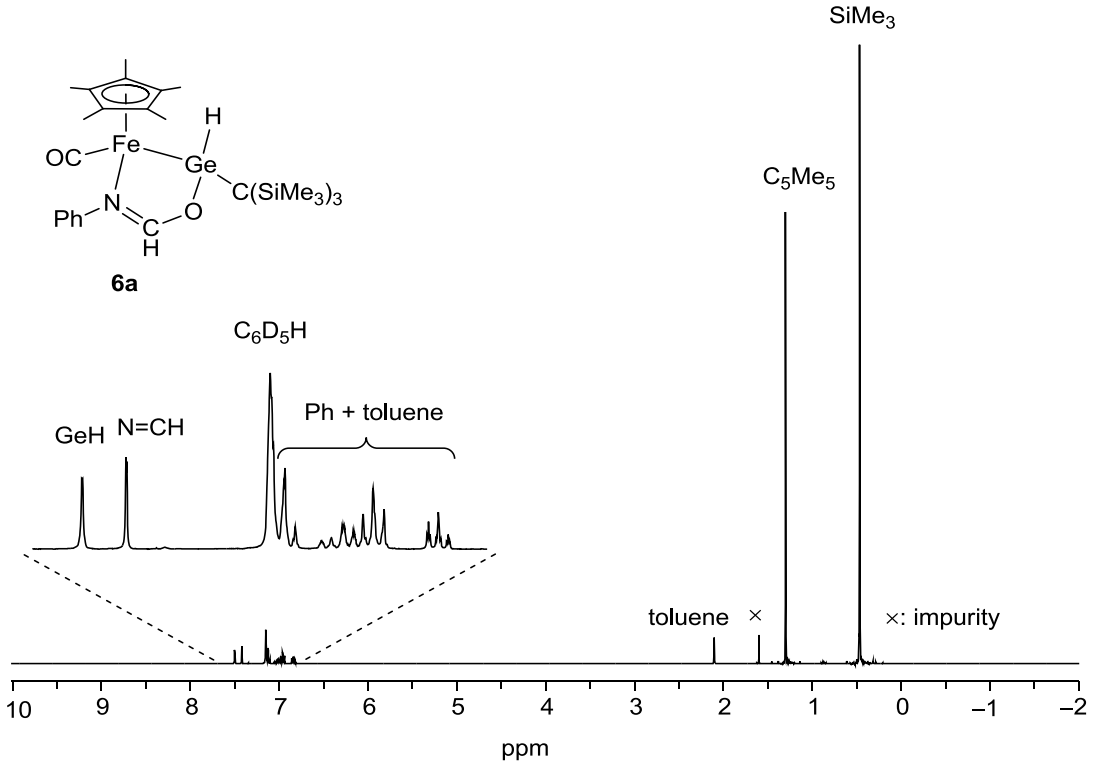

Figure S37. ^{1}H NMR spectrum of Cp*(CO)Fe[κ^2(*N*,*Ge*)-Ge(H)(OC(H)=NPh){C(SiMe$_3$)$_3$}] (**6a**·0.5C_7H_8) (400 MHz, C_6D_6).

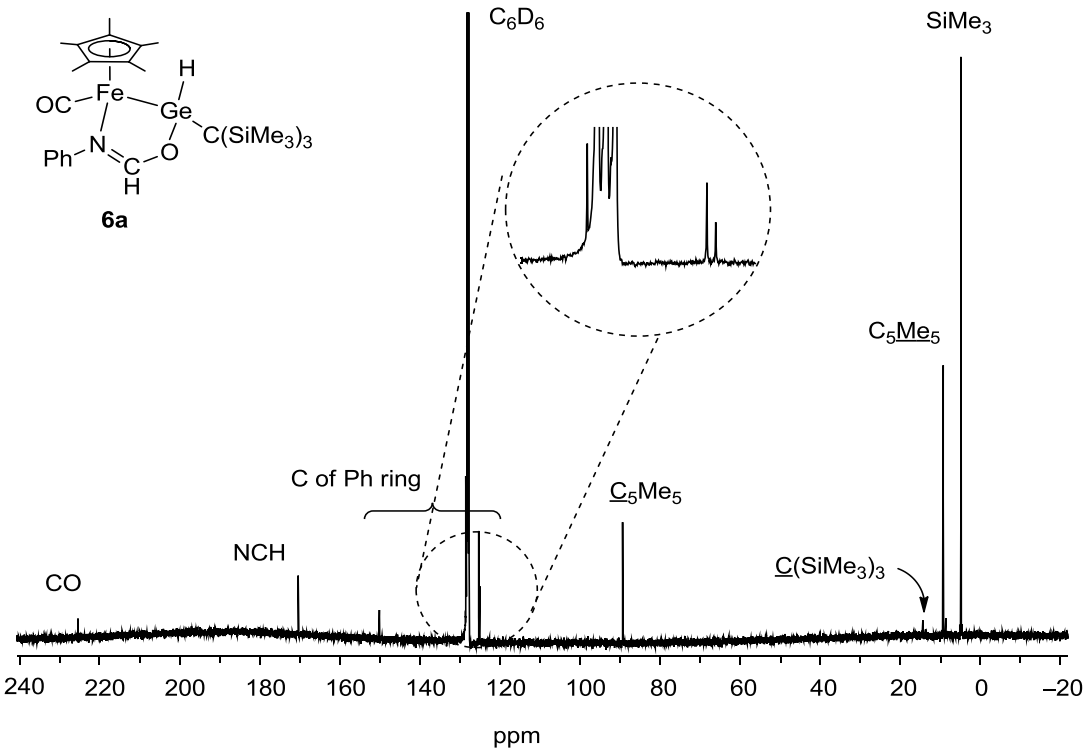

Figure S38. $^{13}C\{^{1}H\}$ NMR spectrum of Cp*(CO)Fe[κ^2(*N*,*Ge*)-Ge(H)(OC(H)=NPh){C($SiMe_3$)$_3$}] (**6a**) (100 MHz, C_6D_6).

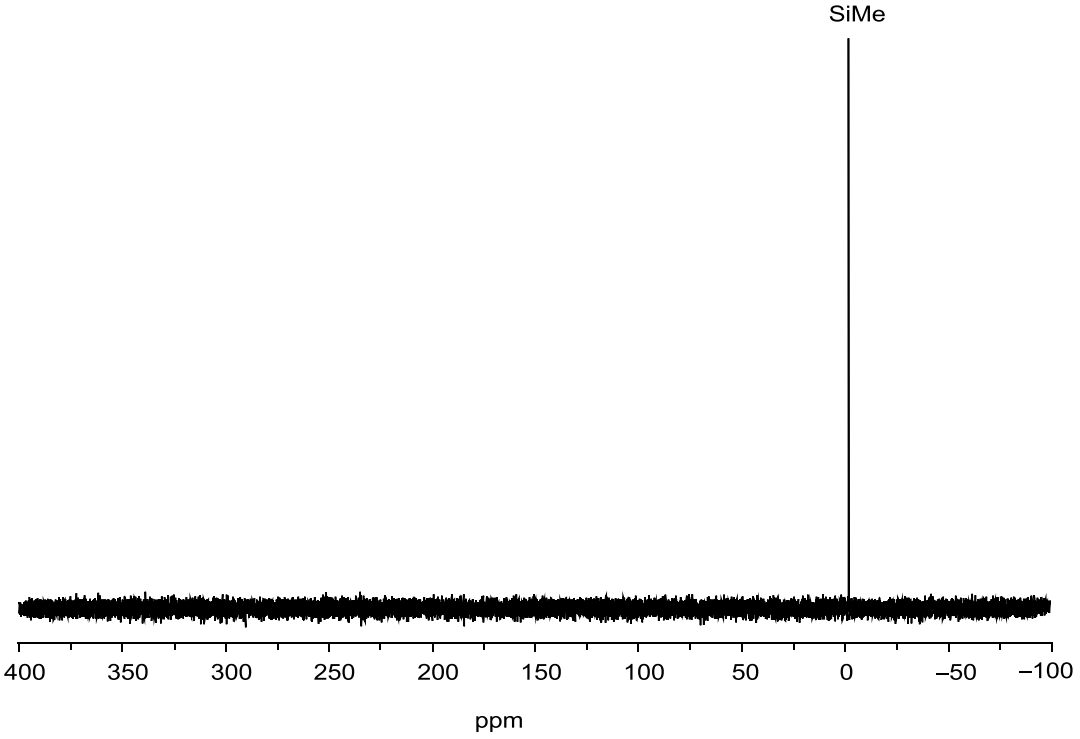

Figure S39. $^{29}Si\{^{1}H\}$ spectrum of Cp*(CO)Fe[κ^2(*N*,*Ge*)-Ge(H)(OC(H)=NPh){C($SiMe_3$)$_3$}] (**6a**) (79.5 MHz, C_6D_6).

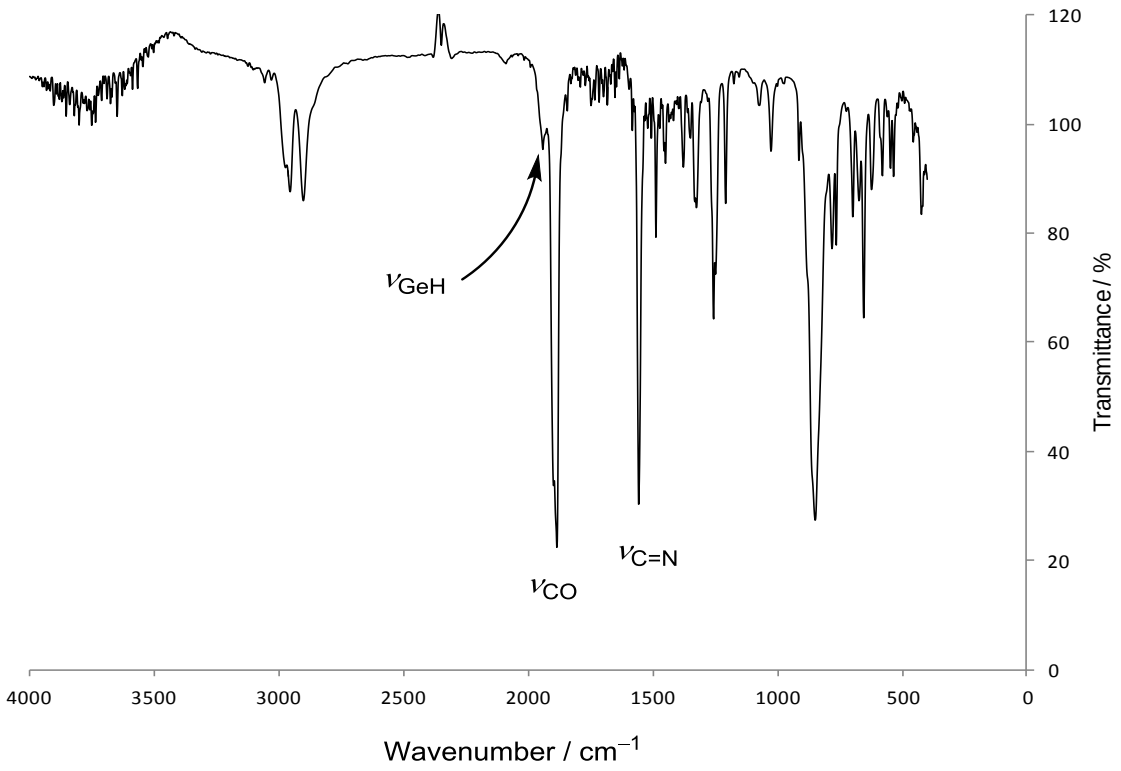

Figure S40. IR spectrum of Cp*(CO)Fe[κ^2(*N*,*Ge*)-Ge(H)(OC(H)=NPh){C(SiMe$_3$)$_3$}] (**6a**·0.5C$_7$H$_8$) (KBr).

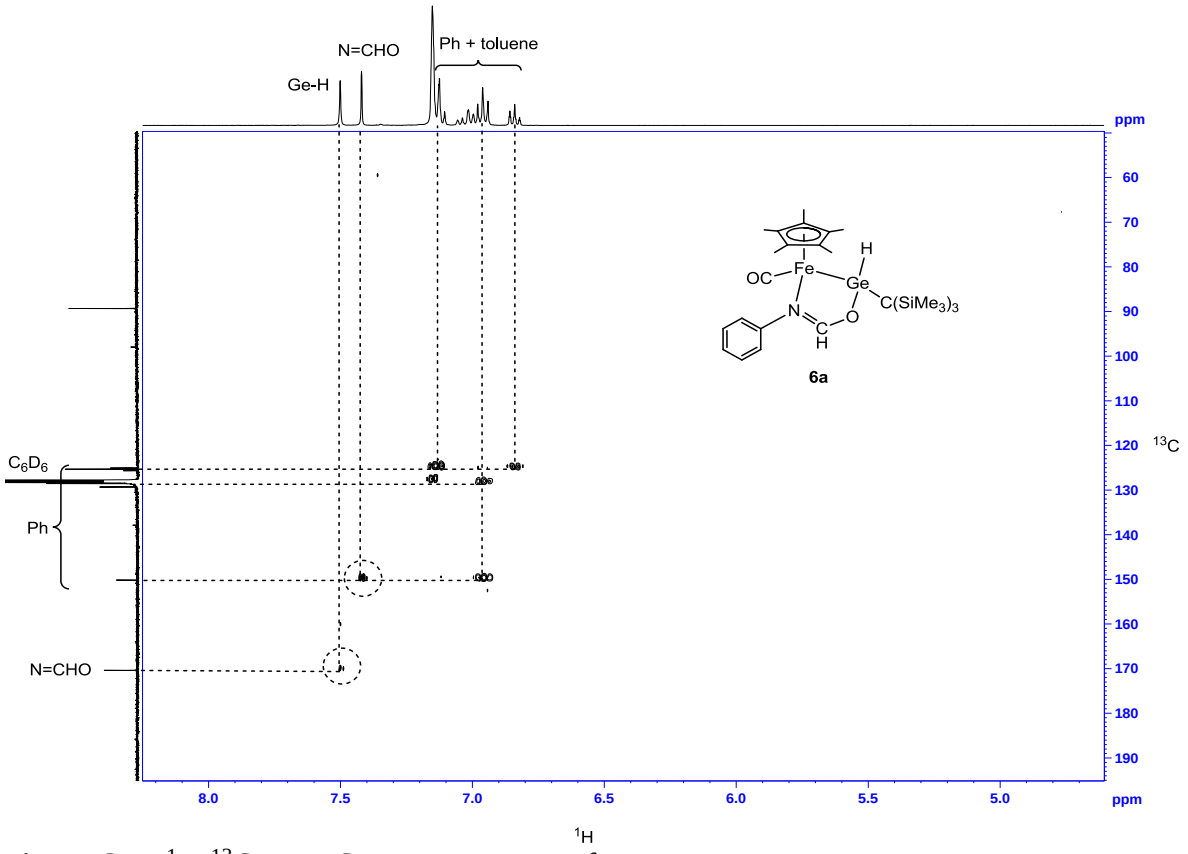

Figure S41. ^{1}H-^{13}C HMBC NMR spectrum of Cp*(CO)Fe[κ^2(*N*,*Ge*)-Ge(H)(OC(H)=NPh){C(SiMe$_3$)$_3$}] (**6a**·0.5 C$_7$H$_8$) (400 MHz, C$_6$D$_6$).

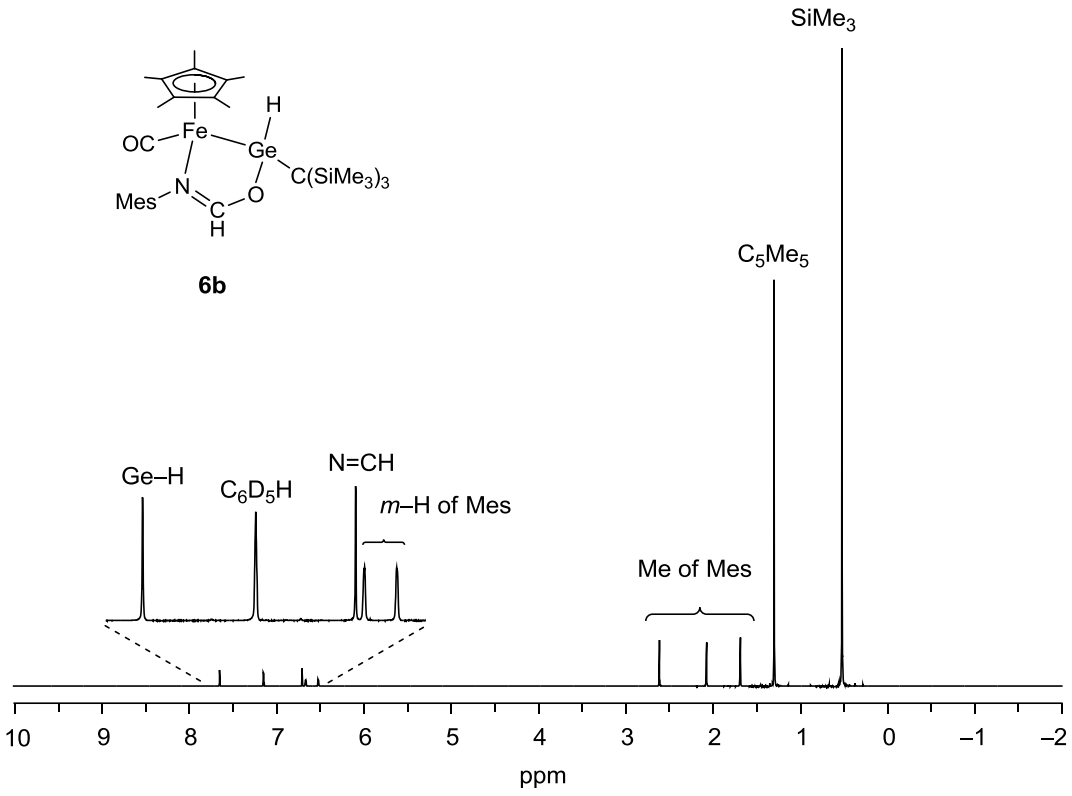

Figure S42. ^{1}H NMR spectrum of Cp*(CO)Fe[κ^{2}(*N*,*Ge*)-Ge(H)(OC(H)=NMes){C(SiMe$_3$)$_3$}] (**6b**) (400 MHz, C_6D_6).

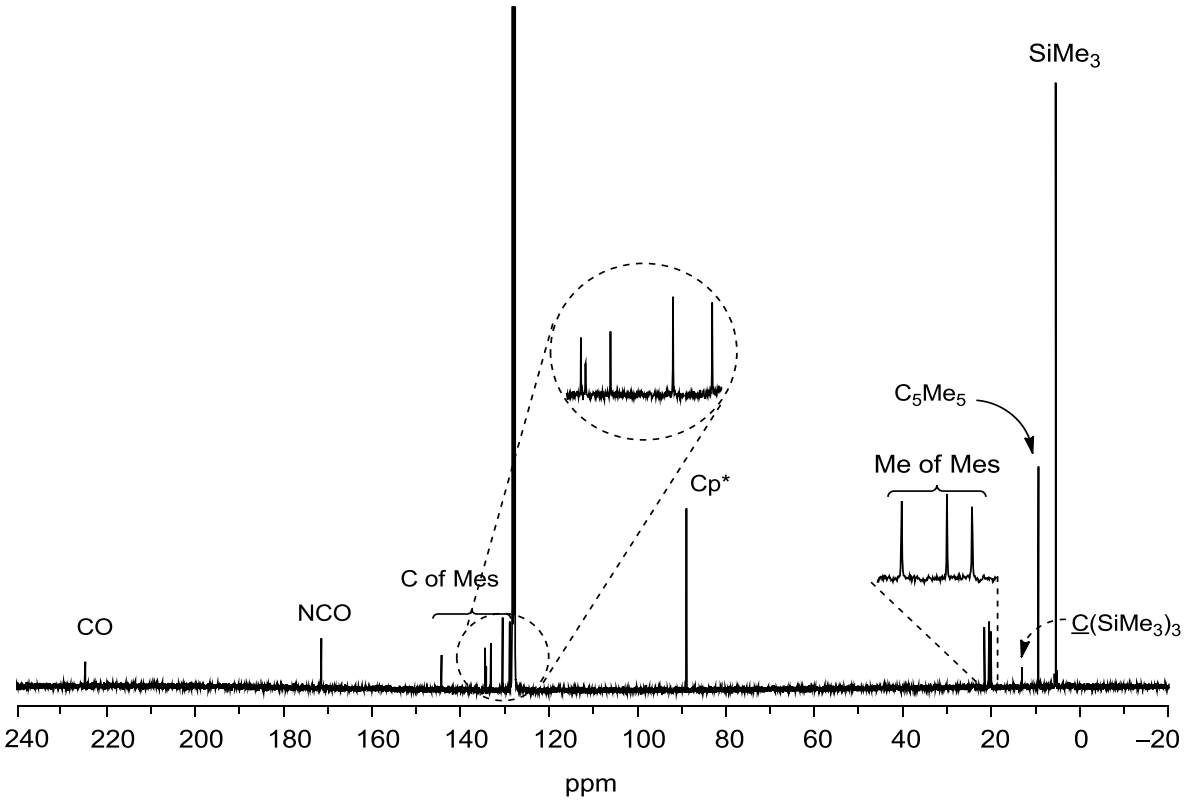

Figure S43. ^{13}C{^{1}H} NMR spectrum of Cp*(CO)Fe[κ^{2}(*N*,*Ge*)-Ge(H)(OC(H)=NMes){C(SiMe$_3$)$_3$}] (**6b**) (100 MHz, C_6D_6).

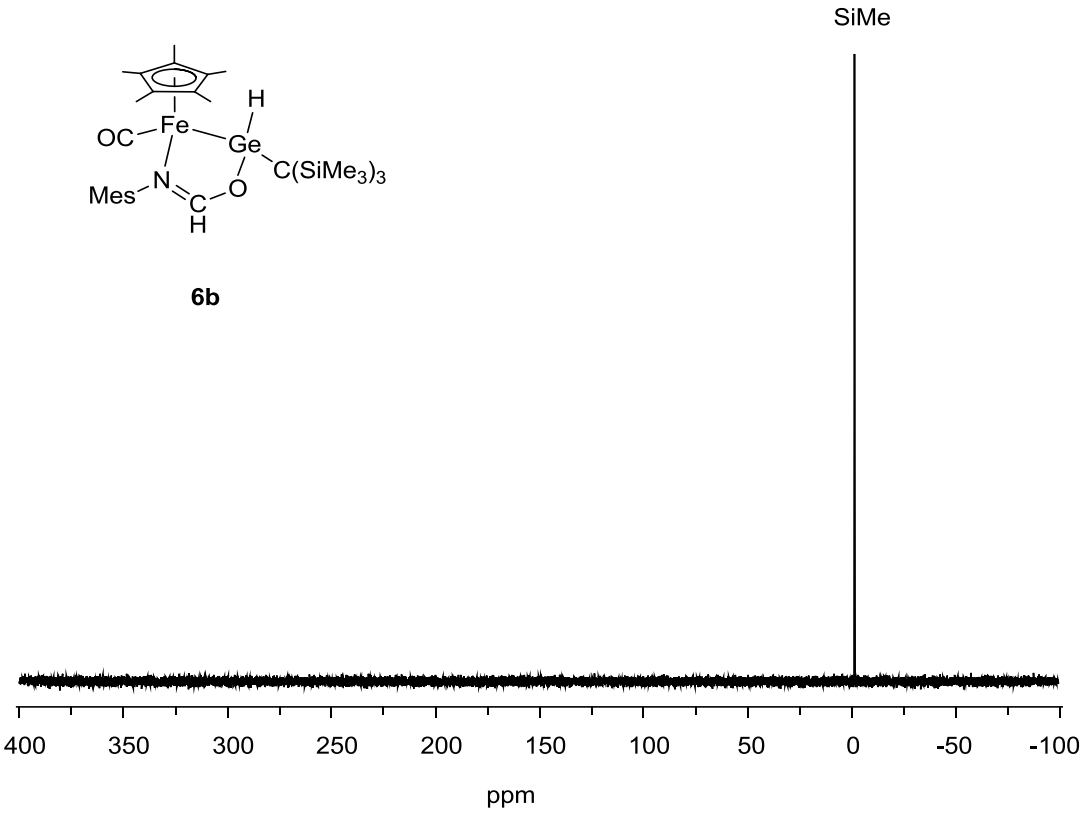

Figure S44. $^{29}Si\{^{1}H\}$ NMR spectrum of Cp*(CO)Fe[κ^2(*N*,*Ge*)-Ge(H)(OC(H)=NMes){C($SiMe_3$)$_3$}] (**6b**) (79.5 MHz, C_6D_6).

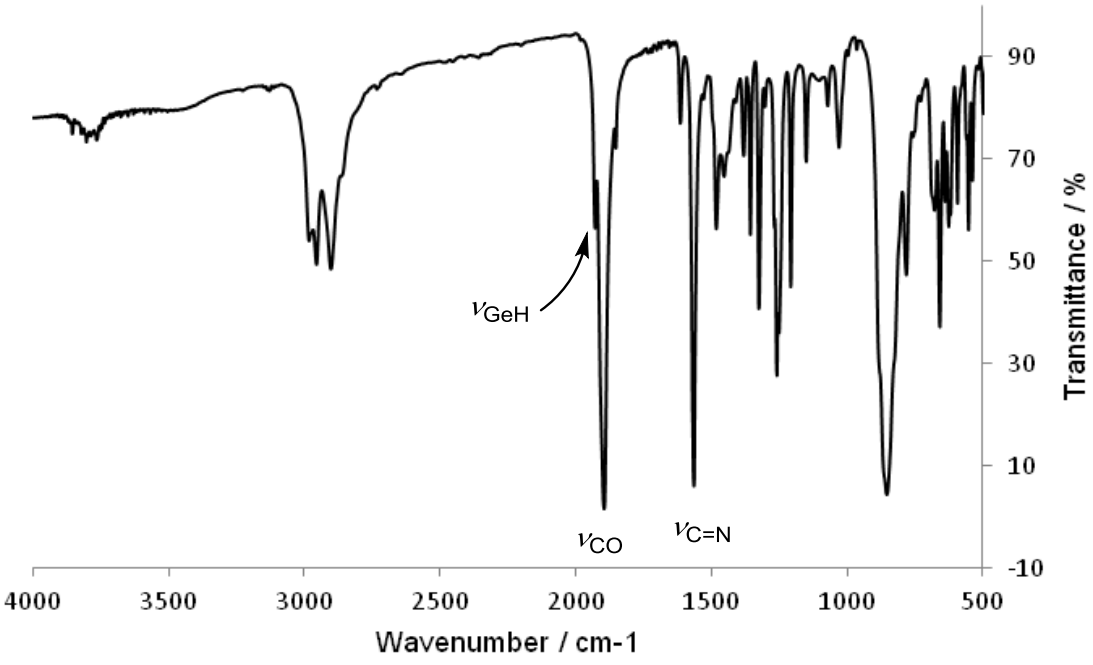

Figure S45. IR spectrum of Cp*(CO)Fe[κ^2(*N*,*Ge*)-Ge(H)(OC(H)=NMes){C($SiMe_3$)$_3$}] (**6b**) (KBr).

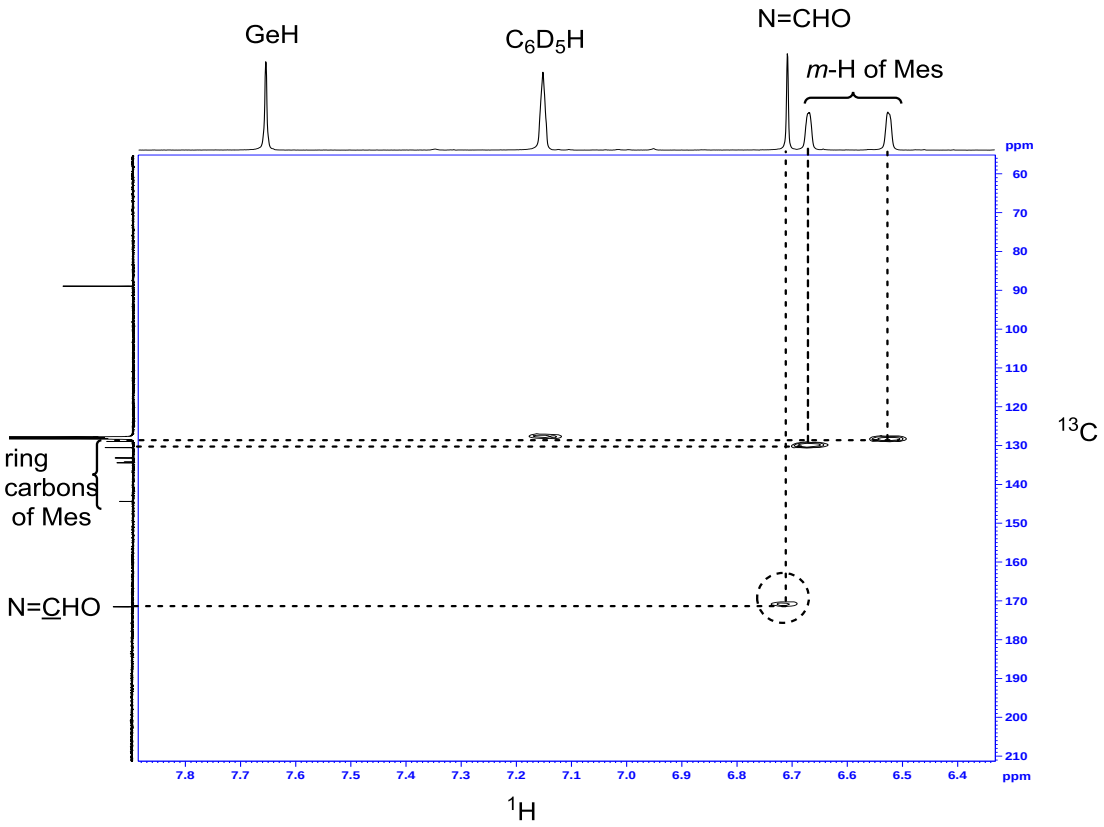

Figure S46. ^{1}H-^{13}C HSQC NMR spectrum of Cp*(CO)Fe[κ^2(*N*,*Ge*)-Ge(H)(OC(H)=NMes){C(SiMe$_3$)$_3$}] (**6b**) (400 MHz, C_6D_6).

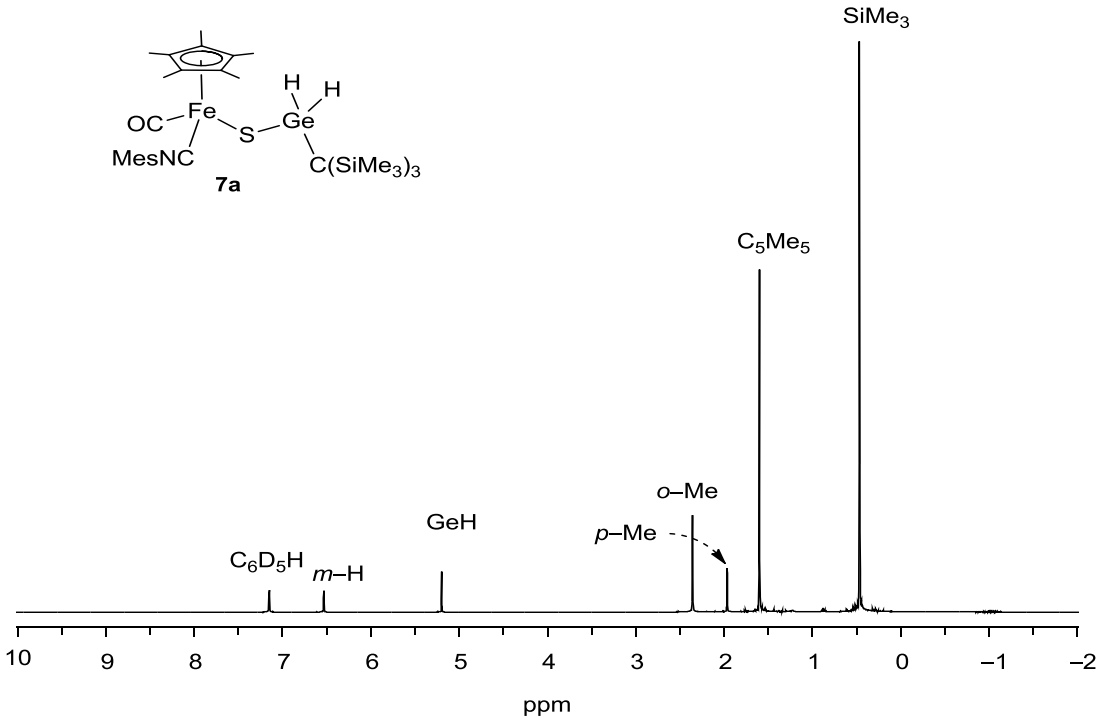

Figure S47. ^{1}H NMR spectrum of Cp*(CO)(MesNC)FeSGeH$_2${C(SiMe$_3$)$_3$} (**7a**) (400 MHz, C_6D_6).

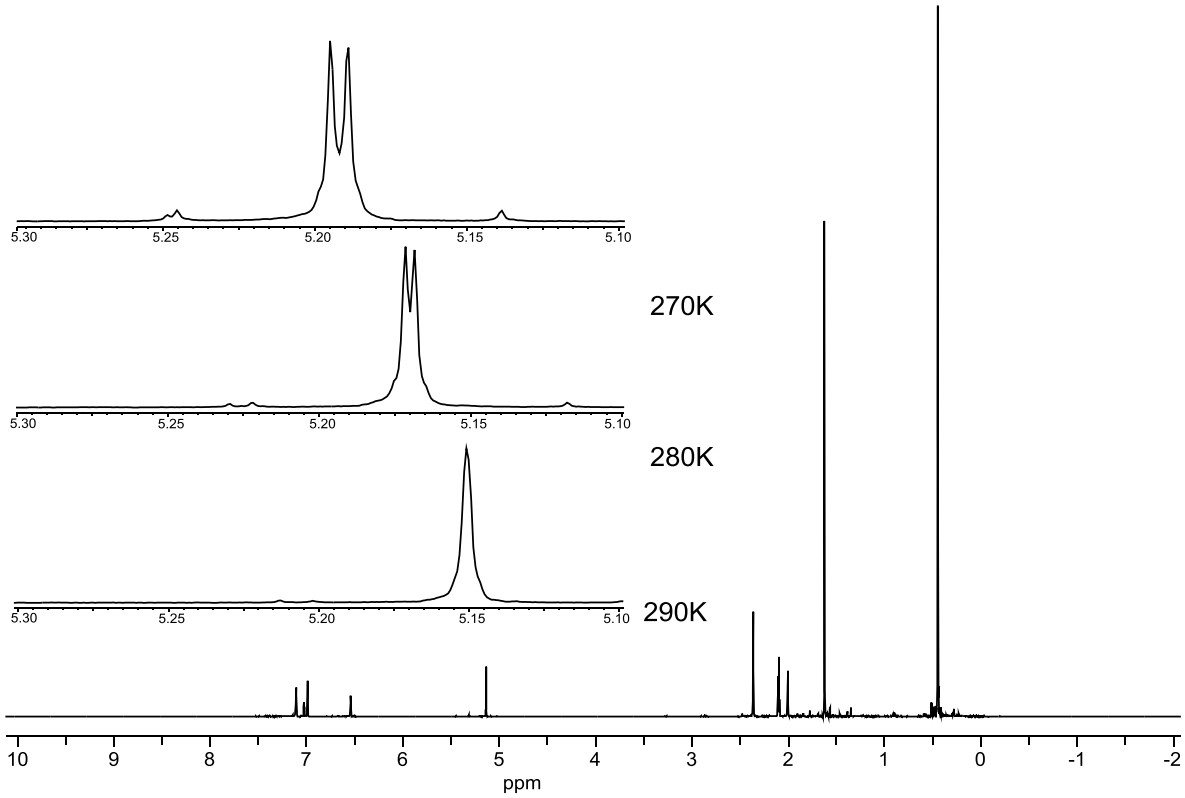

Figure S48. Variable temperature (VT)-^{1}H NMR spectra of Cp*(CO)(MesNC)FeSGeH$_2${C(SiMe$_3$)$_3$} (**7a**) (400 MHz, C_7D_8).

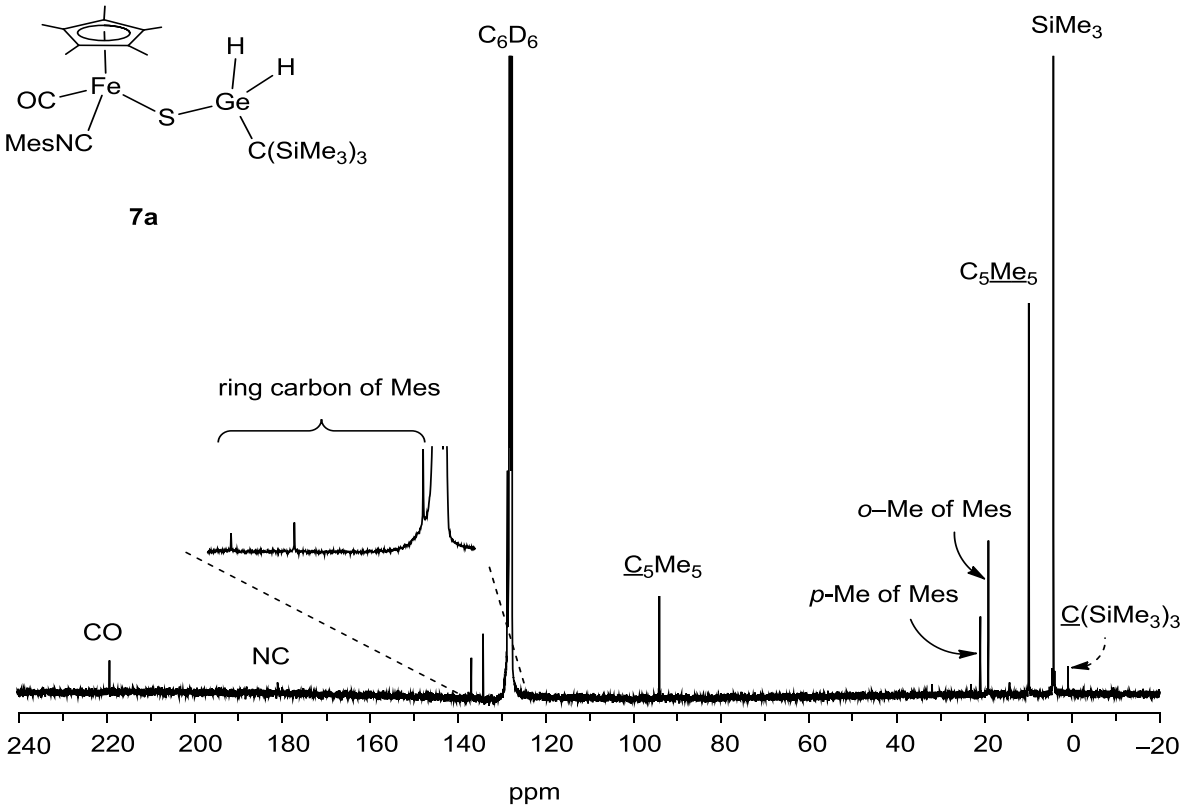

Figure S49. ^{13}C{^{1}H} NMR spectrum of Cp*(CO)(MesNC)FeSGeH$_2${C(SiMe$_3$)$_3$}) (**7a**) (100 MHz. C_6D_6).

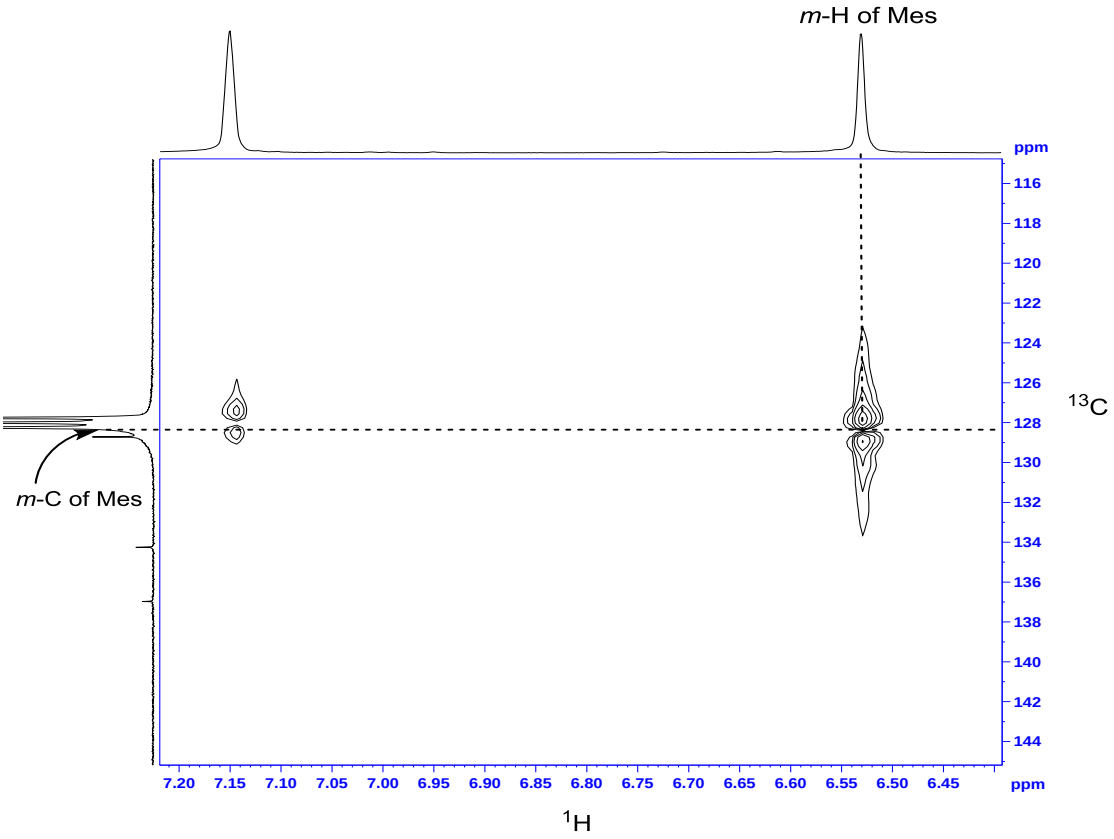

Figure S50. ^{1}H-^{13}C HSQC NMR spectrum of Cp*(CO)(MesNC)FeSGeH$_2${C(SiMe$_3$)$_3$}] (**7a**) (400 MHz, C_6D_6).

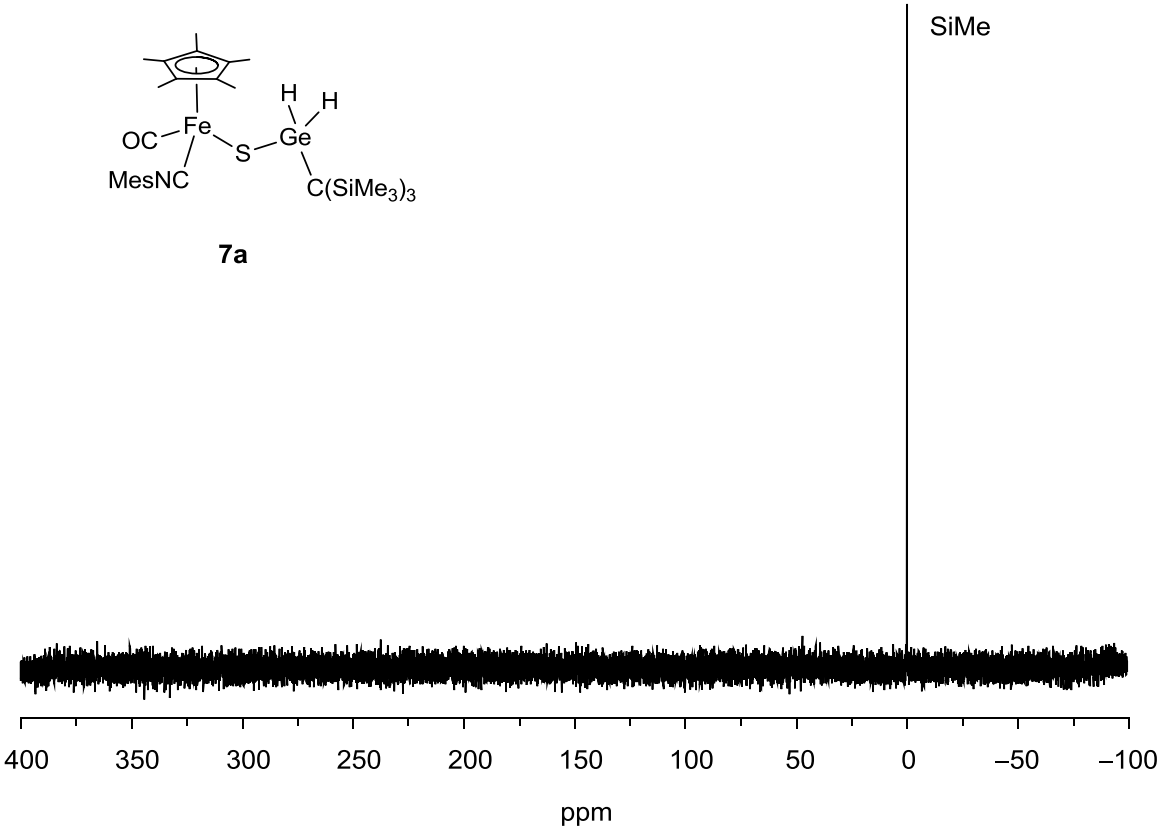

Figure S51. ^{29}Si{^{1}H} NMR spectrum of Cp*(CO)(MesNC)FeSGeH$_2${C(SiMe$_3$)$_3$} (**7a**) (79.5 MHz, C_6D_6).

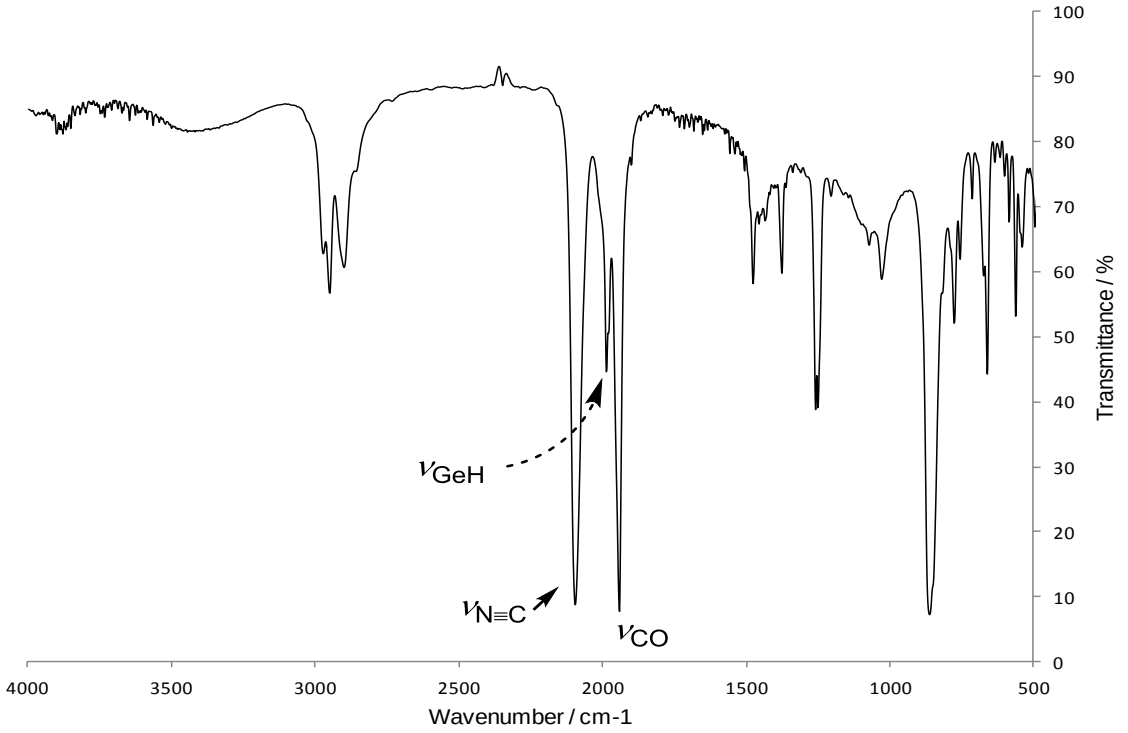

Figure S52. IR spectrum of Cp*(CO)(MesNC)FeSGeH$_2${C(SiMe$_3$)$_3$} (**7a**) (KBr).

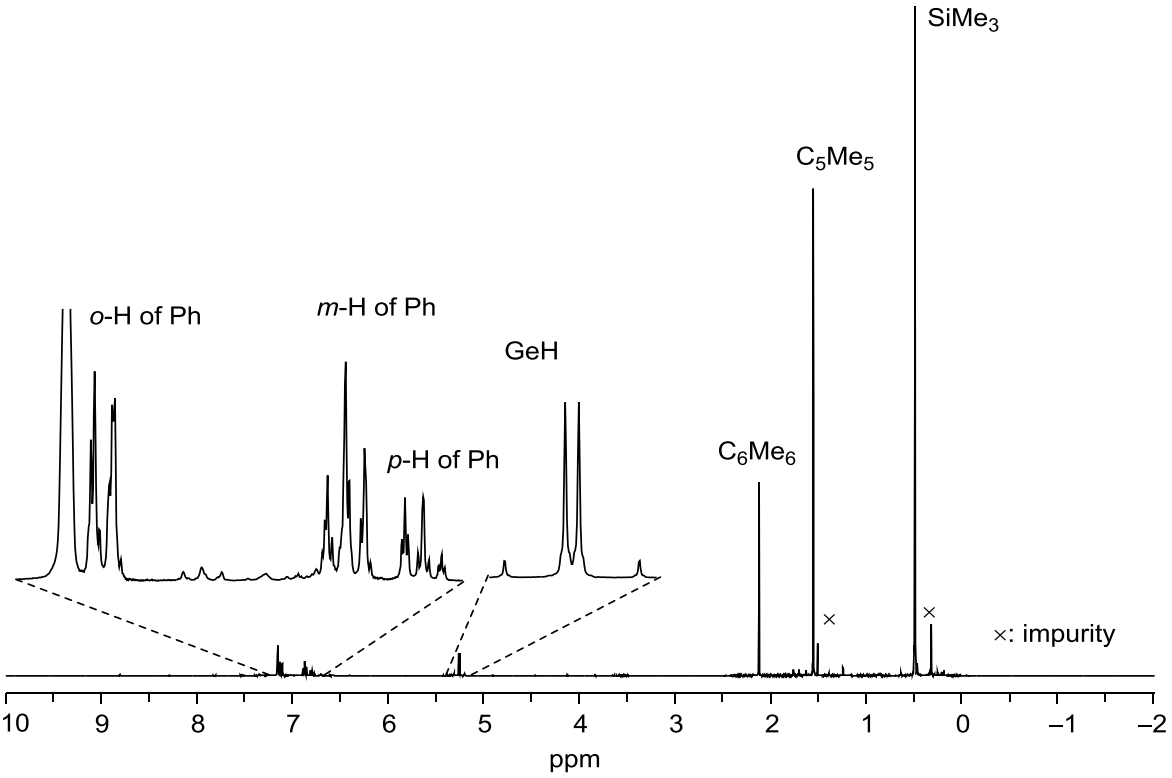

Figure S53. ^{1}H NMR spectrum of Cp*(CO)(PhNC)FeSGeH$_2${C(SiMe$_3$)$_3$} (**7b**) (400 MHz, C$_6$D$_6$).

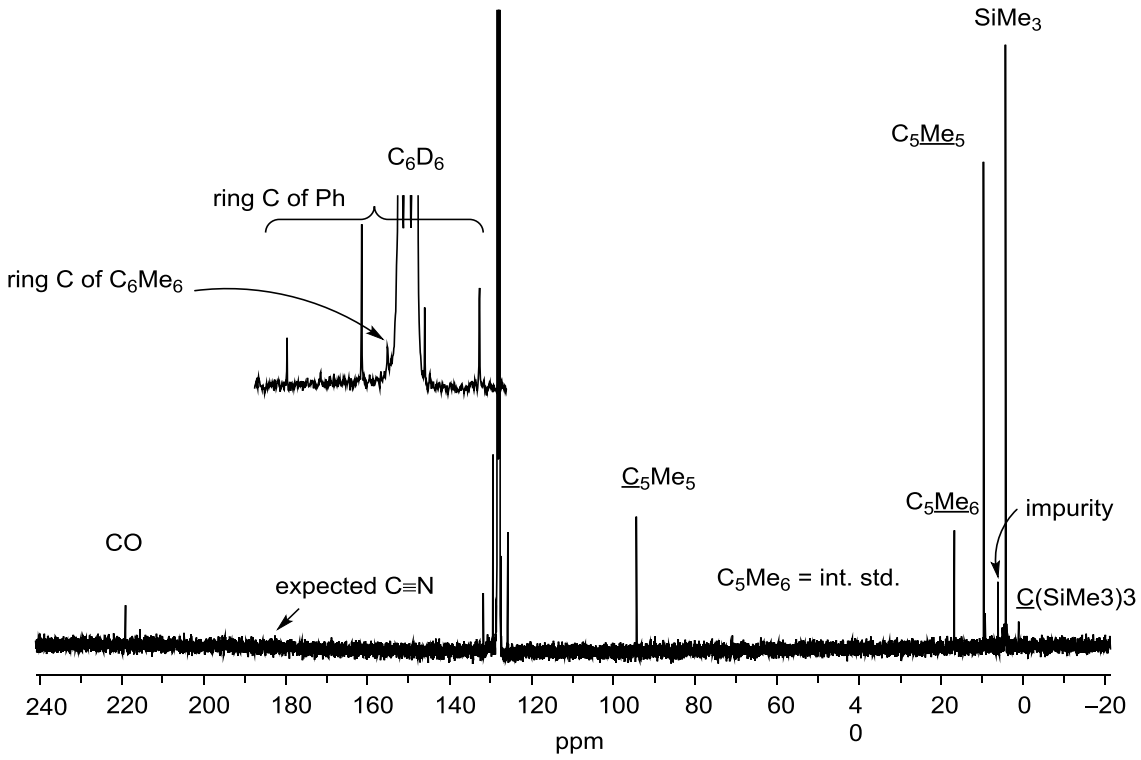

Figure S54. ^{13}C NMR spectrum of Cp*(CO)(PhNC)FeSGeH$_2${C(SiMe$_3$)$_3$} (**7b**) (100 MHz, C_6D_6).

2. X-ray crystallographic analysis (additional comments) and crystal data

Treatment of the positions of hydrogen atoms and some specific comments are as follows:

For Cp*(CO)(H)Fe=Ge(H){C(SiMe$_3$)$_3$} (**1**), the position of both hydrogen atoms of GeH and FeH groups were found from difference Fourier electron density map and were refined with isotropic thermal parameters.

For Cp*(CO)(py)FeGeH$_2${C(SiMe$_3$)$_3$} (**2**), the position of the hydrogen atom of one of two GeH groups for **2** was found and refined isotropically.

For Cp*(CO)(2,4,6-Me$_3$C$_6$H$_2$CN)FeGe(H)$_2${C(SiMe$_3$)$_3$·0.5C$_7$H$_8$ (**3b**·0.5 C$_7$H$_8$), 0.5 molecule of C$_7$H$_8$ was contained in a unit cell of the crystal. The Ge atoms were disordered in two positions (Ge1:95%, Ge2:5%), and the Ge1 atom was refined anisotropically, while the Ge2 atom was refined isotropically. The positions of both hydrogen atoms bound to the Ge1 atom were found and refined isotropically.

For Cp*(CO)(H)Fe=Ge(OCH$_2$Mes){C(SiMe$_3$)$_3$} (**5a**), the position of the hydrogen atom of Fe-H was not found from the difference Fourier electron density map. The positions of C(1) and O(2) were disordered in two positions (61%, 39%) and refined aniisotropically.

For Cp*(CO)Fe[κ^2(*N*,*Ge*)-Ge(H)(O-C(H)=NPh){C(SiMe$_3$)$_3$} (**6a**·C$_7$H$_8$), one molecule of toluene (C$_7$H$_8$) was incorporated in a unit cell in the crystal. The position of the hydrogen atom of Ge-H was found and refined isotropically.

For Cp*(CO)Fe[κ^2(*N*,*Ge*)-Ge(H)(O-C(H)=NMes){C(SiMe$_3$)$_3$}(**6b**), the position of the hydrogen atom of Ge-H was found and refined isotropically.

For Cp*(CO)(2,4,6-Me$_3$C$_6$H$_2$NC)Fe[SGeH$_2${C(SiMe$_3$)$_3$}] (**7a**), The positions of both hydrogen atoms of two GeH groups were found and refined isotropically.

Table S2 Crystal data and structure refinement for Cp*(CO)(H)Fe=Ge(H){C(SiMe$_3$)$_3$} (**1**)

Empirical formula	C_{21} H_{44} Fe Ge O Si_3
Formula weight	525.27
Temperature	150(2) K
Wavelength	0.71069 Å
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a = 11.4411(6) Å
	b = 13.8940(9) Å
	c = 16.9772(9) Å
Volume	2698.7(3) Å^3
Z	4
Density (calculated)	1.293 g/cm^3
Absorption coefficient	1.794 mm^{-1}
F(000)	1112
Crystal size	0.25 x 0.25 x 0.25 mm^3
Theta range for data collection	1.89 to 27.47°
Index ranges	$-14 \le h \le 14$, $-18 \le k \le 17$, $-21 \le l \le 22$
Reflections collected	35610
Independent reflections	6169 [R(int) = 0.1125]
Reflections with $I > 2\sigma(I)$	5716
Completeness to θ = 25.24°	100.0 %
Absorption correction	Numerical
Max. and min. transmission	0.831153 and 0.695998
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6169 / 0 / 266
Goodness-of-fit on F^2	1.081
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0462, wR2 = 0.0997
R indices (all data)	R1 = 0.0519, wR2 = 0.1024
Absolute structure parameter	0.020(10)
Largest diff. peak and hole	0.674 and –0.447 e Å^{-3}

$R1 = \Sigma||Fo| - |Fc|| / \Sigma|Fo|$.

$wR2 = [\Sigma[w(Fo^2 - Fc^2)^2] / \Sigma[w(Fo^2)^2]]^{0.5}$,

calc $w=1/[\sigma^2 (Fo^2)+(0.0341P)^2+3.6620P]$ where $P=(Fo^2+2Fc^2)/3$.

Table S3 Crystal data and structure refinement for Cp*(CO)(py)FeGeH$_2${C(SiMe$_3$)$_3$} (**2**)

Empirical formula	C_{26} H_{49} Fe Ge N O Si_3
Formula weight	604.37
Temperature	140(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 8.4986(4) Å
	b = 18.5971(10) Å β = 100.5527(11)°
	c = 20.0553(9) Å
Volume	3116.1(3) Å^3
Z	4
Density (calculated)	1.288 g/cm^3
Absorption coefficient	1.564 mm^{-1}
F(000)	1280
Crystal size	0.25 x 0.20 x 0.20 mm^3
Theta range for data collection	2.422 to 27.442°
Index ranges	$-10 \le h \le 11$, $-24 \le k \le 24$, $-25 \le l \le 25$
Reflections collected	42629
Independent reflections	7068 [R(int) = 0.0713]
Reflections with $I > 2\sigma$(I)	6218
Completeness to θ = 25.242°	99.8 %
Absorption correction	Numerical
Max. and min. transmission	1.0000 and 1.0000
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7068 / 0 / 316
Goodness-of-fit on F^2	1.146
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0452, wR2 = 0.1430
R indices (all data)	R1 = 0.0543, wR2 = 0.1487
Largest diff. peak and hole	0.591 and –0.822 e Å^{-3}

$R1 = \Sigma||Fo| - |Fc|| / \Sigma|Fo|$.

$wR2 = [\Sigma[w(Fo^2 - Fc^2)^2] / \Sigma[w(Fo^2)^2]]^{0.5}$,

calc $w = 1/[\sigma^2(Fo^2)+(0.1000P)^2+0.0000P]$ where $P=(Fo^2+2Fc^2)/3$.

Table S4 Crystallographic data and structure refinement for Cp*(CO)(2,4,6-$Me_3C_6H_2CN$)FeGe$(H)_2${$C(SiMe_3)_3$}·0.5C_7H_8 (**3b**·0.5 C_7H_8)

Empirical formula	$C_{34.5}H_{59}$ Fe Ge N O Si_3
Formula weight	716.54
Temperature	140(2) K
Wavelength	0.71069 Å
Crystal system	Monoclinic
Space group	*C*2/*c*
Unit cell dimensions	*a* = 32.8319(14) Å
	b = 12.2428(5) Å β = 109.345(2)°
	c = 20.4141(9) Å
Volume	7742.2(6) $Å^3$
Z	8
Density (calculated)	1.229 g/cm^3
Absorption coefficient	1.269 mm^{-1}
F(000)	3048
Crystal size	0.21 × 0.17 × 0.16 mm^3
Theta range for data collection	1.964 to 27.483°
Index range	$-42 \le h \le 41$, $-15 \le k \le 15$, $-26 \le l \le 26$
Reflections collected	55443
Independent reflections	8863 [*R*(int) = 0.1133]
Reflections with $I > 2\sigma(I)$	6985
Completeness to θ = 25.240°	100.0 %
Absorption correction	Numerical
Max. and min. transmission	1.0000 and 1.0000
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8863 / 0 / 431
Goodness-of-fit on F^2	1.185
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0753, *wR*2 = 0.1393
R indices (all data)	*R*1 = 0.1019, *wR*2 = 0.1484
Largest diff. peak and hole	2.026 and –0.666 e $Å^{-3}$

$R1 = \Sigma||Fo| - |Fc|| / \Sigma|Fo|$

$wR2 = [\Sigma[w(Fo^2 - Fc^2)^2] / \Sigma[w(Fo^2)^2]]^{0.5}$

calc $w=1/[\sigma^2(Fo^2)+(0.0348P)^2+57.6127P]$ where $P=(Fo^2+2Fc^2)/3$.

Table S5 Crystal data and structure refinement for Cp*(CO)(H)Fe=Ge(OCH$_2$Mes){C(SiMe$_3$)$_3$} (**5a**)

Empirical formula	$C_{31}H_{56}FeGeO_2Si_3$
Formula weight	673.46
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 8.9028(5) Å
	b = 25.0183(11) Å β = 91.6874(14)°
	c = 15.9058(6) Å
Volume	3541.2(3) Å^3
Z	4
Density (calculated)	1.263 g/cm^3
Absorption coefficient	1.384 mm^{-1}
F(000)	1432
Crystal size	0.190 x 0.170 x 0.160 mm^3
Theta range for data collection	2.429 to 27.484°
Index ranges	$-11 \le h \le 11$, $-31 \le k \le 32$, $-20 \le l \le 20$
Reflections collected	32577
Independent reflections	8120 [R(int) = 0.1224]
Reflections with $I > 2\sigma(I)$	6730
Completeness to θ = 25.242°	99.9 %
Absorption correction	Numerical
Max. and min. transmission	0.8859 and 0.8578
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8120 / 0 / 380
Goodness-of-fit on F^2	1.164
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0635, $wR2$ = 0.1053
R indices (all data)	$R1$ = 0.0825, $wR2$ = 0.1108
Largest diff. peak and hole	0.520 and –0.582 e Å^{-3}

$R1 = \Sigma||Fo| - |Fc|| / \Sigma|Fo|$.
$wR2 = [\Sigma[w(Fo^2 - Fc^2)^2] / \Sigma[w(Fo^2)^2]]^{0.5}$,
$w=1/[\sigma^2(Fo^2)+(0.0221P)^2+6.5474P]$ where $P=(Fo^2+2Fc^2)/3$.

Table S6 Crystal data and structure refinement for Cp*(CO)Fe[κ^2(*N*,*Ge*)-Ge(H)(O-C(H)=NPh){C(SiMe$_3$)$_3$}] (**6a**·0.5 C$_7$H$_8$)

Empirical formula	C_{35} H_{57} Fe Ge N O_2 Si_3	
Formula weight	736.52	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	*a* = 8.6833(7) Å	α = 77.427(2)°
	b = 12.7710(10) Å	β = 86.298(3)°
	c = 17.5545(9) Å	γ = 80.826(2)°
Volume	1874.8(2) Å^3	
Z	2	
Density (calculated)	1.305 g/cm^3	
Absorption coefficient	1.315 mm^{-1}	
F(000)	780	
Crystal size	0.40 × 0.36 × 0.35 mm^3	
Theta range for data collection	2.230 to 27.483°	
Index ranges	$-11 \le h \le 11$, $-16 \le k \le 16$, $-22 \le l \le 22$	
Reflections collected	26076	
Independent reflections	8525 [*R*(int) = 0.0542]	
Reflections with $I > 2\sigma(I)$	7525	
Completeness to theta = 25.242°	99.4 %	
Max. and min. transmission	0.7690 and 0.7116	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8525 / 0 / 459	
Goodness-of-fit on F^2	1.059	
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0412, *wR*2 = 0.0933	
R indices (all data)	*R*1 = 0.0487, *wR*2 = 0.0970	
Largest diff. peak and hole	0.367 and –0.508 e Å^{-3}	

R1 = $\Sigma||Fo| - |Fc|| / \Sigma|Fo|$.

*wR*2 = $[\Sigma[w(Fo^2 - Fc^2)^2] / \Sigma[w(Fo^2)^2]]^{0.5}$,

calc *w*=$1/[\sigma^2 (Fo^2)+(0.0425P)^2+1.3738P]$ where $P=(Fo^2+2Fc^2)/3$.

Table S7 Crystal data and structure refinement for Cp*(CO)Fe[κ^2-N,Ge)-Ge(H)(O-C(H)=NMes){C(SiMe$_3$)$_3$}(**6b**)

Empirical formula	C_{31} H_{55} Fe Ge N O_2 Si_3
Formula weight	686.47
Temperature	140(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	*Pna*2$_1$
Unit cell dimensions	*a* = 16.4196(8) Å
	b = 23.5939(8) Å
	c = 9.1101(3) Å
Volume	3529.3(2) Å^3
Z	4
Density (calculated)	1.292 g/cm^3
Absorption coefficient	1.391 mm^{-1}
F(000)	1456
Crystal size	0.21 × 0.20 × 0.17 mm^3
Theta range for data collection	2.126 to 27.432°
Index ranges	$-21 \le h \le 21$, $-30 \le k \le 30$, $-11 \le l \le 10$
Reflections collected	46667
Independent reflections	7744 [*R*(int) = 0.1026]
Reflections with $I > 2\sigma(I)$	6990
Completeness to θ = 25.242°	99.9 %
Absorption correction	Numerical
Max. and min. transmission	0.8686 and 0.8010
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7744 / 1 / 373
Goodness-of-fit on F^2	1.069
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0444, *wR*2 = 0.0951
R indices (all data)	*R*1 = 0.0521, *wR*2 = 0.0989
Absolute structure parameter	0.075(9)
Largest diff. peak and hole	0.411 and –0.489 e Å^{-3}

*R*1 = Σ||*F*o| - |*F*c|| / Σ|*F*o|.
*wR*2 = [Σ[*w*(*F*o^2 - *F*c^2)^2] / Σ[*w*(*F*o^2)^2]]$^{0.5}$,
calc *w*=1/[σ^2(*F*o^2)+(0.0421*P*)^2+3.0989*P*] where *P*=(*F*o^2+2*F*c^2)/3.

Table S8 Crystal data and structure refinement for
Cp*(CO)(2,4,6-$Me_3C_6H_2NC$)Fe[$SGeH_2${$C(SiMe_3)_3$}] **(7a)**

Empirical formula	C_{31} H_{55} Fe Ge N O S Si_3
Formula weight	702.53
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 12.8979(6) Å
	b = 16.6926(6) Å β = 97.6371(13)°
	c = 17.0382(7) Å
Volume	3635.8(3) $Å^3$
Z	4
Density (calculated)	1.283 g/cm^3
Absorption coefficient	1.405 mm^{-1}
F(000)	1488
Crystal size	0.41 × 0.40 × 0.27 mm^3
Theta range for data collection	1.593 to 27.452°
Index ranges	$-16 \le h \le 16$, $-21 \le k \le 21$, $-22 \le l \le 22$
Reflections collected	54145
Independent reflections	8270 [R(int) = 0.0846]
Reflections with $I > 2\sigma(I)$	7095
Completeness to θ = 25.242°	99.9 %
Absorption correction	Numerical
Max. and min. transmission	0.8181 and 0.6855
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8270 / 0 / 377
Goodness-of-fit on F^2	1.044
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0431, $wR2$ = 0.1287
R indices (all data)	$R1$ = 0.0539, $wR2$ = 0.1367
Largest diff. peak and hole	0.627 and -0.372 e $Å^{-3}$

$R1 = \Sigma||Fo| - |Fc|| / \Sigma|Fo|$.
$wR2 = [\Sigma[w(Fo^2 - Fc^2)^2] / \Sigma[w(Fo^2)^2]]^{0.5}$,
calc $w=1/[\sigma^2(Fo^2)+(0.1000P)^2+0.0000P]$ where $P=(Fo^2+2Fc^2)/3$.