Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

for

$\{Ge_9[Si(SiMe_3)_3]_2\}^{2-}$: A Starting Point for Mixed Substituted Metalloid Germanium Clusters.

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a) Synthetic procedure for the Synthesis of the K_4Ge_9 precursor and $K[Ge_9(Hyp)_3]$ (1) in thf; (Hyp = $Si(SiMe_3)_3$):

Synthesis of K_4Ge_9 . 600 mg of K (15.4 mmol) and 2.0 g of Ge (27.5 mmol, 99.999% ABCR) were heated to 650 ^{o}C for 3 days in a sealed evacuated quartz ampoule. The ampoule was then opened in a glove-box and the product was collected. The yield is approximately 2.5 g with a chemically available content of ca. 30-35% of K_4Ge_9. ***Caution!*** *At elevated temperature potassium is highly aggressive to quartz. Experiments should be performed with precautions against explosion and burning in case of depressurization of the ampoule. Also opening of the ampoule requires somewhat more accuracy, as due to reaction with potassium quartz glass become breakable.*

Estimation of chemically available K_4Ge_9 content in used precursor. According to XRPD (**Figure S1**) the K_4Ge_9 precursor contains certain amount of elemental germanium besides the desired product K_4Ge_9. However, XPRD analysis is limited to crystalline compounds; hence, the presence of amorphous phases inside the bulk product of composition $KGe_{2.25}$ cannot be excluded. Therefore, despite the powder diffraction of the obtained precursor was done (figure S1), we cannot rely on this data too much, and due to the quality of the spectrum it can only be said that the bulk precursor contains K_4Ge_9 and also other phases e.g. elemental germanium in not determined amounts. Nevertheless, for the gram-quantity synthesis of $K[Ge_9Hyp_3]$ it is more important to estimate the chemically accessible amount of K_4Ge_9 for substitution by HypCl. As this amount cannot be determined by powder XRPD as outlined above it was done practically in a chemical way (see below). Therefore we estimated the quantity of $K[Ge_9Hyp_3]$ obtained from a certain amount of the easily accessible K_4Ge_9 precursor (synthesized in quartz ampoules). Hence by this procedure we obtained the synthetically available amount of K_4Ge_9 inside the precursor irrespective of the amount of other impurities which is most important for synthetic purposes.

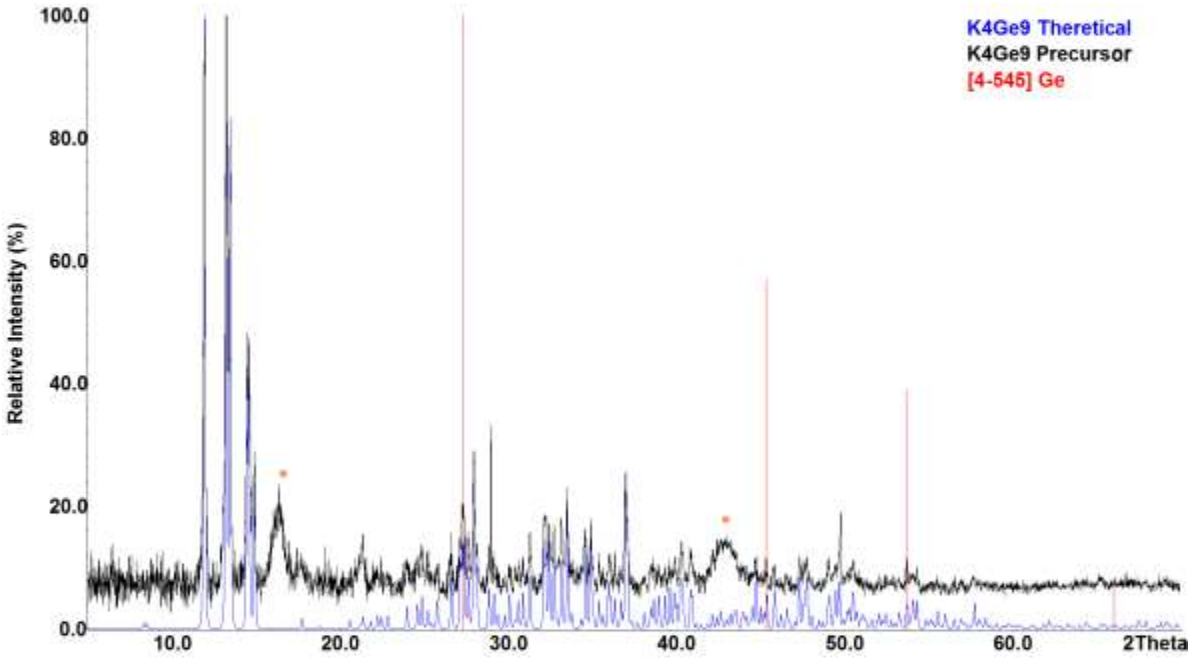

Figure S1: XPRD diffractogram of the K_4Ge_9 precursor (black). Picture shows that synthetic product consist of K_4Ge_9 (blue) and Ge (red), though quantitative estimation is problematic and was not performed therefore (*artefacts of the device not related to the measured sample).

a) 0.4 mL of HypCl (1.24 mmol) required 1.5 g of K_4Ge_9 precursor (added by several portions) to be completely transferred to $K_2[Ge_9(Hyp)_2]$, **2** in MeCN, yielding after work-up procedures 590 mg of **2** which is 77% yield with respect to HypCl. The content of K_4Ge_9 in the precursor was therefore calculated to 33%.

b) 2.0 g of K_4Ge_9 precursor reacts with excess of HypCl (5-6 eq of HypCl to 1 eq of K_4Ge_9 estimated) in thf giving 1090 mg of $K[Ge(Hyp)_3]$ after purification. Assuming 100% yield of the reaction and minimal loses of the product during work-up procedures, the content of K_4Ge_9 in the precursor was estimated as 31%, though this value is a bit understated due to the assumptions applied.

Synthesis of K[Ge_9(Hyp)$_3$] (1). 2.0 g of K_4Ge_9 precursor (supposedly 0.81 mmol of K_4Ge_9) was suspended in ca. 15 ml of thf by stirring at -78°C. 0.8 mL of molten ClSi(SiMe$_3$)$_3$ (2.48 mmol; melting point: 50°C) was added by syringe and the reaction mixture was kept cold for 5-7 hours; ClSi(SiMe$_3$)$_3$ can be cooled to room temperature without solidification. After warming to room temperature the solution was stirred for 5 days. Afterwards the solvent was completely evaporated and the solid residue was heated up to 50°C for 20 minutes in vacuum in order to remove solvated thf molecules. Afterwards the solid was washed by a large amount of pentane (ca. 50 ml) and **1** was extracted by thf (ca. 10 ml) leading to an orange-red solution (980 mg of **1**, 83% with respect to applied HypCl). *NMR* (thf-d$_8$): ^{1}H (400 MHz) 0.25 ppm (s, -Si*Me$_3$*); ^{13}C (50 MHz) 3.26 ppm (-Si*Me$_3$*); ^{29}Si (50 MHz) -9.52 ppm (dezet, J = 6.5 Hz, -*Si*Me$_3$), -107.80 ppm (-*Si*(SiMe$_3$)$_3$). When the product of the reaction was not dried enough, a small amount of **1** can also dissolve in pentane in form of its thf solvate and can be crystallized as orange needle-like crystals of [K(thf)$_3$][Ge_9(Hyp)$_3$]*C_5H_{12} (**1*thf**).

Byproducts from the reaction of K_4Ge_9 silylation in thf. An interesting observation for the reaction system K_4Ge_9 + 3HypCl in thf is that the starting compounds show a higher reactivity and are thus less selective. During the first experiments we observed a high amount of different silyl-containing species by 1H NMR spectroscopy of the reaction mixture (signals at 0.24 ppm, 0.31-0.32 ppm, **Figure S2**). All these compounds are completely extracted by pentane and several of them were crystallized and analyzed which resulted in known silanes Si{Si(SiMe$_3$)$_3$}$_4$ (0.24 ppm) and Si$_2${Si(SiMe$_3$)$_3$}$_6$ (within the group of signals 0.31-0.32 ppm). On this point we stopped further investigations of the pentane extract, assuming that besides small amount of **1*thf** (0.25 ppm) there are no other compounds containing a germanium core. We assumed that formation of silanes in thf begins from the reduction of HypCl to KHyp after the starting compounds are mixed with further non-selective reactions between KHyp and HypCl. It is worth to note, that we never observed such silane products in the reactions performed in MeCN which underlines the great importance of the solvent on the reaction course. However, when the reaction in thf is started at -78 °C for the first 5-7 hours and then continued at room temperature, the amount of the by-products decreases dramatically.

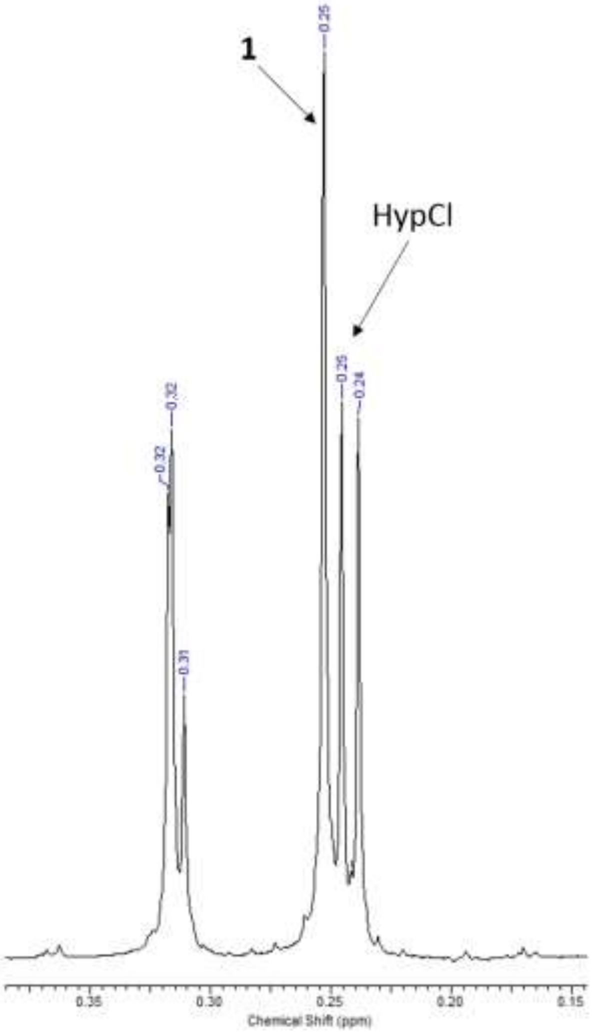

Figure S2 Proton NMR spectrum (in thf -d_8) of the product mixture from the reaction between K_4Ge_9 and excess of HypCl performed at room temperature, indicating a high amount of different silyl-containing species in addition to the main product $K[Ge_9(Hyp)_3]$ (**1**) and unreacted HypCl.

b) Crystal structures of $[K(Tol)_3][Ge_9(Hyp)_3]$*Tol (1*Tol) and $[K(thf)_3][Ge_9(Hyp)_3]\cdot C_5H_{12}$ (1*thf) (Hyp = $Si(SiMe_3)_3$; Tol = toluene; thf = tetrahydrofurane).

Crystal structure data for:

a) $C_{27}H_{81}Ge_9Si_{12}C_7H_8K*3(C_7H_8)$ (**1*Tol)**: $C_{55}H_{113}Ge_9KSi_{12}$: M_r = 1804.13 g/mol, crystal size 0.335 x 0.138 x 0.136 mm, monoclinic, space group: $P2_1/c$, a = 15.8387(9), b = 20.2949(13), c = 27.3283(16) Å, β = 91.293(1)°, V = 8782.3(9) Å^3, Z = 4, $\rho_{calc.}$ = 1.365 gcm^{-3}, μ = 3.274 mm^{-1}, $2\theta_{max}$ = 46.60°, 12589 collected reflections, 9222 independent reflections (R(int.) = 0.0405), Absorption correction: numerical (min/max-transmission 0.696 / 1.000), R_1 [$I > 2\sigma(I)$] = 0.0620, wR_2 (all Data) = 0.1638. Bruker APEX II - Diffraktometer ($Mo_{K\alpha}$-radiation, (λ = 0.71073 Å), 150K)

b) $C_{27}H_{81}Ge_9Si_{12}C_{12}H_{24}KO_3*C_5H_{12}$ (**1*thf)**: $C_{44}H_{117}Ge_9KO_3Si_{12}$: M_r = 1724.05 g/mol, crystal size 0.388 x 0.133 x 0.028 mm, monoclinic, space group: $P2_1/c$, a = 26.448(4), b = 11.2469(18), c = 30.221(4) Å, β = 112.221(4), V = 8322(2) Å^3, Z = 4, $\rho_{calc.}$ = 1.376 gcm^{-3}, μ = 3.454 mm^{-1}, $2\theta_{max}$ = 46.42°, 11828 collected reflections, 7249 independent reflections (R(int.) = 0.0661), Absorption correction: numerical (min/max-transmission 0.517 / 0.745), R_1 [$I > 2\sigma(I)$] = 0.0562, wR_2 (all Data) = 0.1339. Bruker APEX II - Diffraktometer ($Mo_{K\alpha}$-radiation, (λ = 0.71073 Å), 150K).

The structures were solved by direct methods and refined by full-matrix least-square techniques (programs used: SHELXS and SHELXL[1]) The non hydrogen atoms were refined anisotropically and the hydrogen atoms were calculated using a riding model. CCDC-1418081 (**1*Tol**) and ccdc-1418084 (**1*thf)** contains the supplementary crystallographical data for this paper. These data can be obtained online free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ; Fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk.

Simplified molecular structures of **1*Tol** and **1*thf** are shown in **Figure S3** together with the structure of **3*thf**. Interesting similarity between the structures of **3*thf**, **1*Tol** and **1*thf** is that all clusters form in the solid state ionic pairs with a KL_3^+ (L = Tol, thf) cation coordinated to two or three Ge atoms of one triangular face of the anion with K-Ge distances of 3.6-3.9 Å.

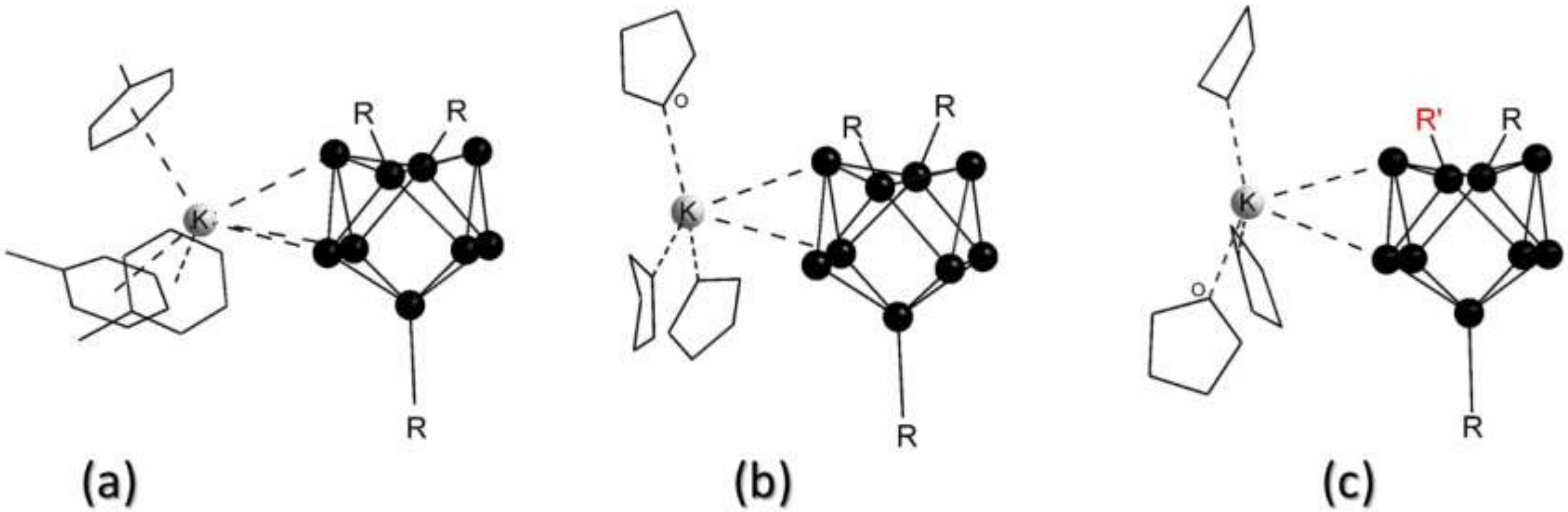

Figure S3 Schematic presentation of ionic pairs observed in the crystal structures of **1*Tol** (a), **1*thf** (b) **and 3*thf** (c) indicating similar cation-anion interactions in all these compounds. H-atoms are omitted, C-atoms are drawn transparently, Hyp and Hyp^{Ph3} ligands are simplified to R and R' symbols respectively. K-Ge bond lengths are within the range of 3.6-3.9 Å.

c) Mass spectrometric and NMR investigations of K{Ge_9[Hyp]$_2$[FeCp(CO)$_2$]}; (Hyp = Si(SiMe$_3$)$_3$).

The anionic cluster compounds were brought into the gas phase by electrospraying[2] a thf solution of K{Ge_9[Hyp]$_2$[FeCp(CO)$_2$]}. The end-plate of the electrospray source was typically held at a potential of +3.2 kV relative to the electrospray needle, which was grounded. A potential of +3.3 kV was applied to the entrance of the metal-coated quartz capillary.

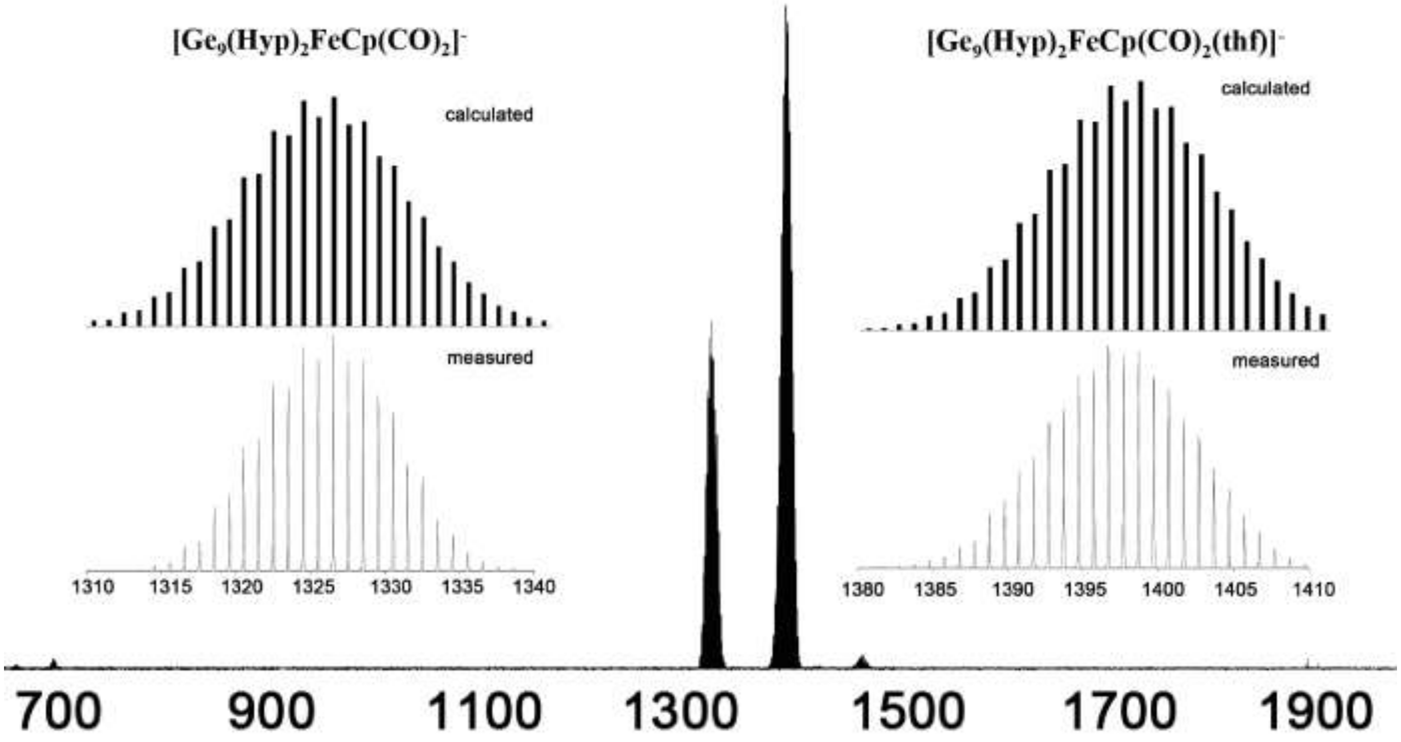

Figure S4 Overall ESI mass spectrum of the reaction solution (thf) of [$Ge_9(Hyp)_2$]$^{2-}$ and $BrFeCp(CO)_2$ measured in the anionic mode. The two observed intense signals could be identified by comparison of the measured and the calculated isotopic pattern as {$Ge_9(Hyp)_2$[FeCp(CO)$_2$]}$^-$ (left highlighted) and {$Ge_9(Hyp)_2$[FeCp(CO)$_2$]}$^-$ • 1 thf (right highlighted).

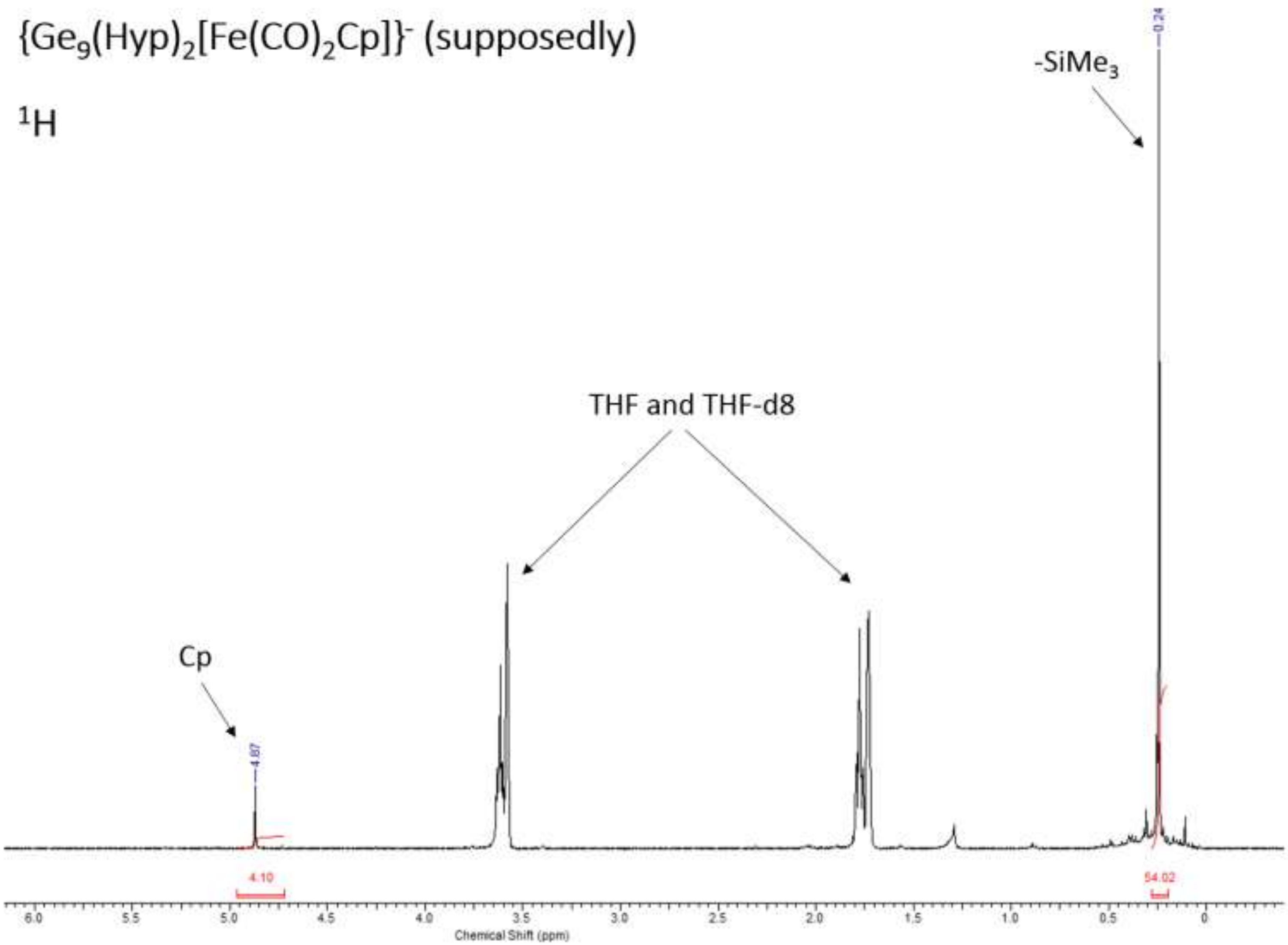

Figure S5 ^{1}H NMR spectrum (in thf -d8) of the reaction mixture of $[Ge_9(Hyp)_2]^{2-}$ and $BrFeCp(CO)_2$ in thf indicating transformation of disubstituted cluster (initial $SiMe_3$ protons shift at 0.17 ppm) to trisubstituted one (observed $SiMe_3$ protons shift at 0.24 ppm).

d) NMR data for [K-crypt]$_2$[Ge$_9$(Hyp)$_2$]*3 thf (2-crypt) and [K(thf)$_3$][Ge$_9$(Hyp)$_2$(Hyp^{Ph3})] (3*thf).

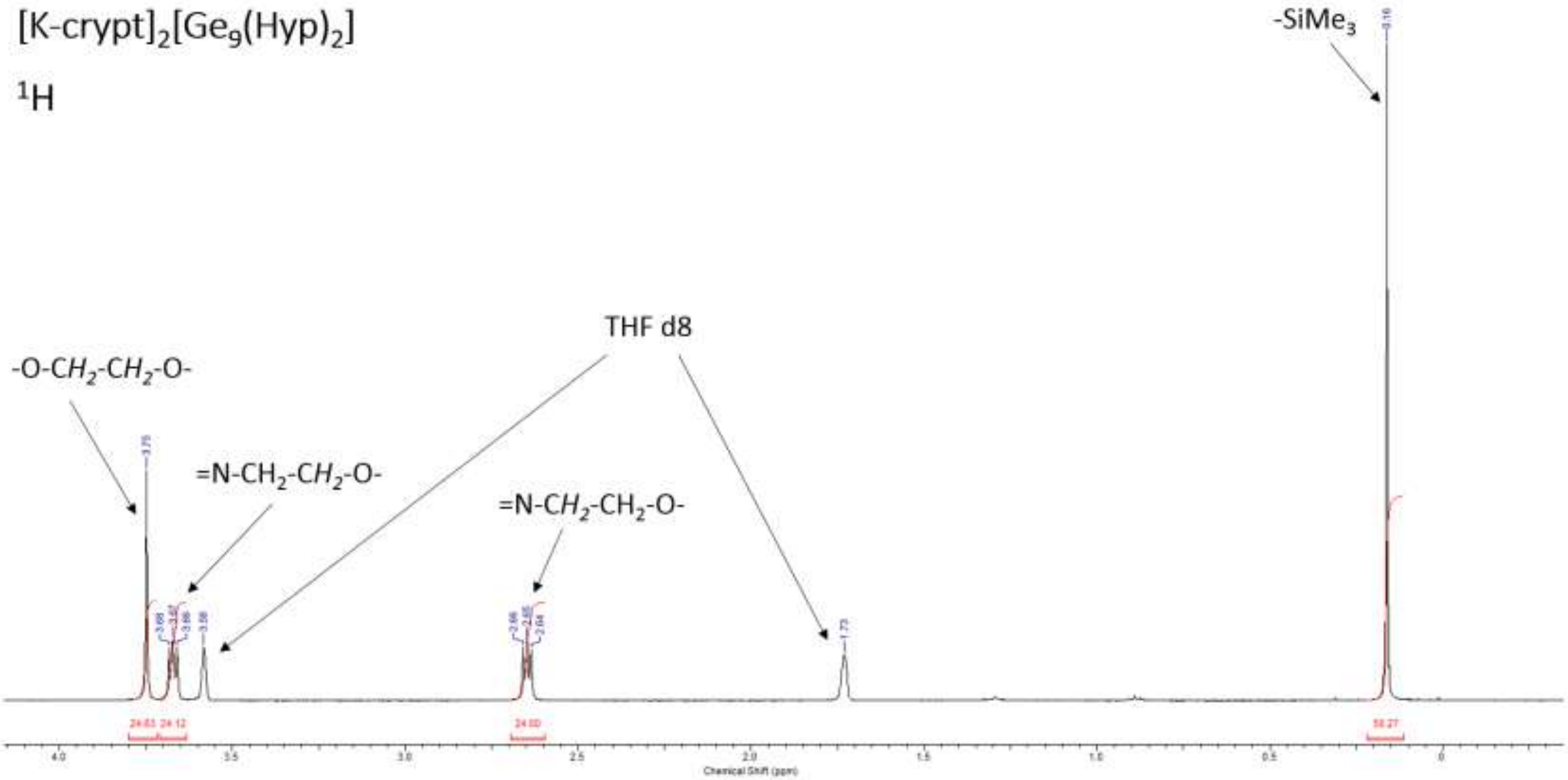

Figure S6 ^{1}H NMR spectrum of [K-crypt]$_2$[Ge$_9$(Hyp)$_2$] (**2-crypt**).

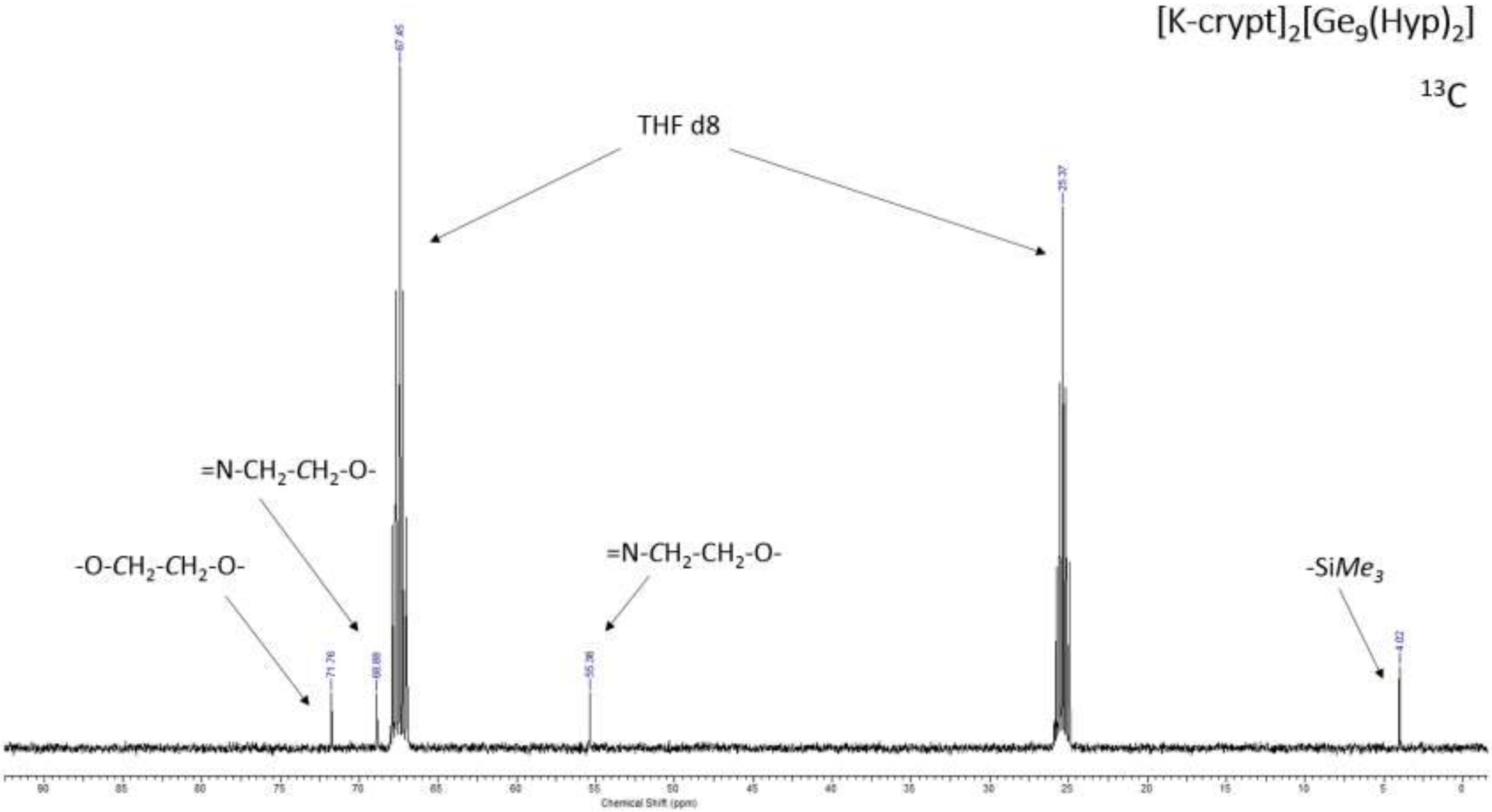

Figure S7 ^{13}C NMR spectrum of [K-crypt]$_2$[Ge$_9$(Hyp)$_2$] (**2-crypt**).

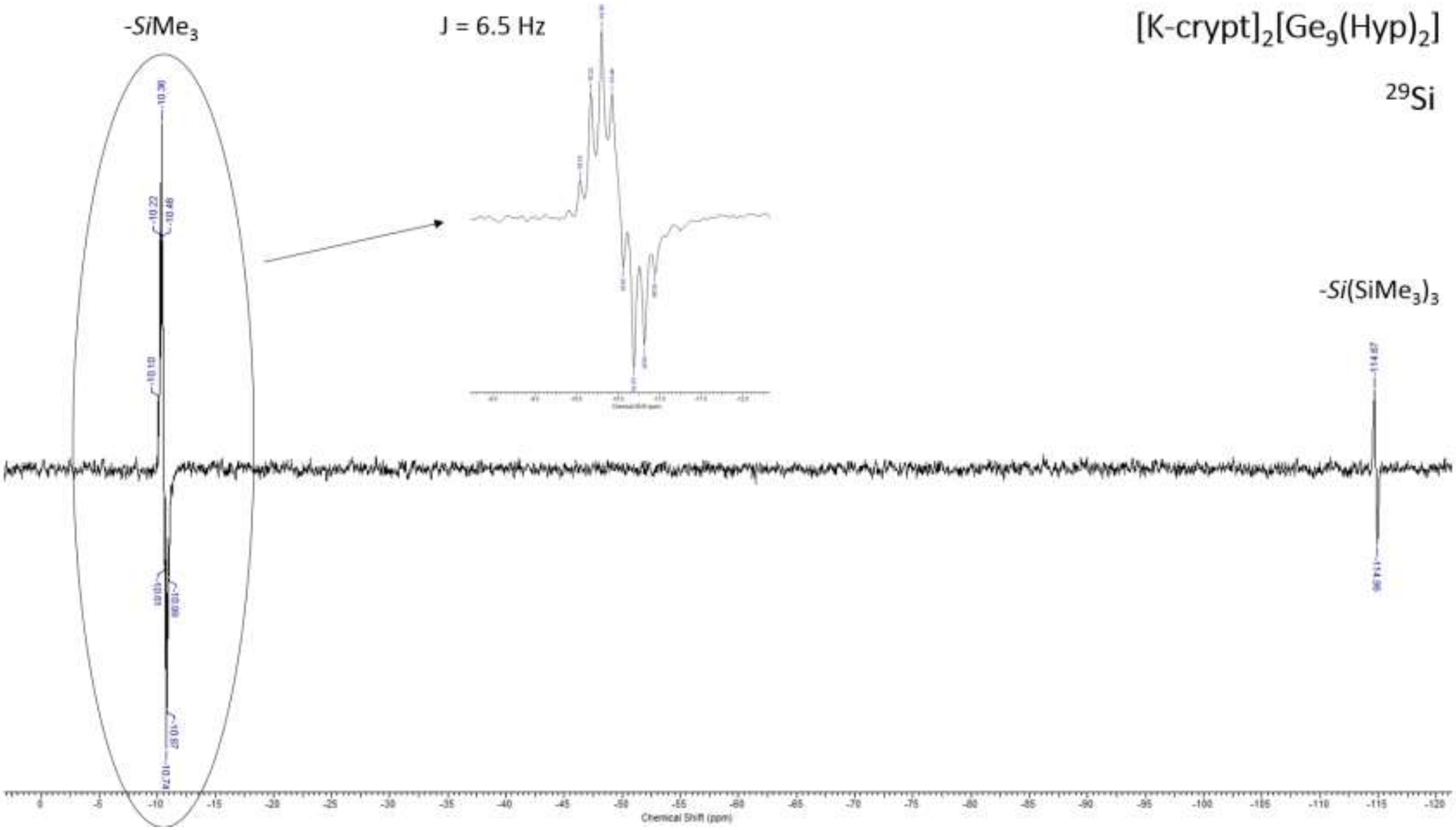

Figure S8 ^{29}Si NMR spectrum of [K-crypt]$_2$[Ge$_9$(Hyp)$_2$] (**2-crypt**) with magnified section of SiMe$_3$ groups region.

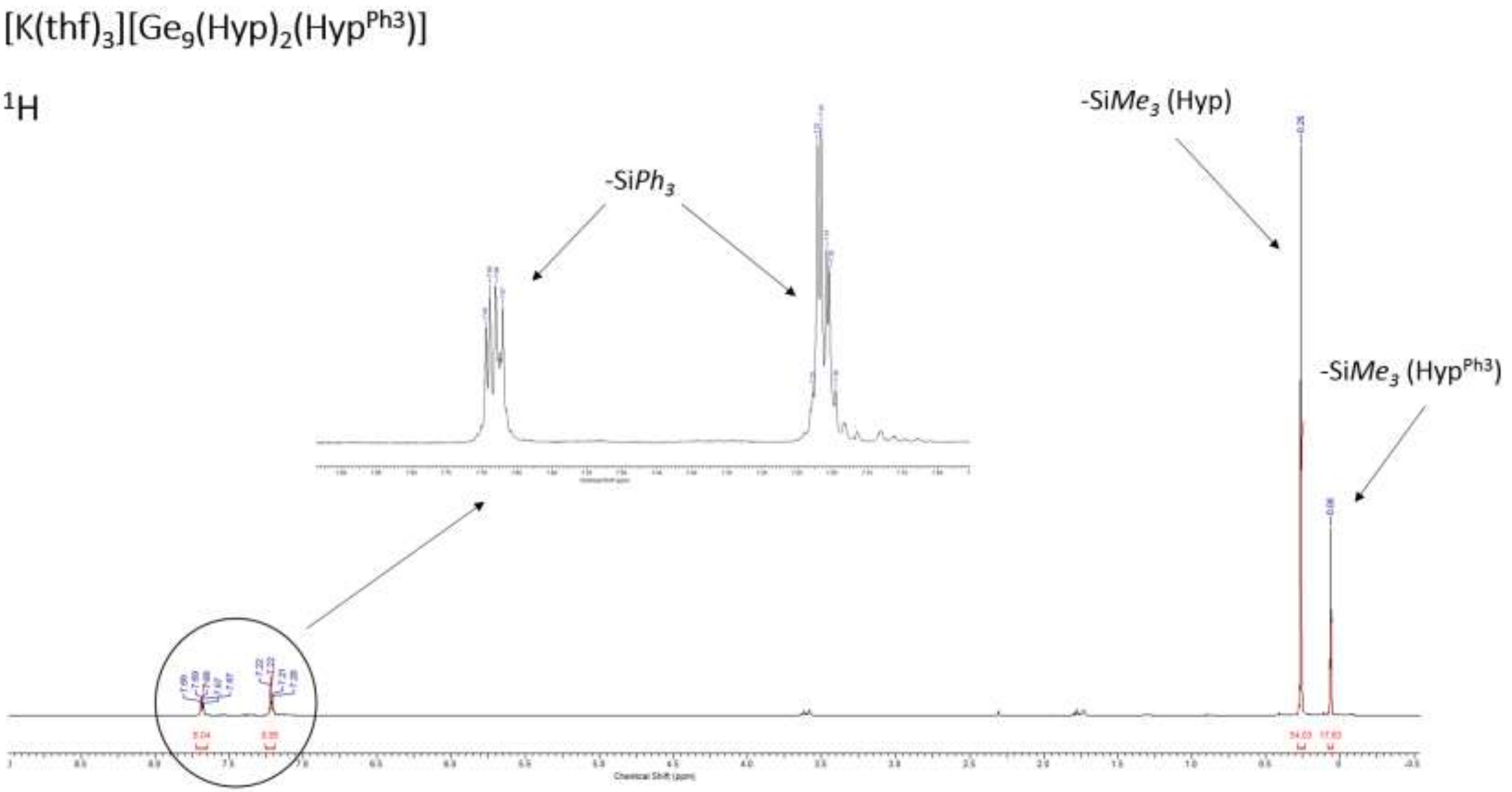

Figure S9 ^{1}H NMR spectrum of K[Ge$_9$(Hyp)$_2$(Hyp^{Ph3})] (**3**) with magnified section of aromatic hydrogen atoms region.

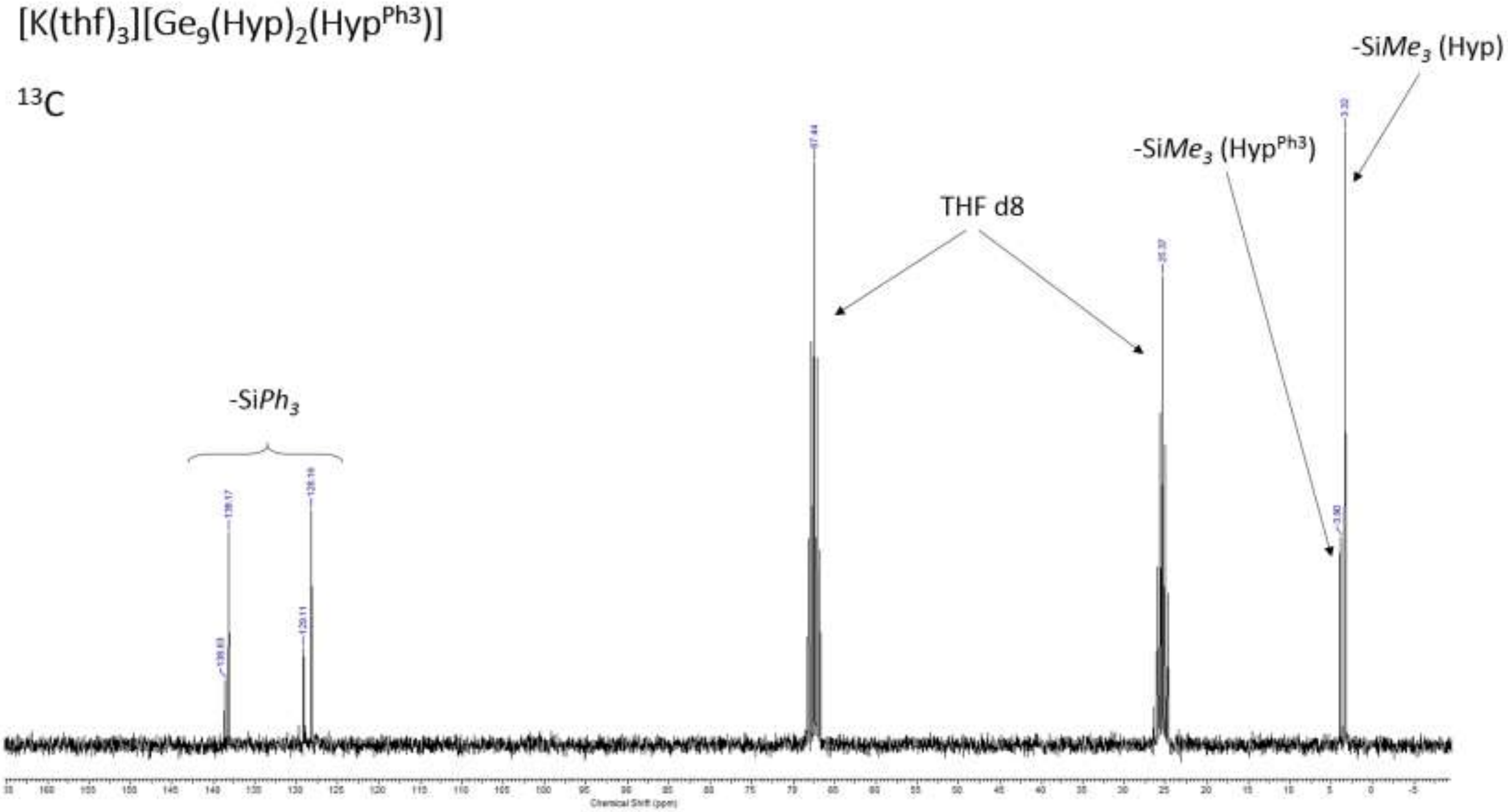

Figure S10 ^{13}C NMR spectrum of K[Ge$_9$(Hyp)$_2$(Hyp^{Ph3})] (**3**).

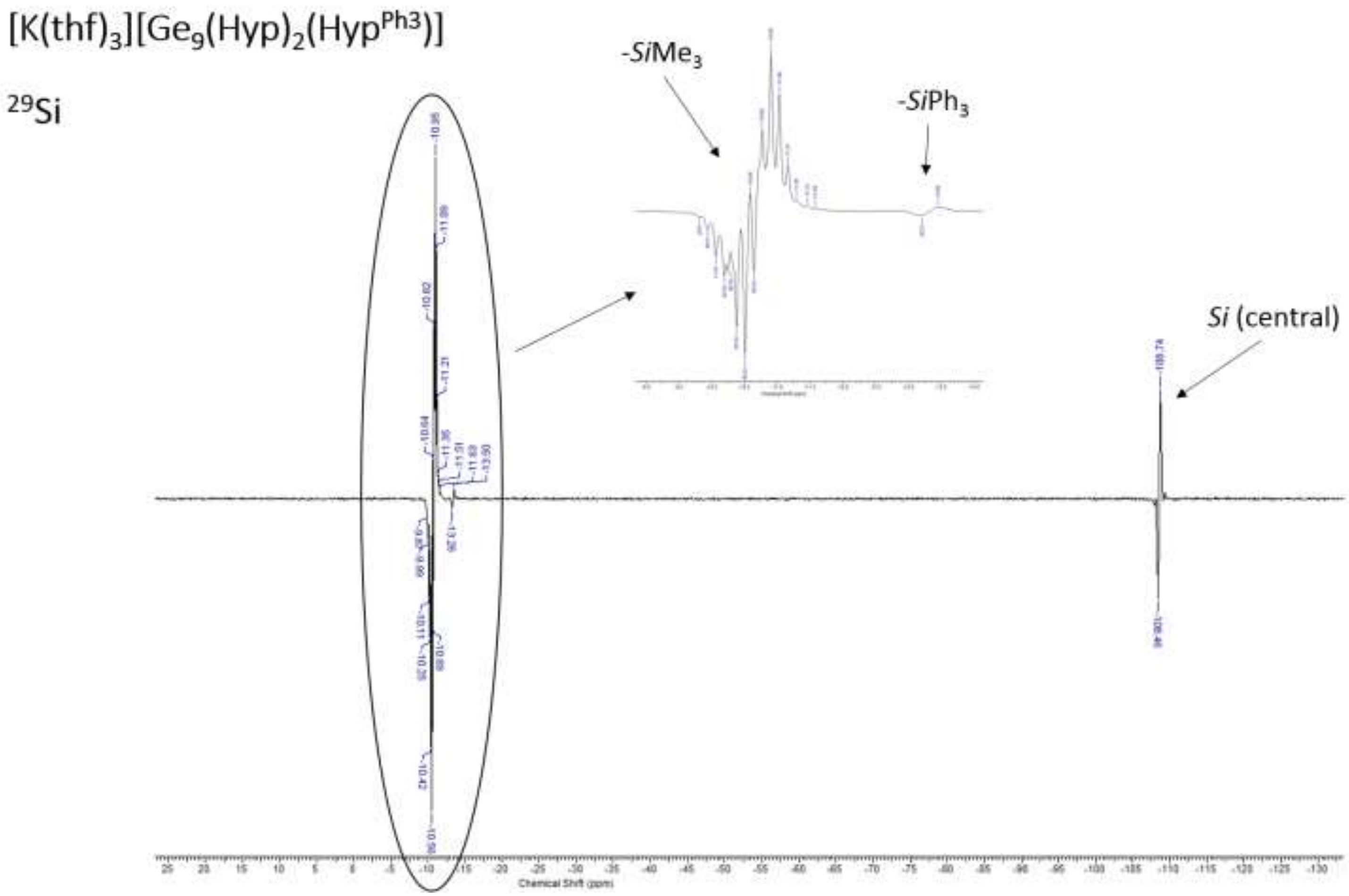

Figure S11 ^{29}Si NMR spectrum of K[Ge$_9$(Hyp)$_2$(Hyp^{Ph3})] (**3**) with magnified section of SiPh$_3$ and SiMe$_3$ groups region.

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[1] G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112 – 122.

[2] J. B. Fenn, *Angew. Chem.* ***2003*****,** *115*, 3999–4024; *Angew. Chem., Int. Ed. 2003*, *42*, 3871–3894.