Derivatization of Phosphine Ligands with Bulky Deltahedral *Zintl* Clusters – Synthesis of Charge Neutral Zwitterionic Tetrel Cluster Compounds $[(Ge_9\{Si(TMS)_3\}_2)^tBu_2P]M(NHC^{Dipp})$ (M: Cu, Ag, Au)

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Content

Selected Distances

Table SI 1: Selected bonding distances [Å] in **1** (Cluster I and Cluster II).

bond	**distance**	**bond**	**distance**
Cluster 1		Cluster 2	
Ge1-Ge2	2.5284(9)	Ge10-Ge11	2.5312(9)
Ge1-Ge3	2.5206(9)	Ge10-Ge12	2.5241(9)
Ge1-Ge4	2.5095(8)	Ge10-Ge13	2.5030(8)
Ge1-Ge5	2.512(1)	Ge10-Ge14	2.498(1)
Ge2-Ge3	2.8285(9)	Ge11-Ge12	2.8284(9)
Ge2-Ge6	2.550(1)	Ge11-Ge15	2.559(1)
Ge2-Ge7	2.669(1)	Ge11-Ge16	2.657(1)
Ge3-Ge7	2.6398(9)	Ge12-Ge16	2.6542(9)
Ge3-Ge8	2.5490(9)	Ge12-Ge17	2.5666(9)
Ge4-Ge5	2.9147(9)	Ge13-Ge14	2.9187(9)
Ge4-Ge8	2.631(1)	Ge13-Ge17	2.635(1)
Ge4-Ge9	2.6232(8)	Ge13-Ge18	2.6142(9)
Ge5-Ge6	2.673(1)	Ge14-Ge15	2.676(1)
Ge5-Ge9	2.6090(9)	Ge14-Ge18	2.5858(9)
Ge6-Ge7	2.586(1)	Ge15-Ge16	2.595(1)
Ge6-Ge9	2.4862(8)	Ge15-Ge18	2.4927(9)
Ge7-Ge8	2.5791(9)	Ge16-Ge17	2.5737(9)
Ge8-Ge9	2.4745(9)	Ge17-Ge18	2.473(1)
Ge1-Si1	2.376(2)	Ge10-Si13	2.374(2)
Ge6-Si2	2.408(2)	Ge15-Si14	2.407(2)
Ge8-Si3	2.391(1)	Ge17-Si15	2.398(2)
Ge9-P1	2.343(2)	Ge18-P2	2.336(2)
Ge2-Ge5	3.0006(7)	Ge11-Ge14	3.0042(7)
Ge3-Ge4	3.0687(7)	Ge12-Ge13	3.0300(7)
Ge7-Ge9	3.6920(8)	Ge16-Ge18	3.7057(8)
P1-C101	1.876(5)	P2-C201	1.863(6)
P1-C26	1.871(5)	P2-C207	1.866(6)

Table SI 2: Selected bonding distances [Å] in **1** (Cluster III).

bond	**distance**
Cluster 3	
Ge19-Ge20	2.5213(9)
Ge19-Ge21	2.5264(9)
Ge19-Ge22	2.507(1)
Ge19-Ge23	2.5118(8)
Ge20-Ge21	2.8262(9)
Ge20-Ge24	2.5681(9)
Ge20-Ge25	2.6317(9)
Ge21-Ge25	2.670(1)
Ge21-Ge26	2.5721(9)
Ge22-Ge23	2.9046(9)
Ge22-Ge26	2.665(1)
Ge22-Ge27	2.6247(9)
Ge23-Ge24	2.643(1)
Ge23-Ge27	2.6146(9)
Ge24-Ge25	2.5706(8)
Ge24-Ge27	2.4966(9)
Ge25-Ge26	2.557(1)
Ge26-Ge27	2.4902(8)
Ge19-Si25	2.375(2)
Ge24-Si26	2.404(2)
Ge26-Si27	2.402(2)
Ge27-P3	2.355(2)
Ge20-Ge23	3.0470(8)
Ge21-Ge22	2.9586(8)
Ge25-Ge27	3.7180(9)
P3-C301	1.869(6)
P3-C307	1.870(6)

Table SI 3: Selected bonding distances [Å] in **4**.

bond	**distance**
Ge1-Ge2	2.5407(7)
Ge1-Ge3	2.530(1)
Ge1-Ge4	2.5468(8)
Ge1-Ge5	2.534(1)
Ge2-Ge5	2.633(1)
Ge2-Ge6	2.552(1)
Ge2-Ge9	2.6967(9)
Ge3-Ge4	2.595(1)
Ge3-Ge6	2.5322(8)
Ge3-Ge7	2.737(1)
Ge4-Ge7	2.714(1)
Ge4-Ge8	2.5271(8)
Ge5-Ge8	2.534(1)
Ge5-Ge9	2.704(1)
Ge6-Ge7	2.5548(1)
Ge6-Ge9	2.553(1)
Ge7-Ge8	2.551(1)
Ge8-Ge9	2.5461(7)
Ge6-Si1	2.380(1)
Ge8-Si2	2.371(1)
Ge1-P1	2.316(1)
Ge2-Ge3	3.620(1)
Ge4-Ge5	3.658(1)
Ge7-Ge9	3.070(1)
Cu1-C1	1.923(3)
Cu1-P1	2.218(1)
P1-C22	1.883(4)
P1-C26	1.883(4)

Computational Analysis

Table SI 4: Selected charges from Hirshfeld[1] and Natural Population Analysis[2] for Compound **4** and [^{t}Bu$_3$PCu(NHC^{Dipp})]$^+$.[3]

	Compound 4		**[^{t}Bu$_3$PCu(NHC^{Dipp})]$^+$**	
Atom	Hirshfeld	NPA	Hirshfeld	NPA
P1	0.08	0.41	0.16	0.85
Cu1	0.16	0.42	0.20	0.41
[Ge$_9$] (Ge1-Ge9)	-0.33	-0.91	-	-

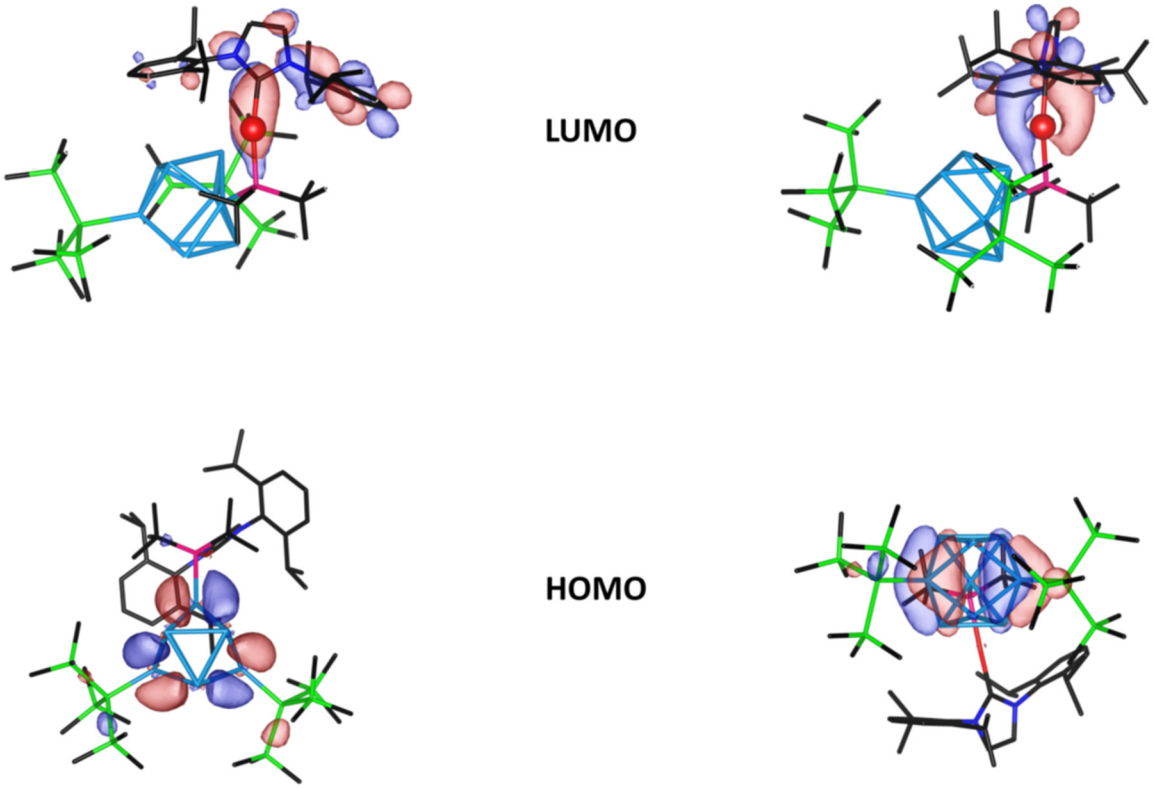

Figure SI 1: HOMO and LUMO orbital of compound **4**. C atoms are shown in black, N atoms in dark blue, P atoms in pink, Si atoms in green, Cu atoms in red and Ge atoms in light blue. Pictures were created using VESTA.[4]

NMR spectra

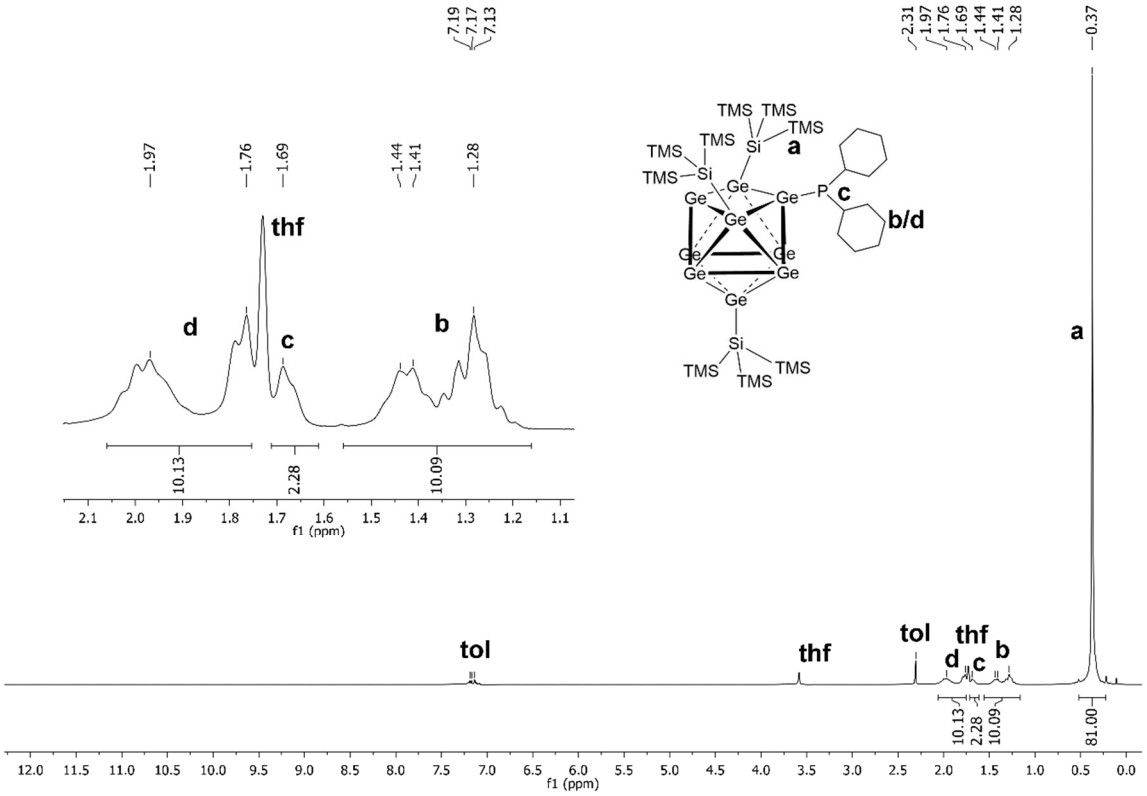

Figure SI 2: ^{1}H NMR spectrum of compound **1** in thf-d_8.

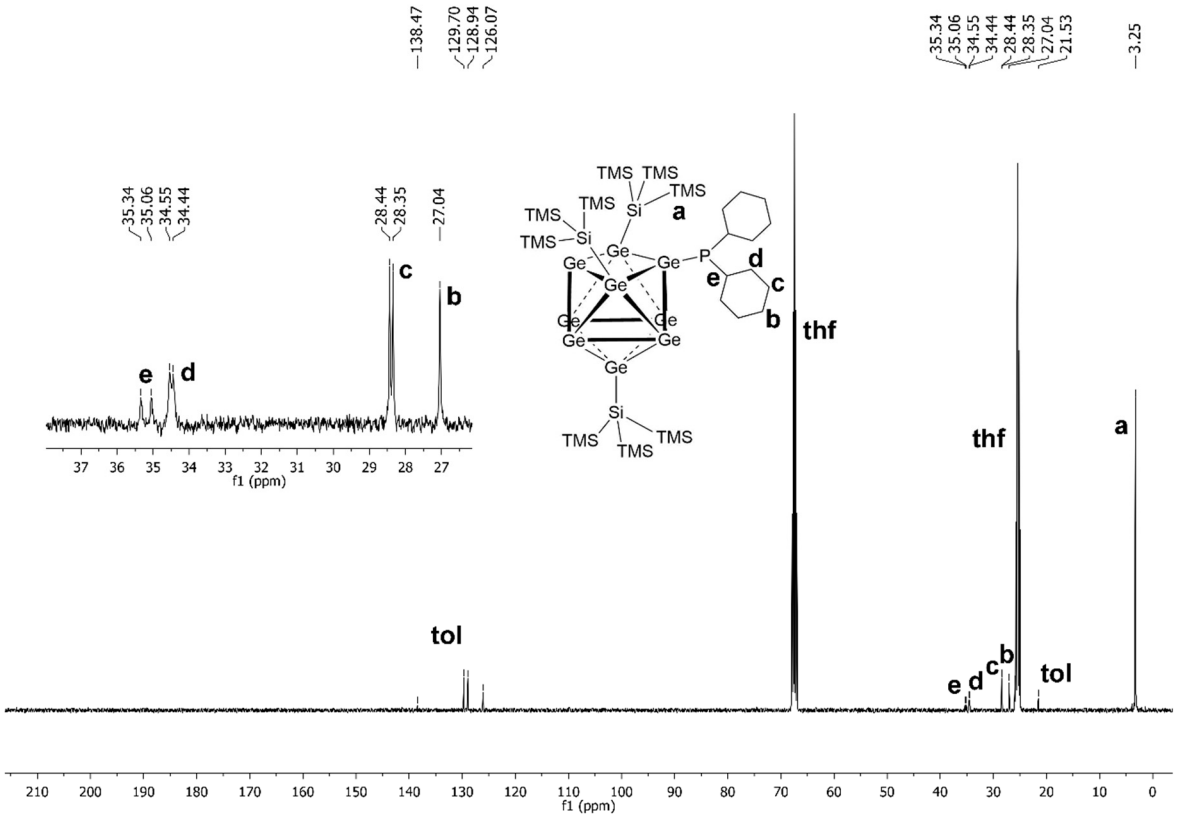

Figure SI 3: ^{13}C NMR spectrum of compound **1** in thf-d_8.

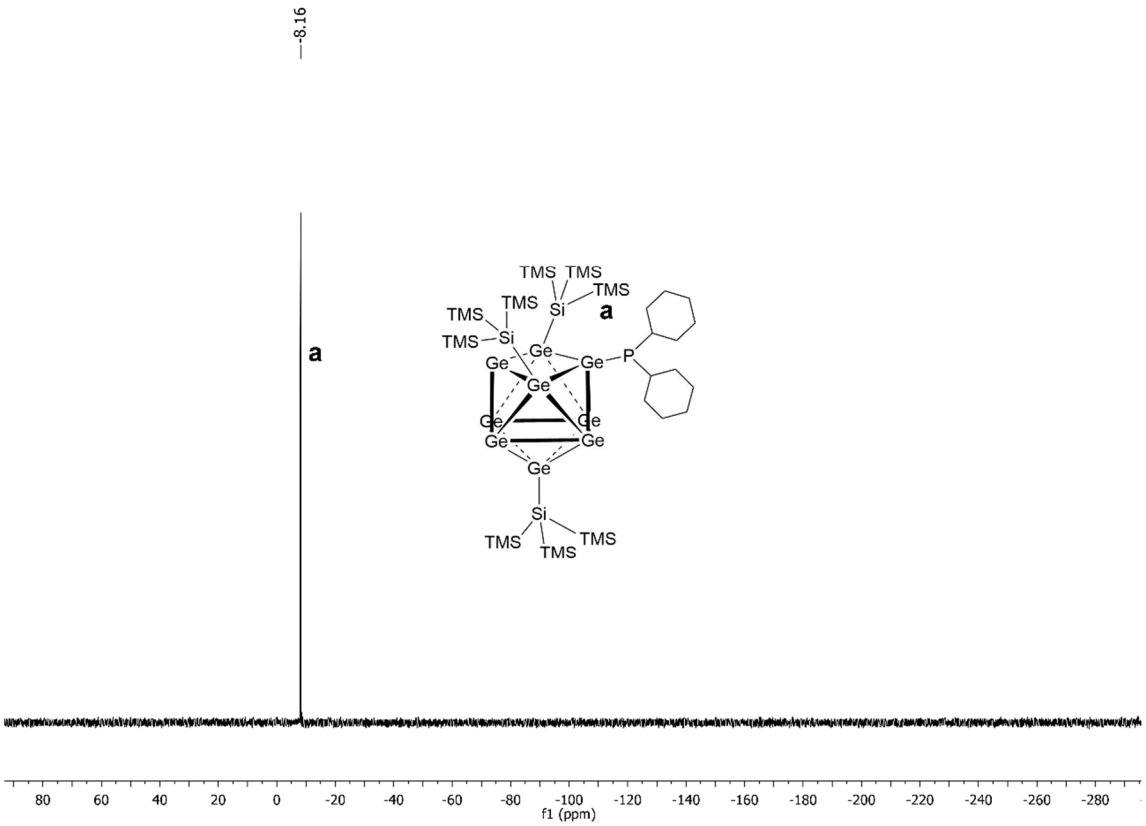

Figure SI 4a: ^{29}Si NMR spectrum of compound **1** in thf-d_8. Measurement was carried out with purified sample and relaxation time of 4s.

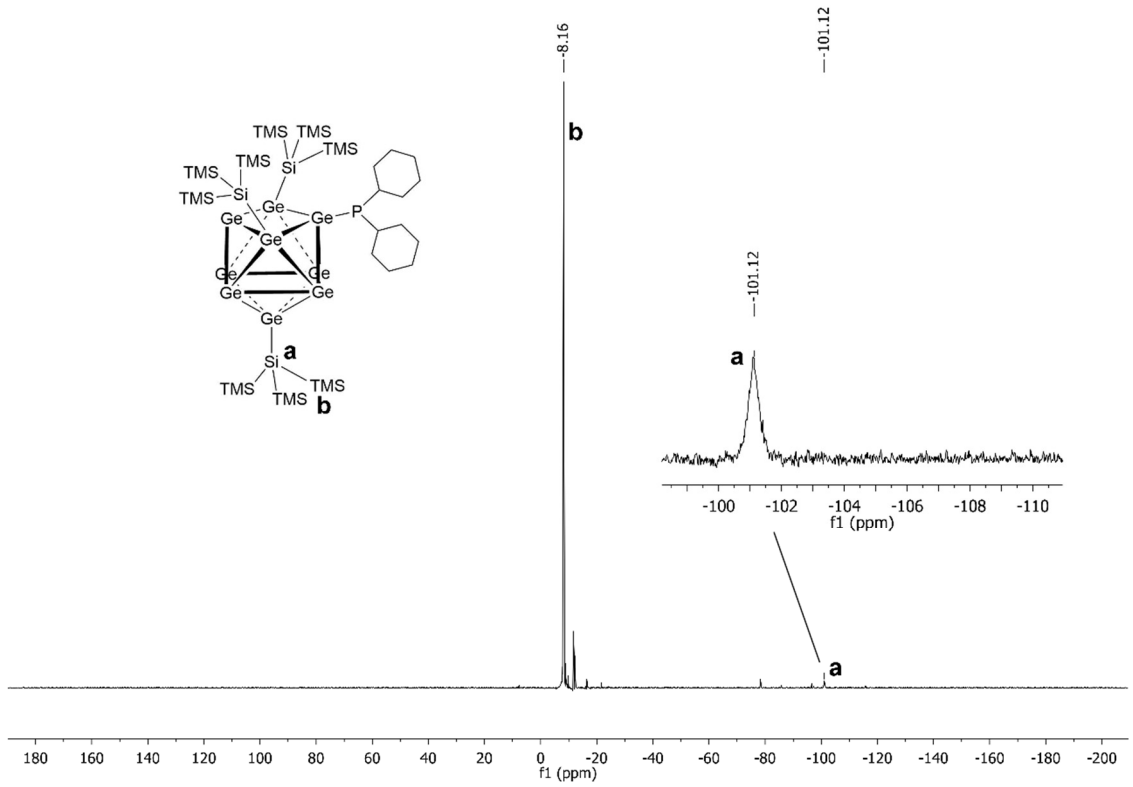

Figure SI 4b: ^{29}Si NMR spectrum of compound **1** in thf-d_8. Measurement was carried out with crude product sample and relaxation time of 15s.

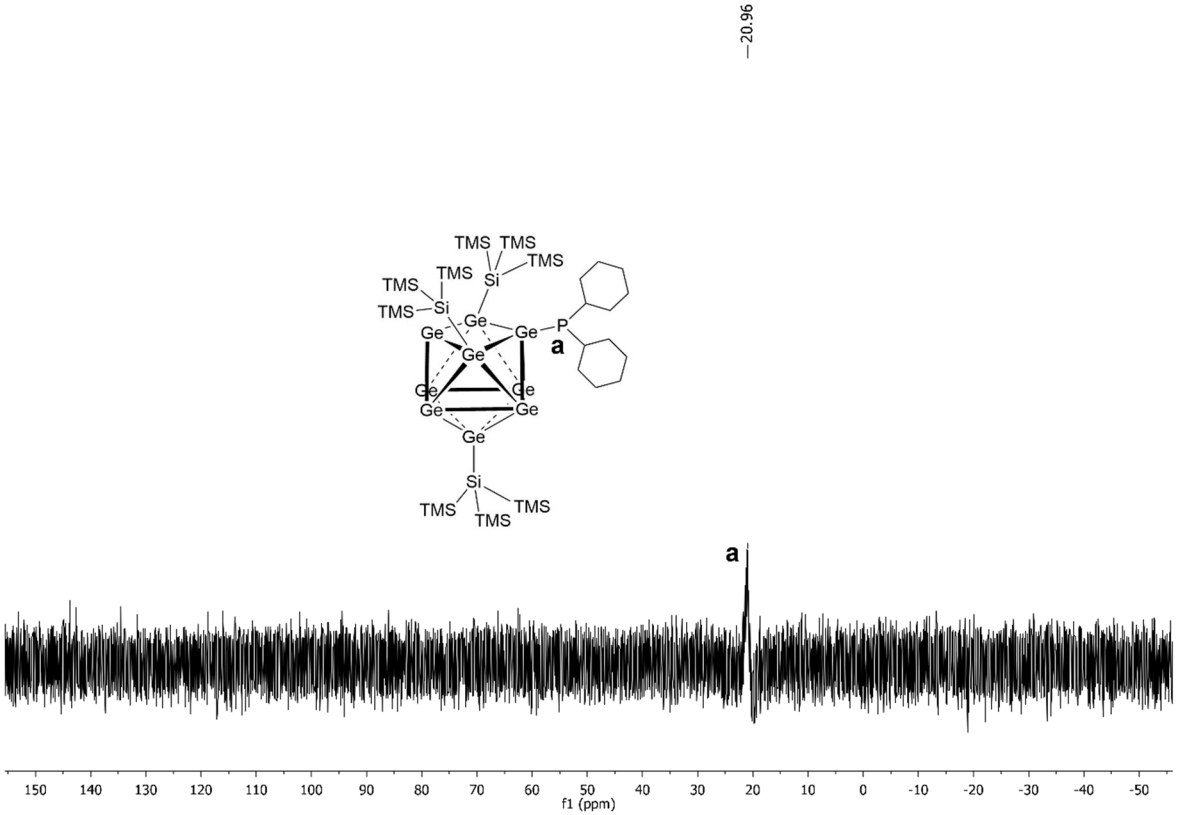

Figure SI 5: ^{31}P NMR spectrum of compound **1** in thf- d_8.

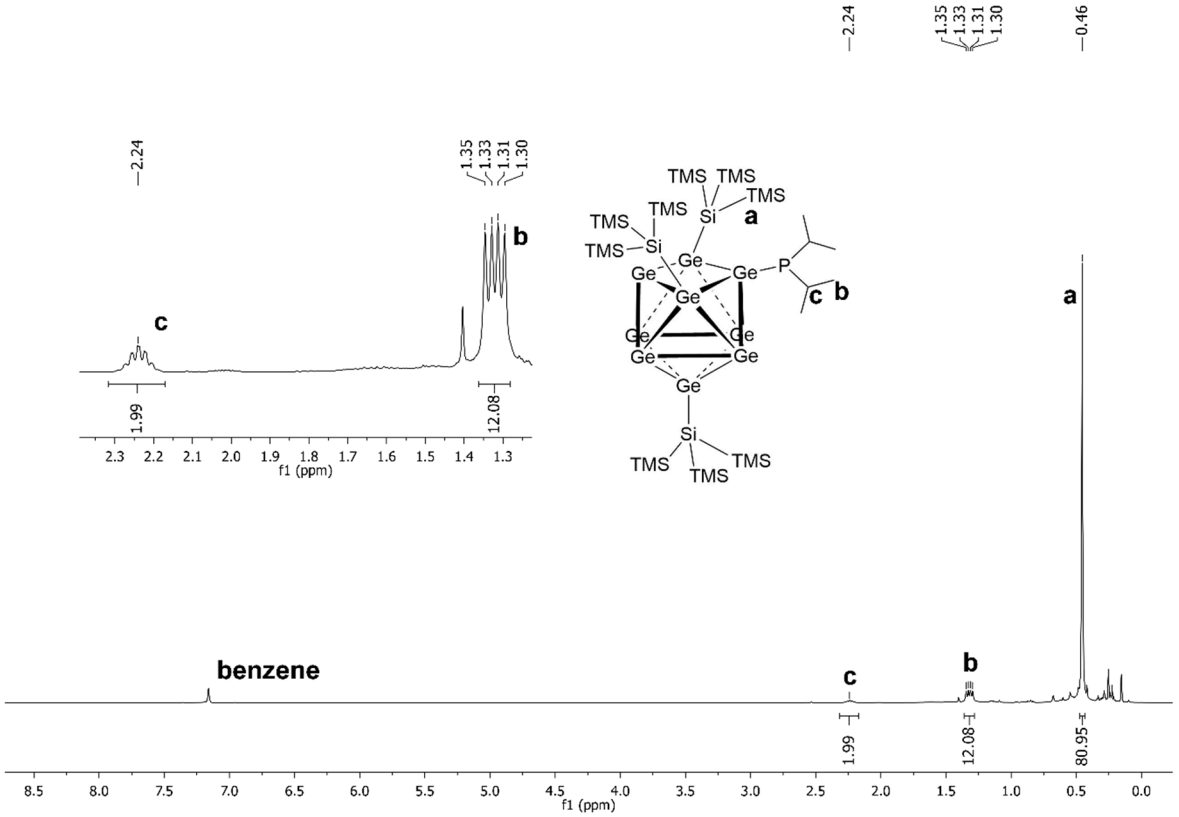

Figure SI 6: ^{1}H NMR spectrum of compound **2** in C_6D_6.

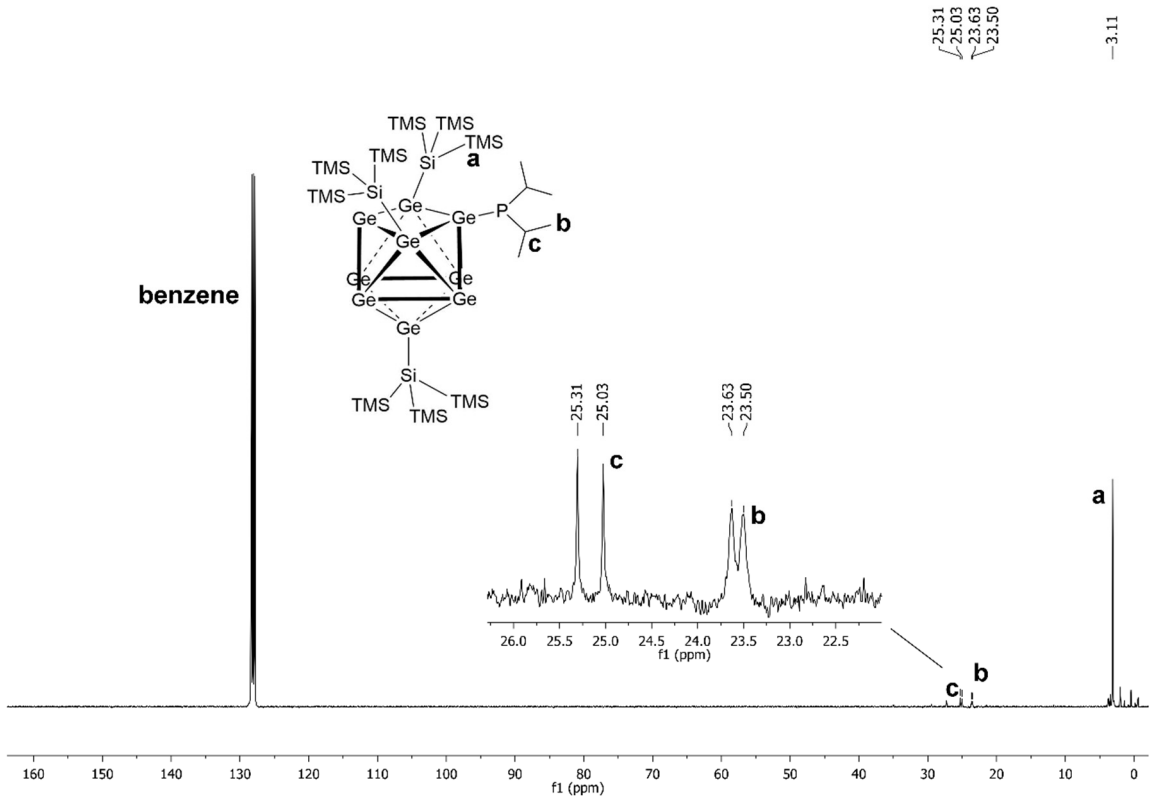

Figure SI 7: ^{13}C NMR spectrum of compound **2** in C_6D_6.

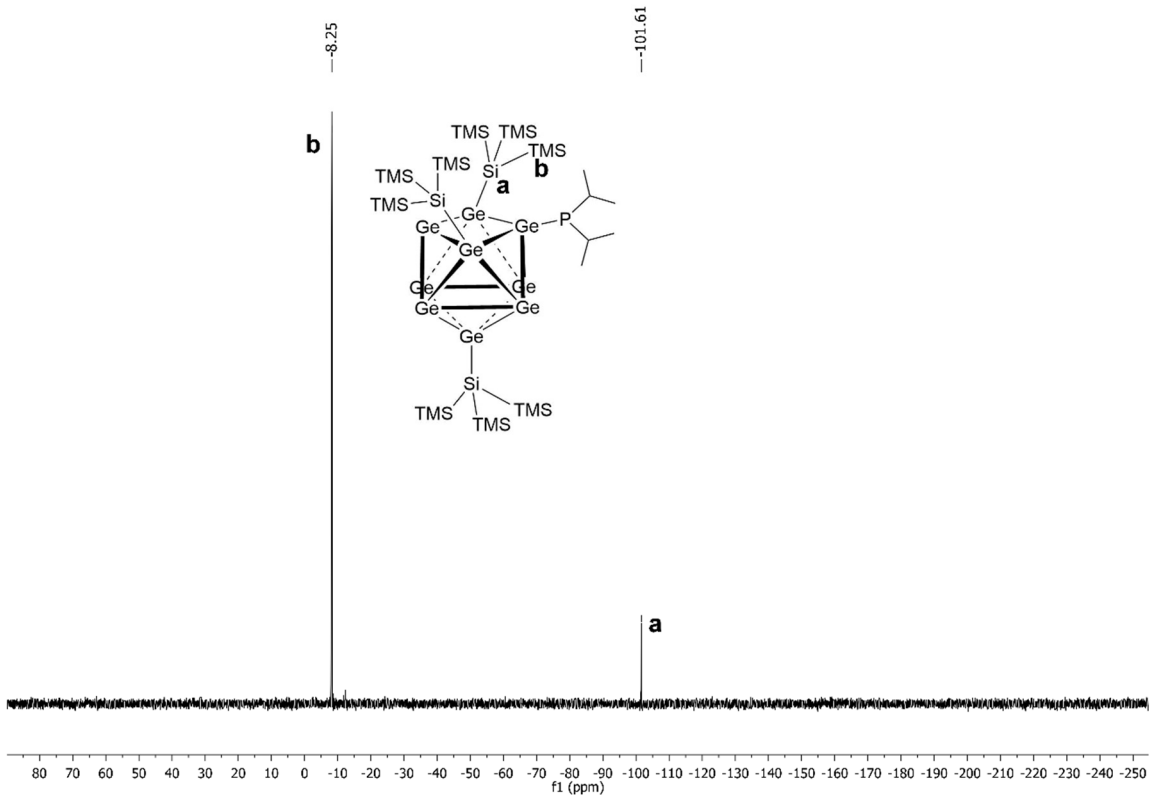

Figure SI 8: ^{29}Si NMR spectrum of compound **2** in C_6D_6.

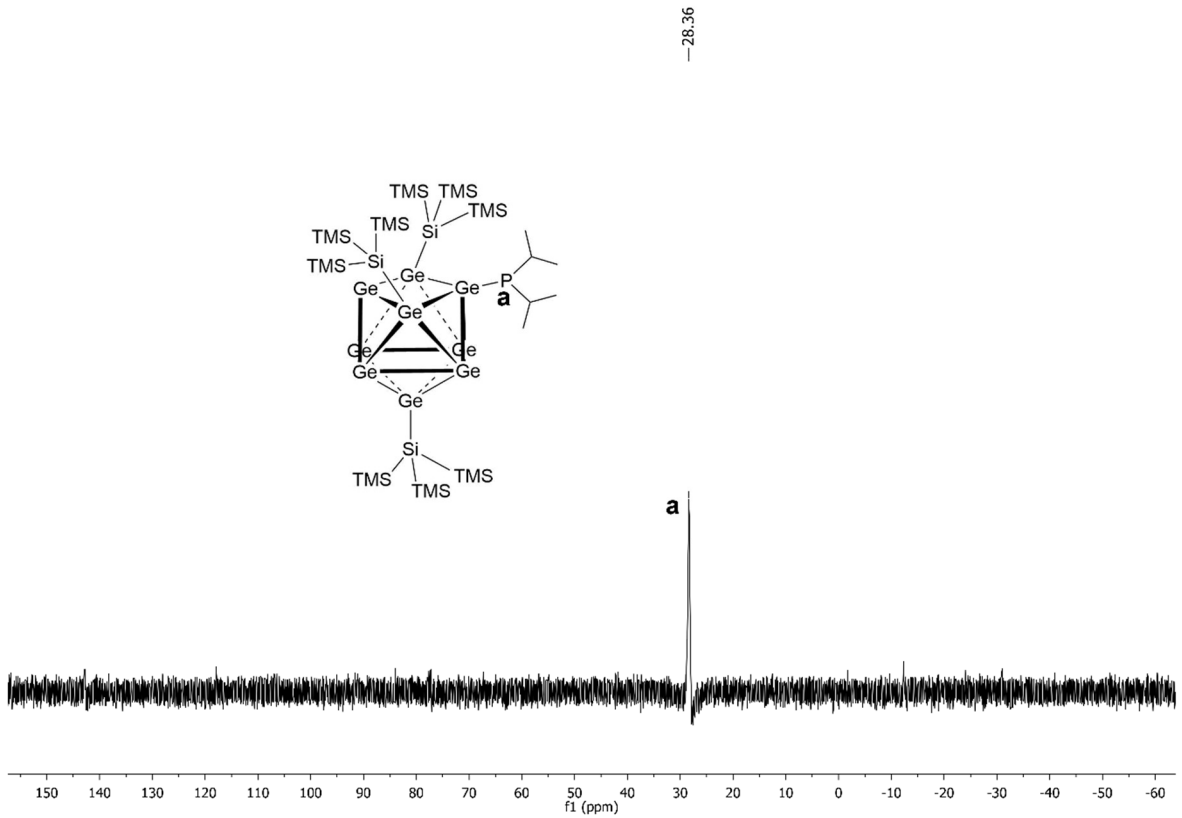

Figure SI 9: ^{31}P NMR spectrum of compound **2** in C_6D_6.

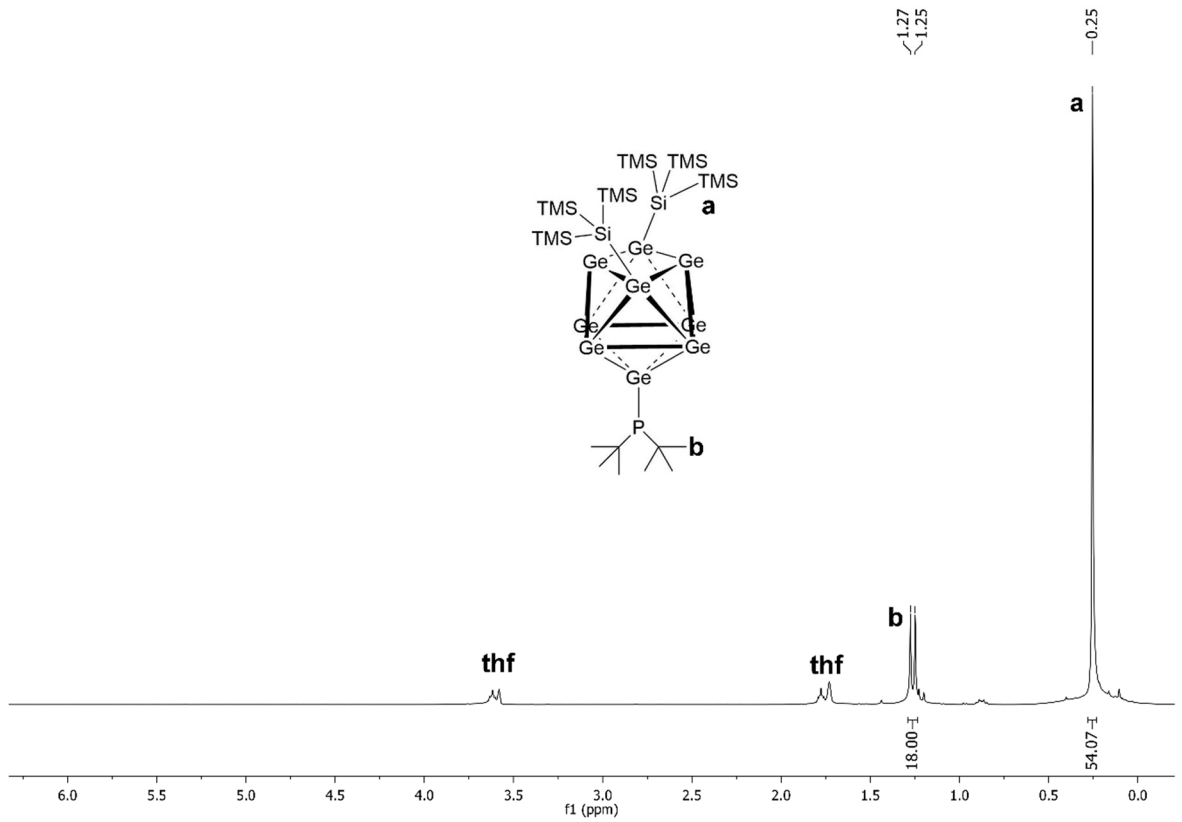

Figure SI 10: ^{1}H NMR spectrum of compound **3** in thf-d_8.

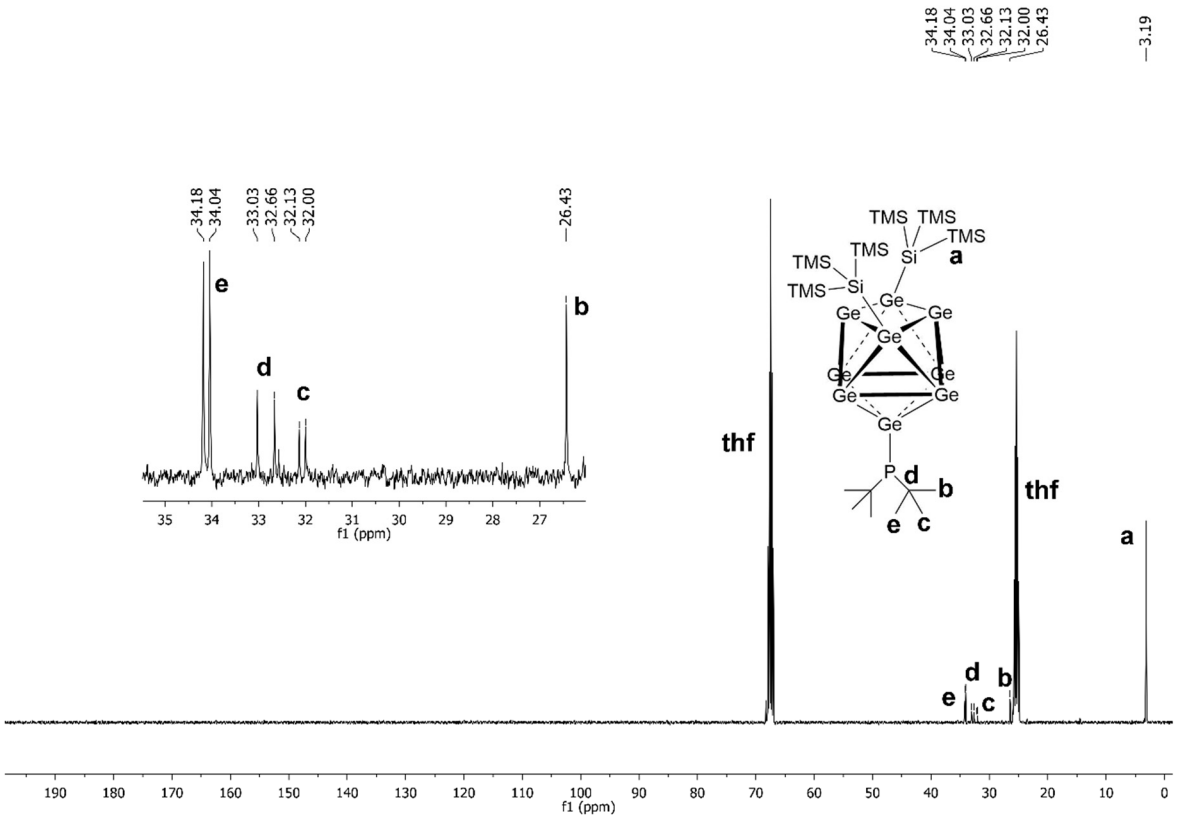

Figure SI 11: ^{13}C NMR spectrum of compound **3** in thf-d_8.

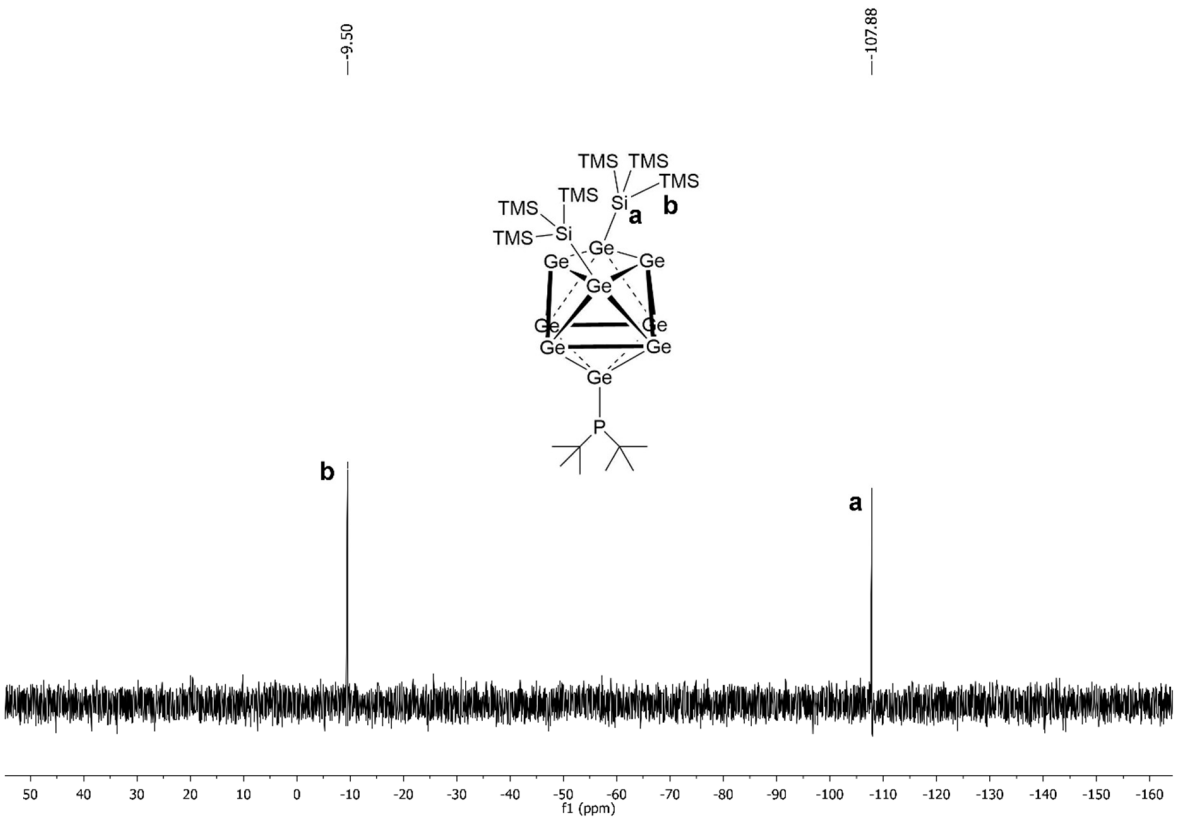

Figure SI 12: ^{29}Si NMR spectrum of compound **3** in thf-d_8.

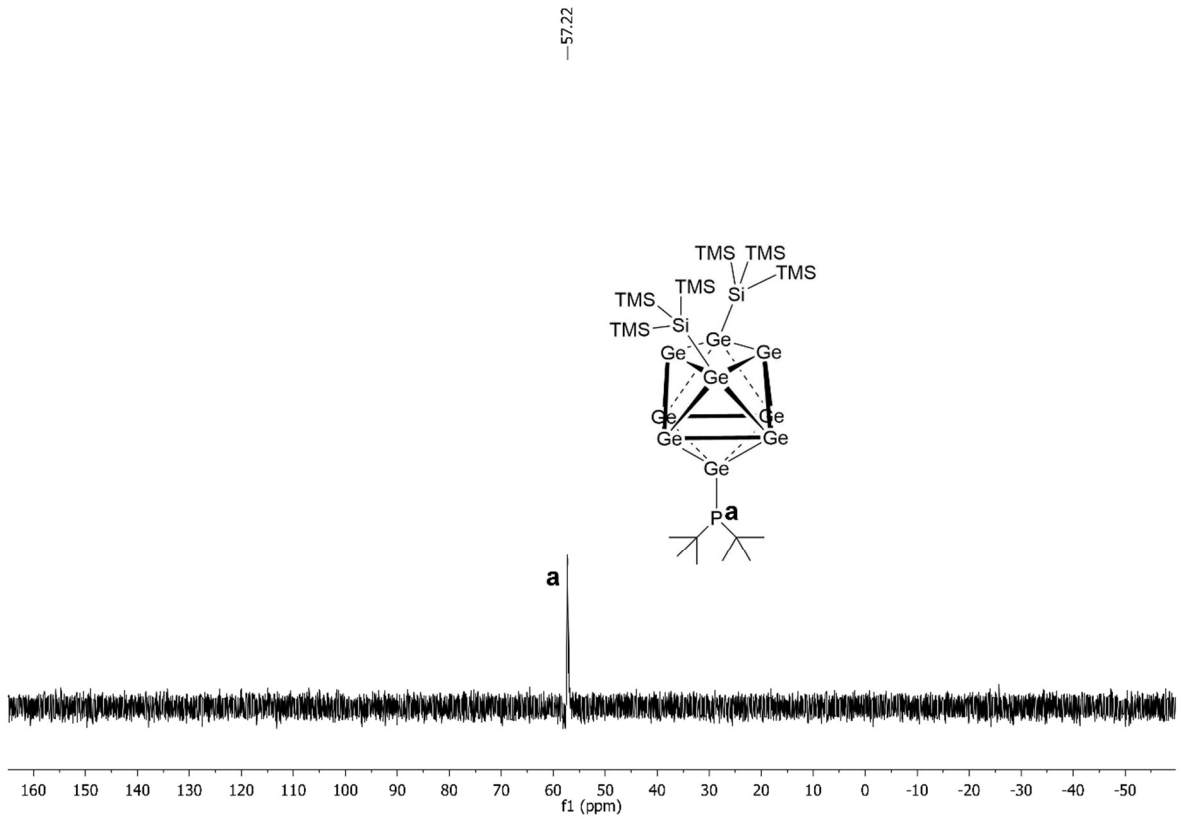

Figure SI 13: ^{31}P NMR spectrum of compound **3** in thf-d_8.

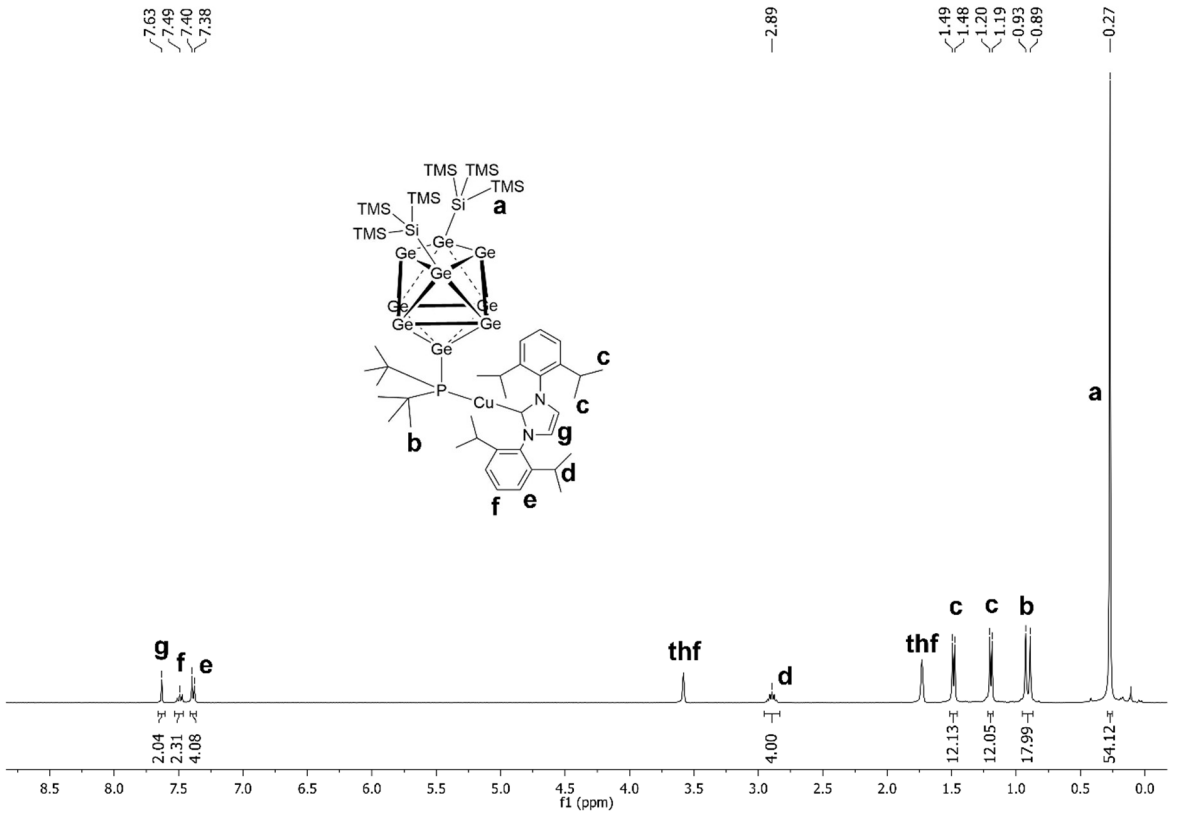

Figure SI 14: ^{1}H NMR spectrum of compound **4** in thf-d_8.

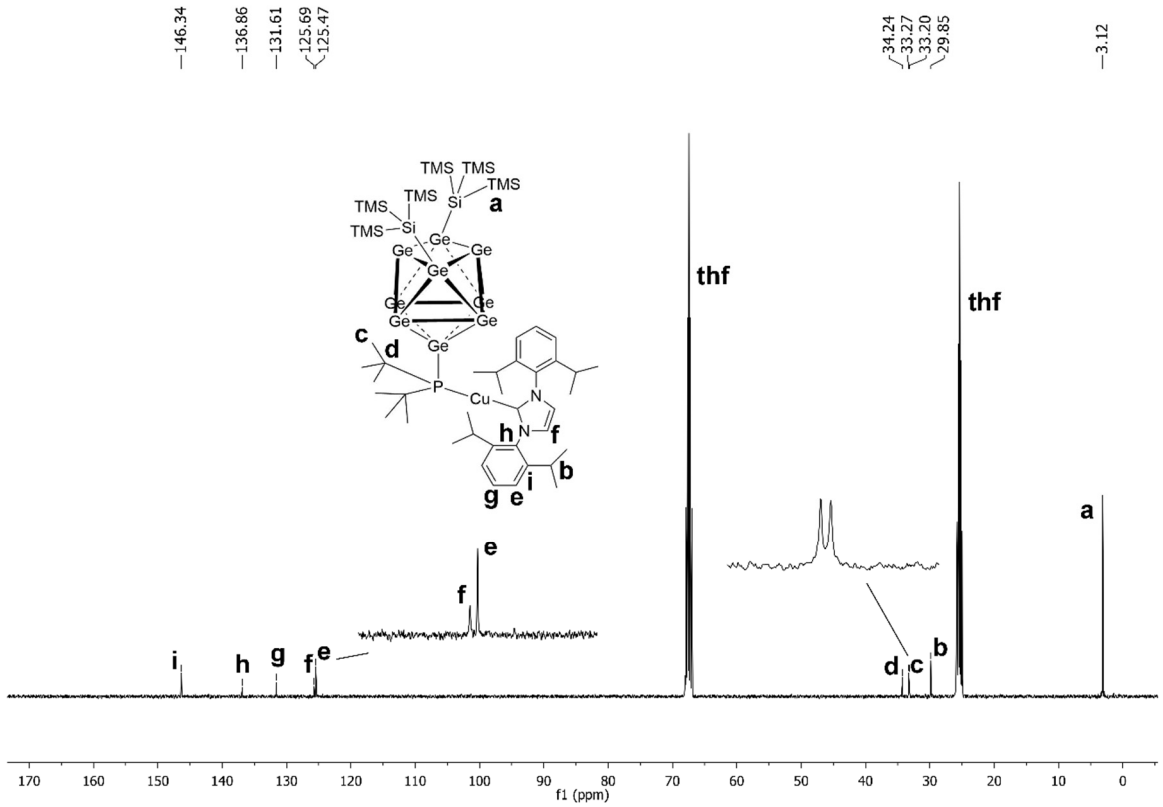

Figure SI 15: ^{13}C NMR spectrum of compound **4** in thf-d_8.

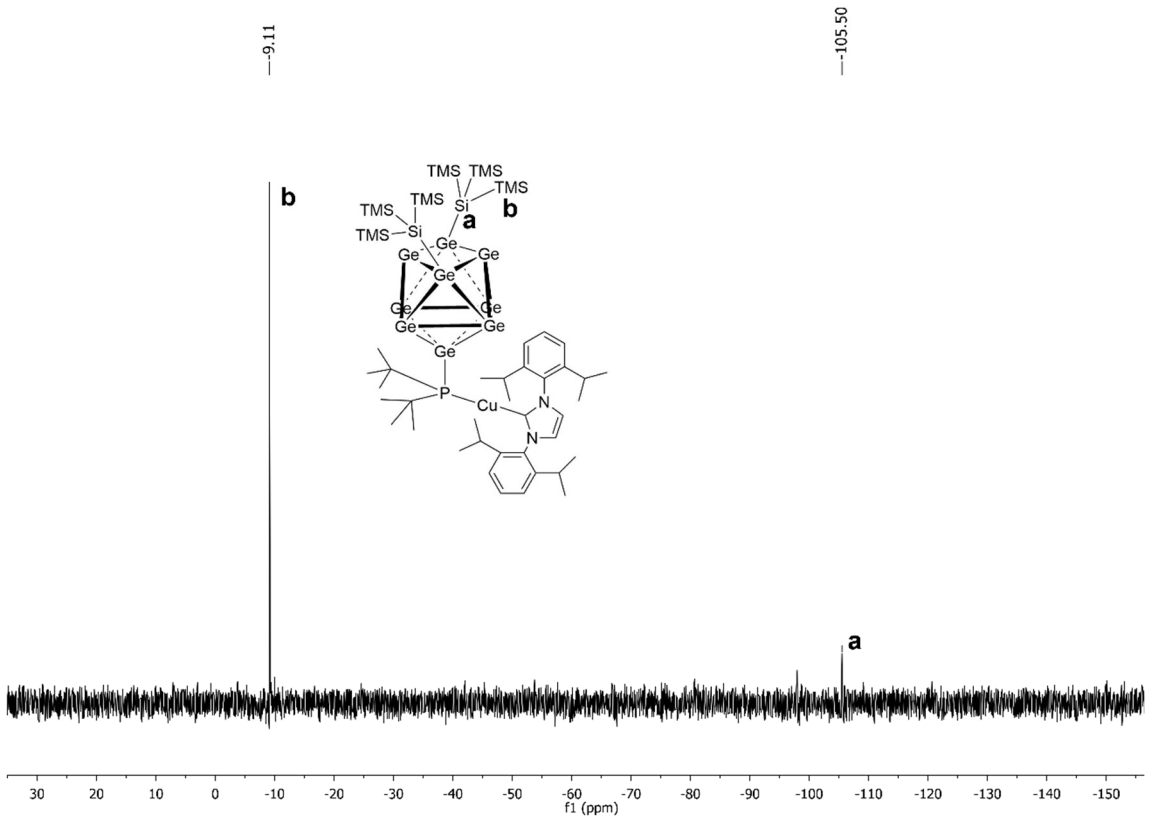

Figure SI 16: ^{29}Si NMR spectrum of compound **4** in thf-d_8.

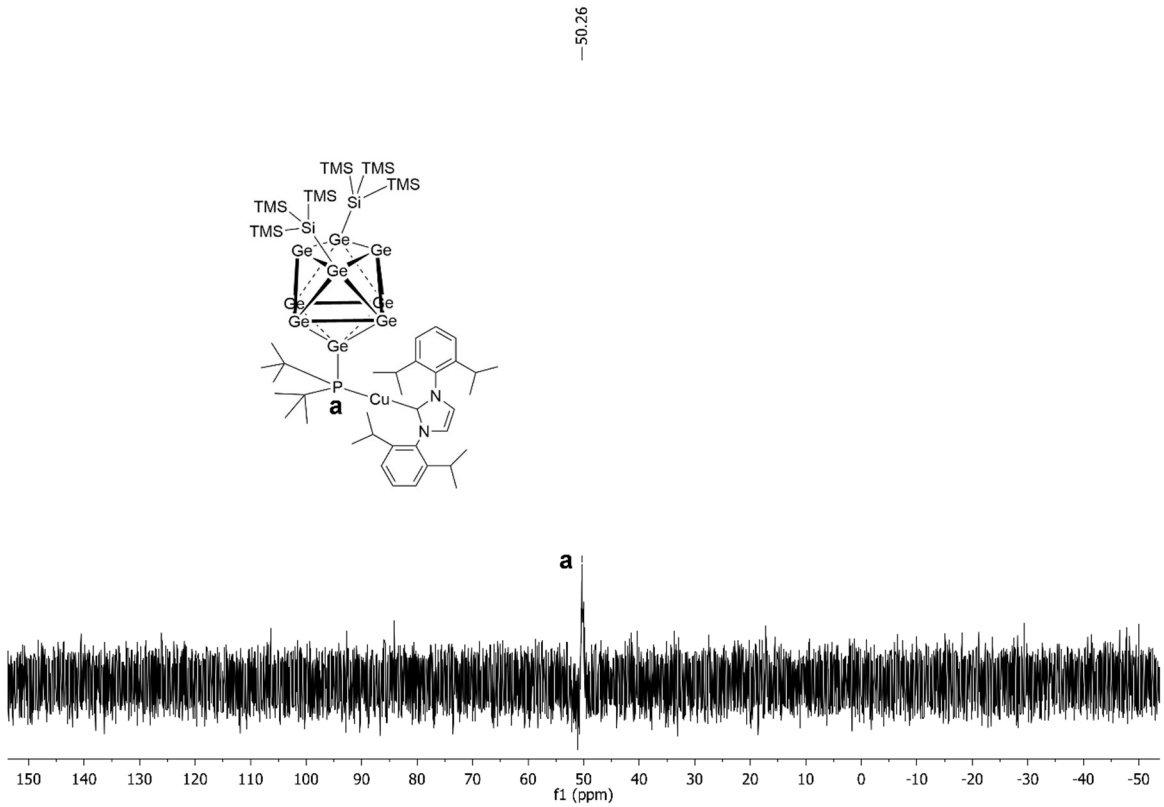

Figure SI 17: ^{31}P NMR spectrum of compound **4** in thf-d_8.

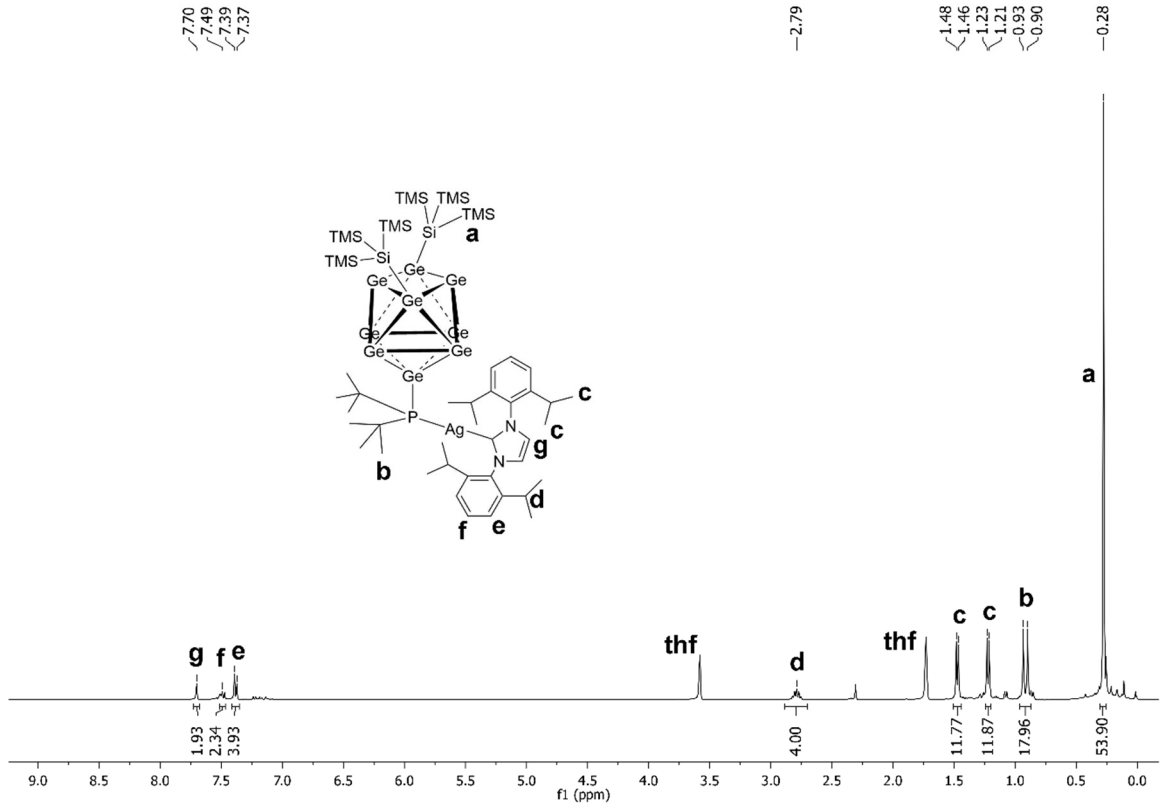

Figure SI 18: ^{1}H NMR spectrum of compound **5** in thf-d_8.

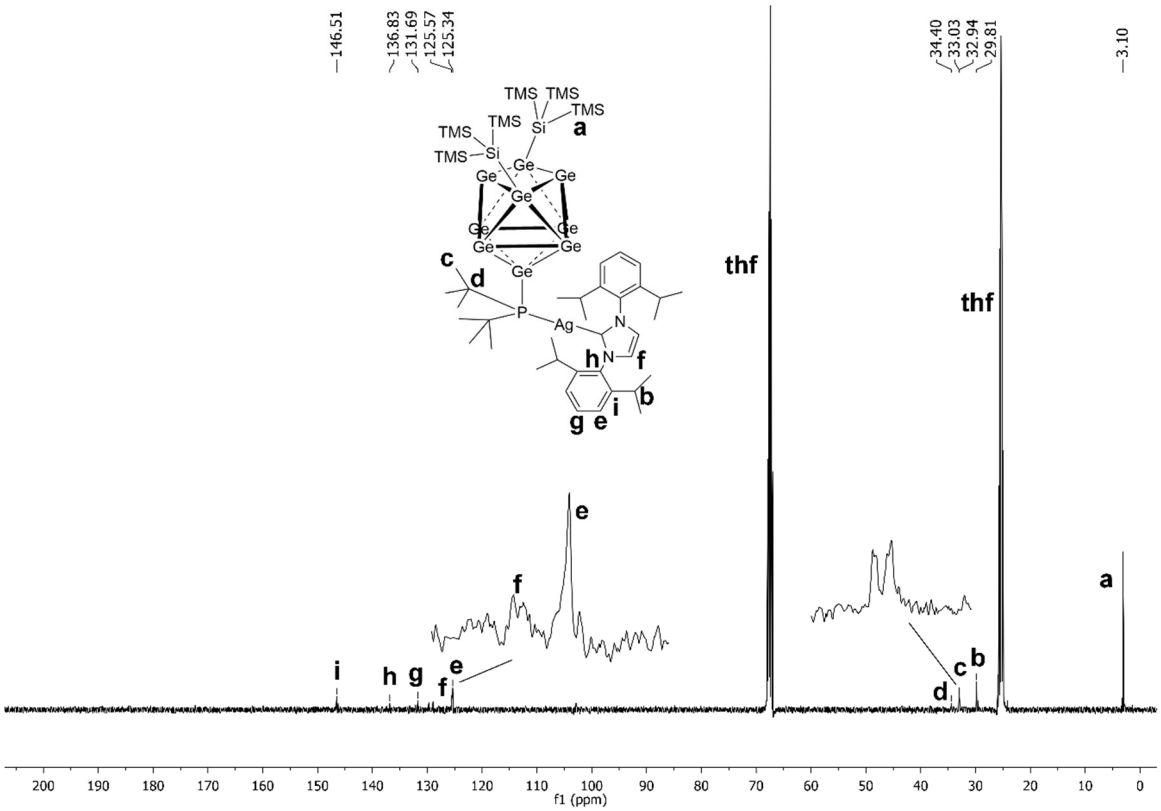

Figure SI 19: ^{13}C NMR spectrum of compound **5** in thf-d_8.

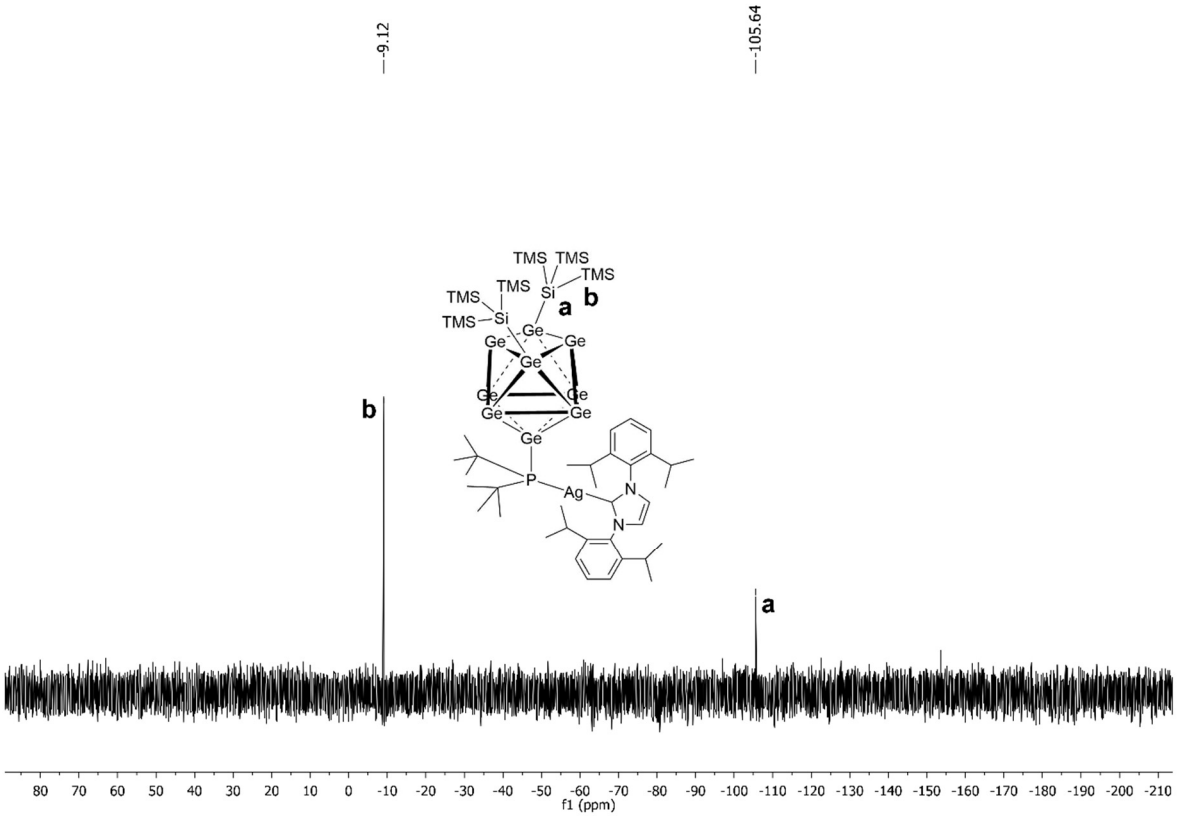

Figure SI 20: ^{29}Si NMR spectrum of compound **5** in thf-d_8.

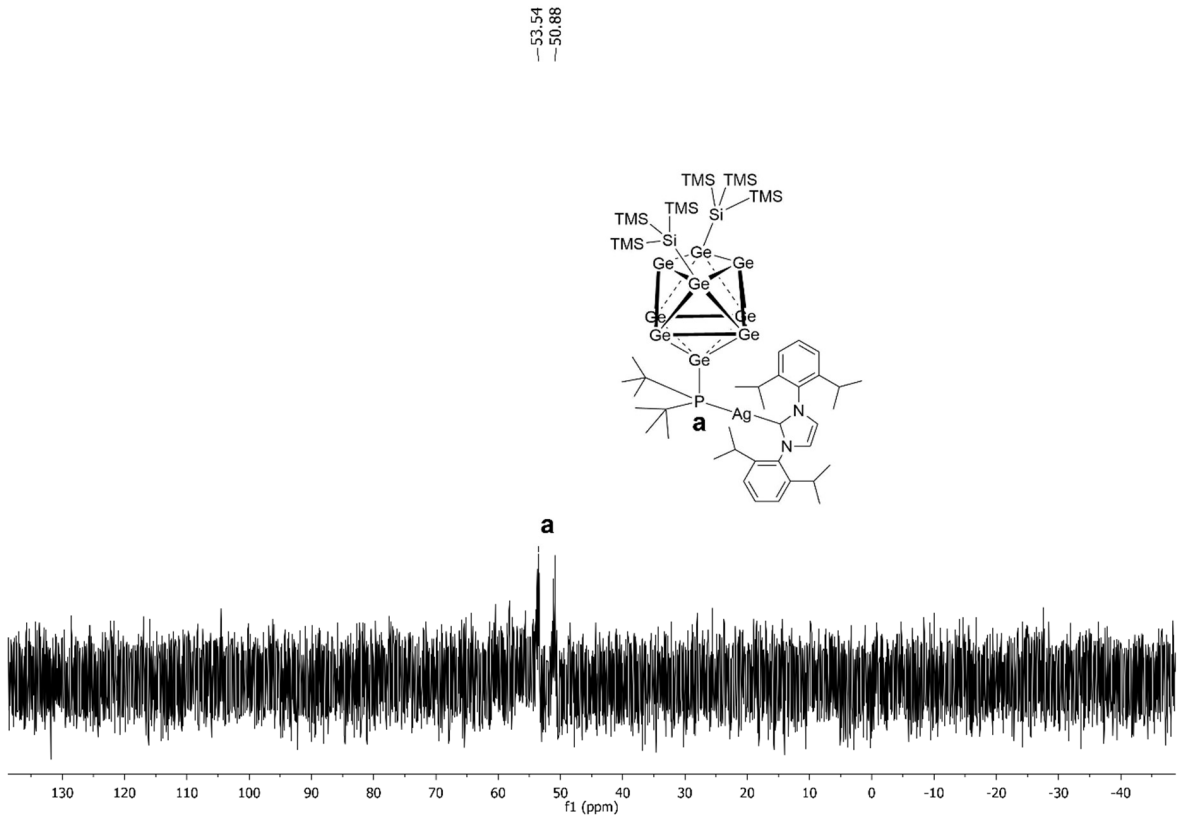

Figure SI 21: ^{31}P NMR spectrum of compound **5** in thf-d_8.

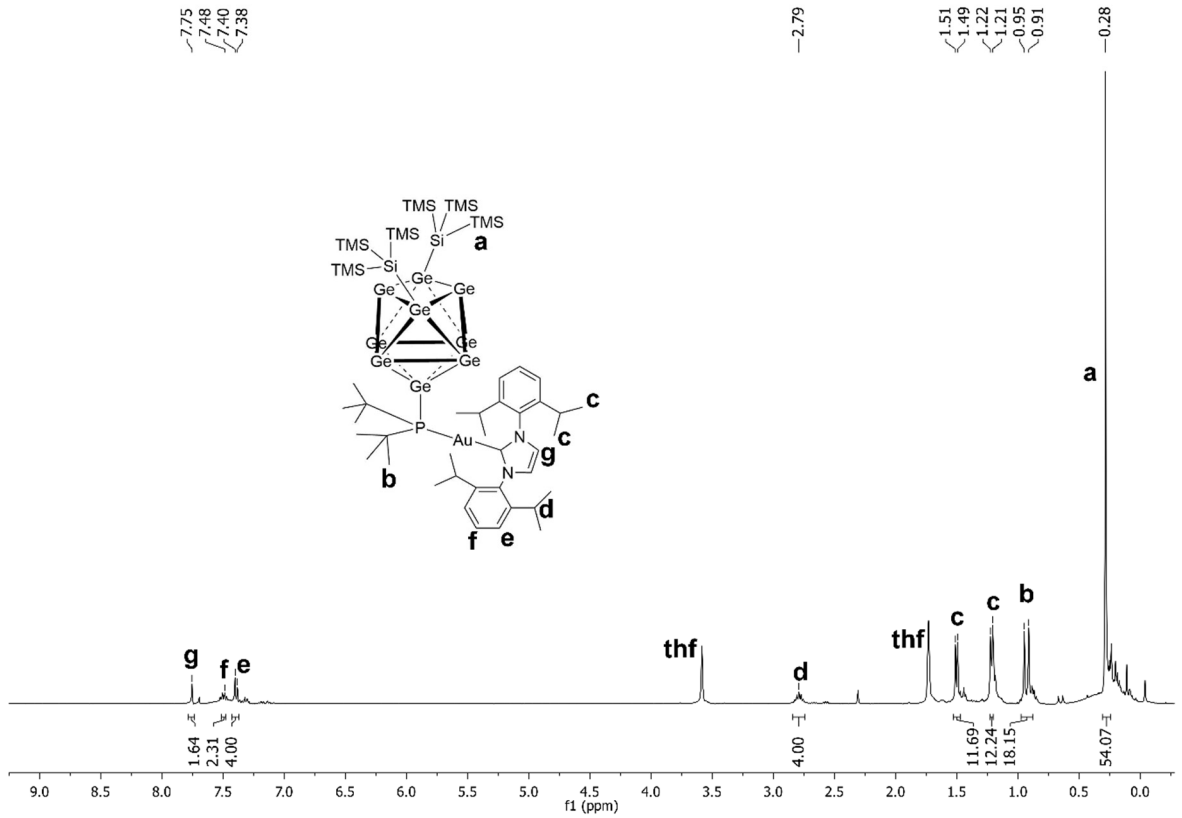

Figure SI 22: ^{1}H NMR spectrum of compound **6** in thf-d_8.

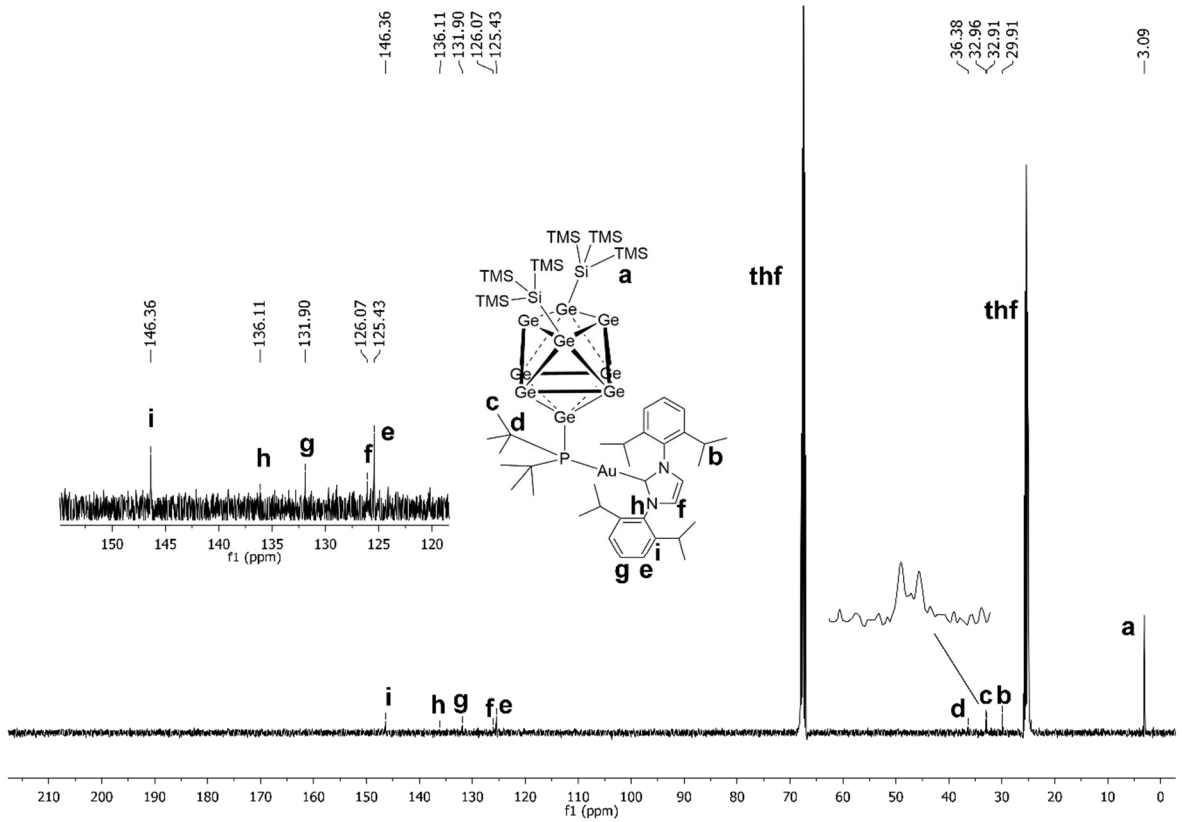

Figure SI 23: ^{13}C NMR spectrum of compound **6** in thf-d_8.

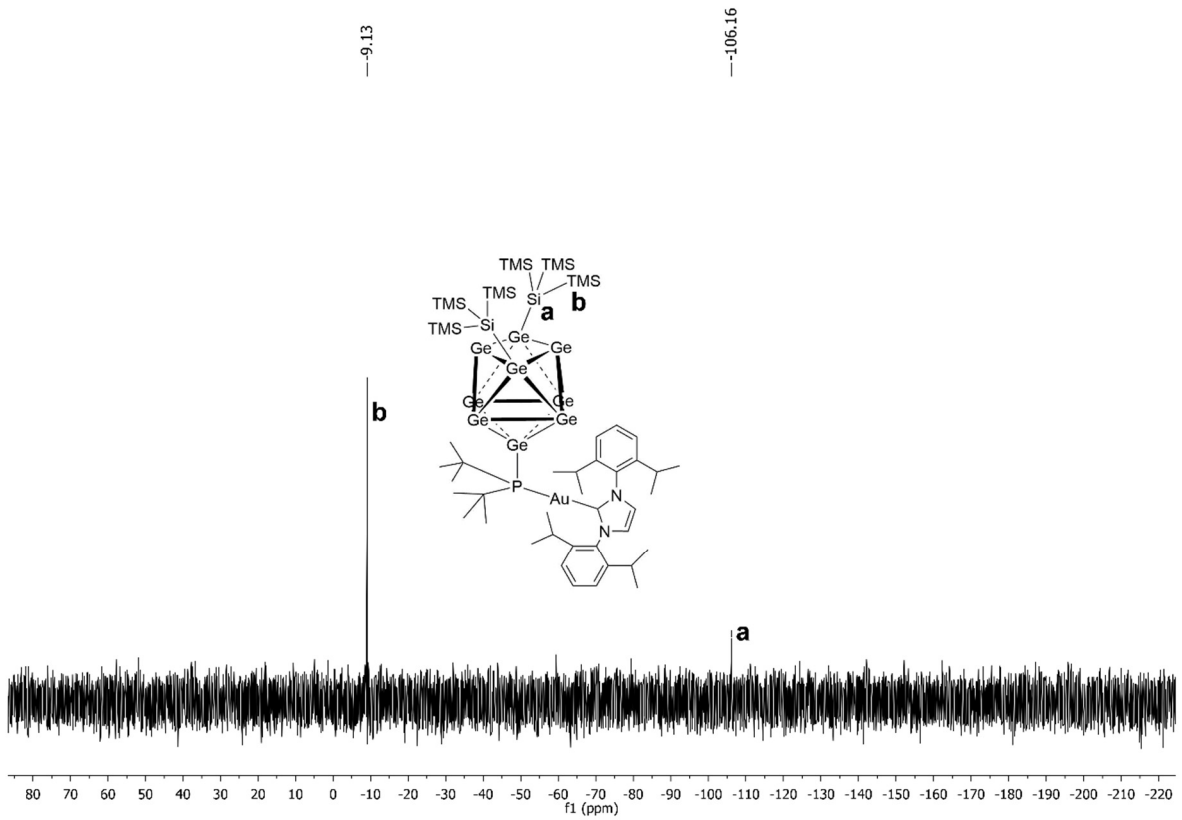

Figure SI 24: ^{29}Si NMR spectrum of compound **6** in thf-d_8.

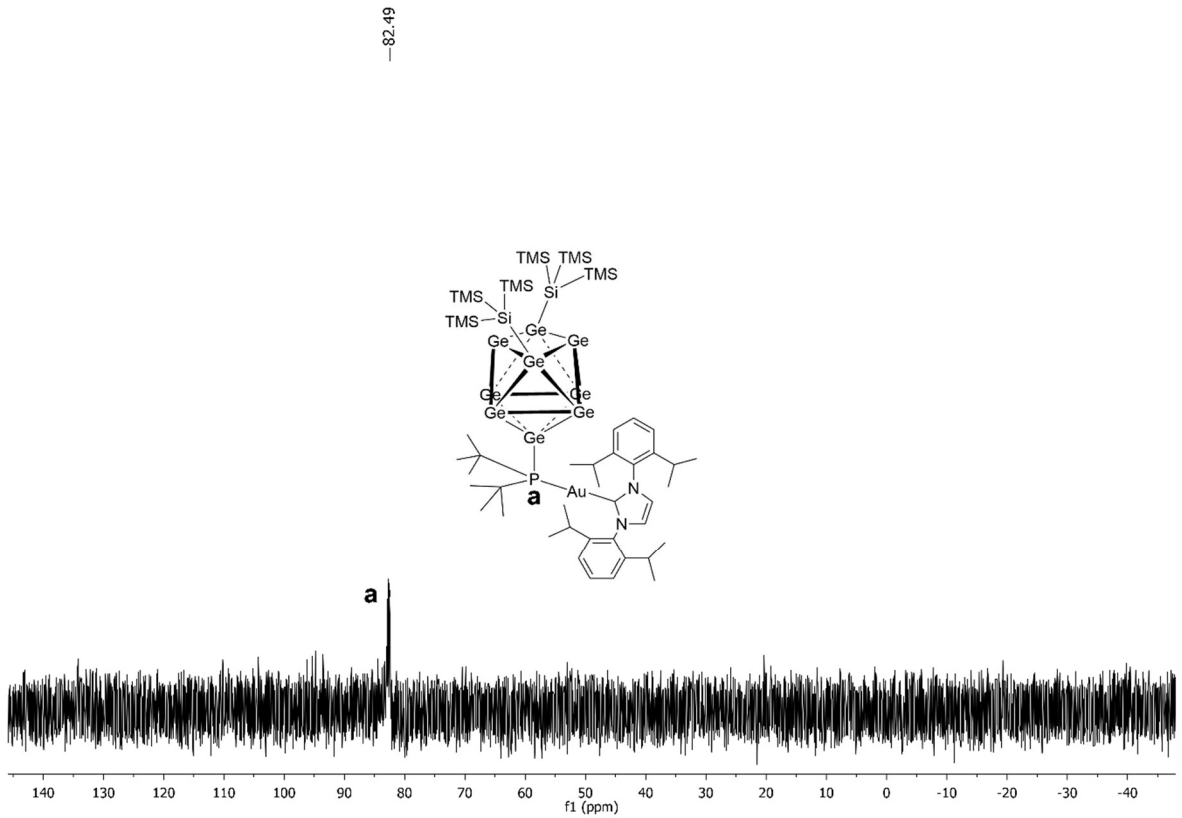

Figure SI 25: ^{31}P NMR spectrum of compound **6** in thf-d_8.

ESI-MS spectra

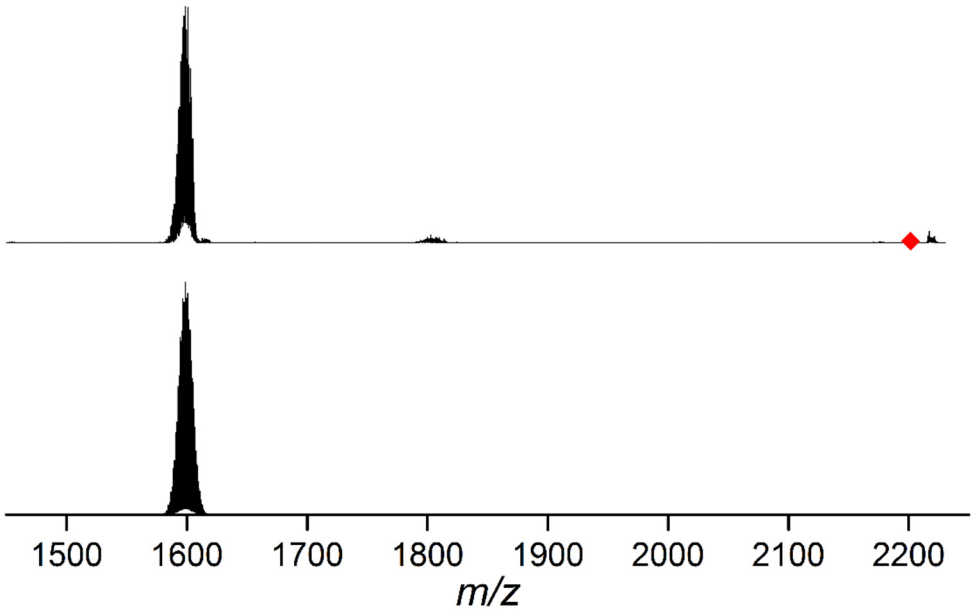

Figure SI 26: MS-MS fragmentation of signal at *m/z* 2199.3 {[(NHC^{Dipp}Cu)[(Ge$_9${Si(TMS)$_3$}$_2$)^{t}Bu$_2$P]Cu(NHC^{Dipp})]$^+$} (red square), yielding signal at *m/z* 1598.7 {[(NHC^{Dipp}Cu)Ge$_9${Si(TMS)$_3$}$_2$]$^+$}, resulting from cleavage of NHC^{Dipp}CuP^{t}Bu$_2$-moiety. Measured spectrum (top) was acquired in positive ion mode (4000 V, 300 °C), calculated spectrum is pictured below.

References

(1) Hirshfeld, F. L. *Theor. Chim. Acta* **1977**, *44*, 129.

(2) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735.

(3) Lazreg, F.; Slawin, A. M. Z.; Cazin, C. S. J. *Organometallics* **2012**, 31, 7969.

(4) Momma, K.; Izumi, F. *J. Appl. Crystallogr.* **2008**, 41, 653.