

Electronic Supplementary Information

The influence of the $\text{FeCp}(\text{CO})_2^+$ moiety on the dynamics of the metalloid $[\text{Ge}_9(\text{Si}(\text{SiMe}_3)_3)_3]^-$ cluster in thf: Synthesis and characterization by time-resolved absorption spectroscopy

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Stationary UV-Vis-NIR absorption spectra

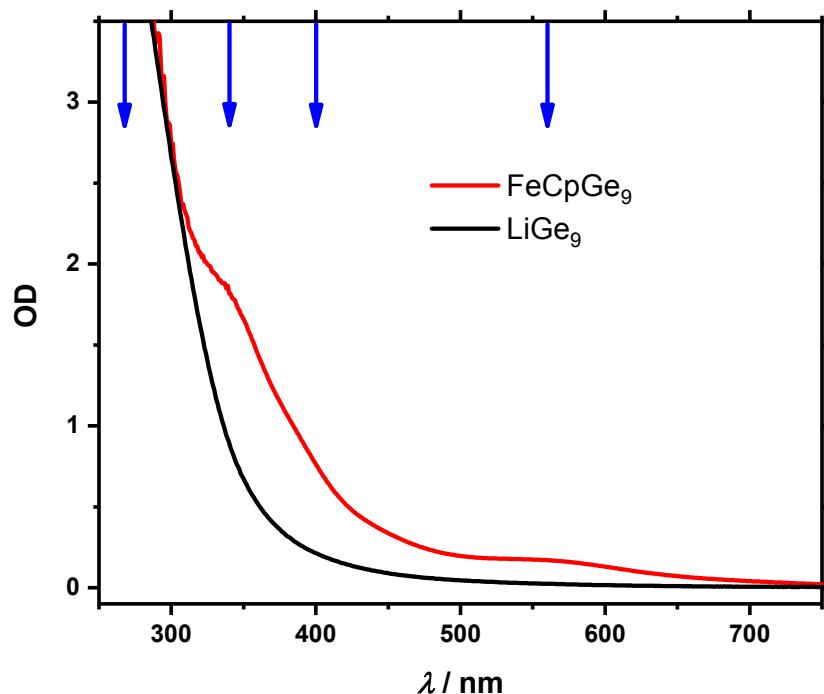


Figure S1: Comparison between the stationary absorption spectra of $[\text{Ge}_9(\text{Hyp})_3\text{FeCp}(\text{CO})_2]$ (FeCpGe_9) and $[\text{Ge}_9(\text{Hyp})_3]$ (LiGe_9), between 250 and 750 nm. Blue arrows mark excitation wavelengths for the fs pump-probe experiments of FeCpGe_9 .

Transient absorption spectra

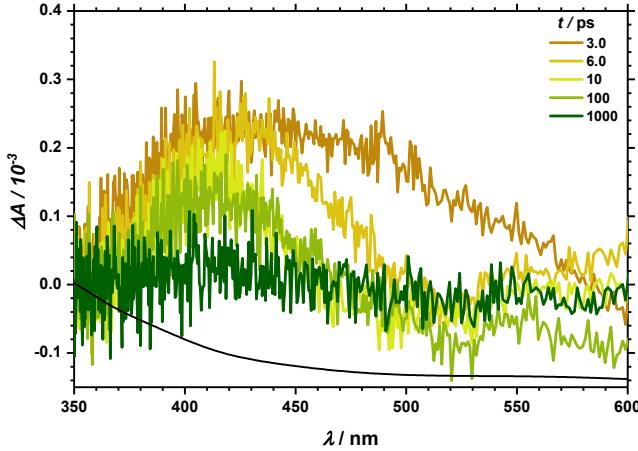


Figure S2: Transient absorption spectra at selected delay times after excitation with 340 nm and steady state absorption spectrum (black line).

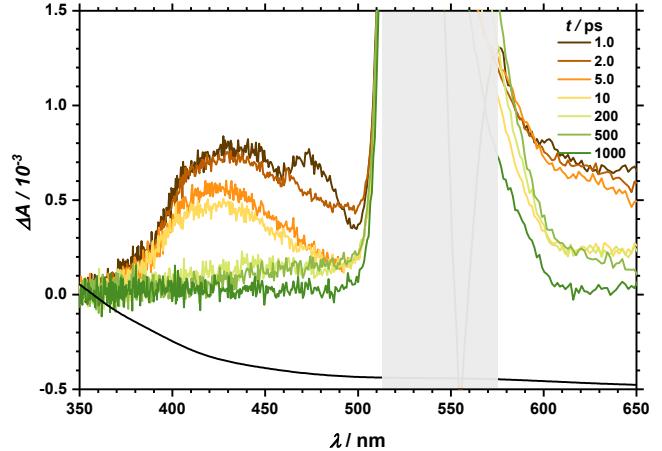


Figure S3: Transient absorption spectra at selected delay times after excitation with 560 nm and steady state absorption spectrum (black line). Global fit near the probe wavelength is not possible due to artifacts caused by scattered light from pump pulse (gray box).

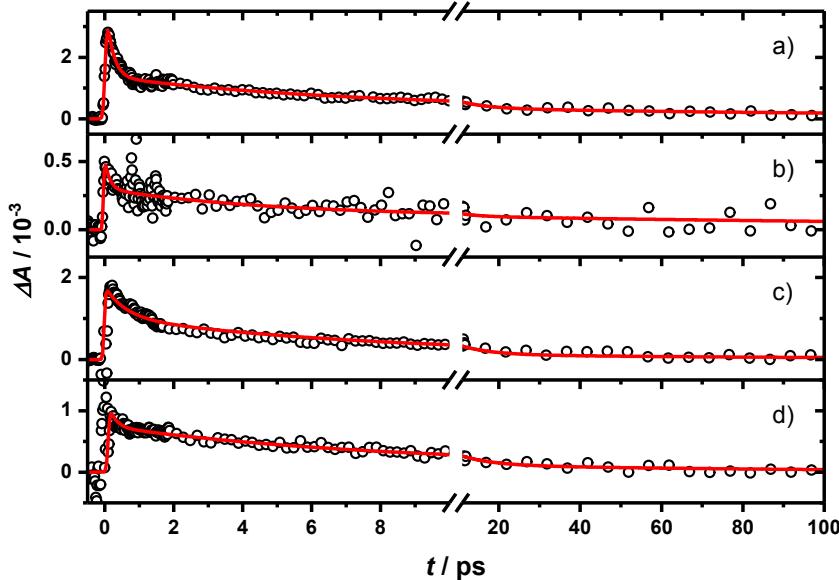


Figure S4: Comparison of transient response at 415 nm probe wavelength after a) 267 nm, b) 340 nm, c) 400 nm and d) 560 nm excitation.

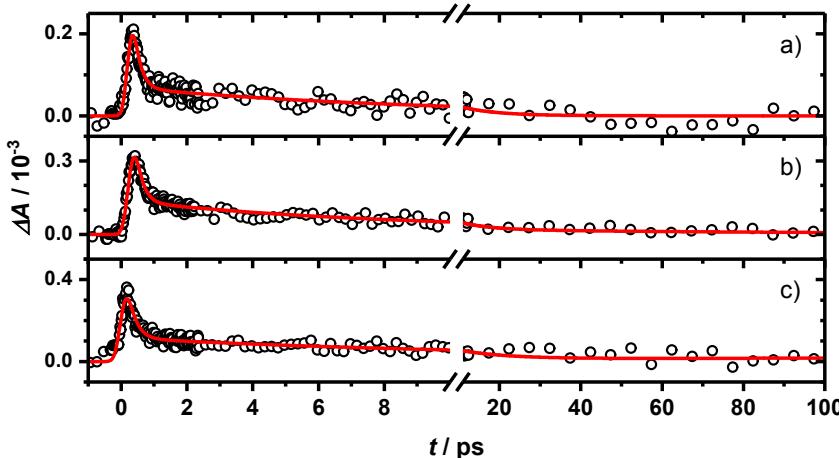


Figure S5: Comparison of transient response at 1000 nm probe wavelength after a) 258 nm, b) 388 nm excitation of $[\text{Ge}_9(\text{Hyp})_3\text{FeCp}(\text{CO})_2]$, c) $\text{Li}[\text{Ge}_9(\text{Hyp})_3]$ after 258 nm excitation at 1000 nm probe wavelength.

Fit parameter and decay associated spectra

Table 1: Exponential fitting procedure reveals the following time constants in ps decay functions for Vis and NIR spectral range. Long time constants after 340 and 560 nm excitations have relatively high errors due to low signal to noise ratio. First three time constants for Li[Ge₉(Hyp)₃] are given for comparison.²³

	267-Vis	258-NIR	340-Vis	400-Vis	388-NIR	560-Vis	LiGe ₉ (Ref. 23)
τ_1	0.2	0.2	0.1	0.6	0.2	0.2	0.5
τ_2	7	9	7	8	7	7	2
τ_3	150		190	100	100	200	>>100

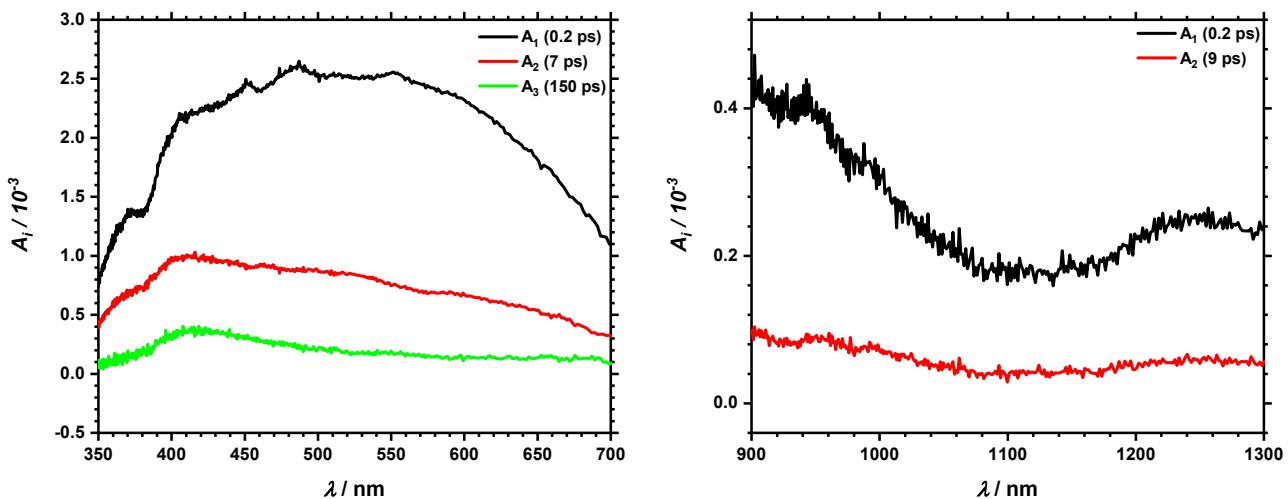


Figure S6: Decay associated spectra (DAS) for given time constants with amplitudes A_i from fits of the experimental data after excitation with 267/258 nm in Vis (left) and NIR (right). In the NIR a third (long) time constant was not necessary.

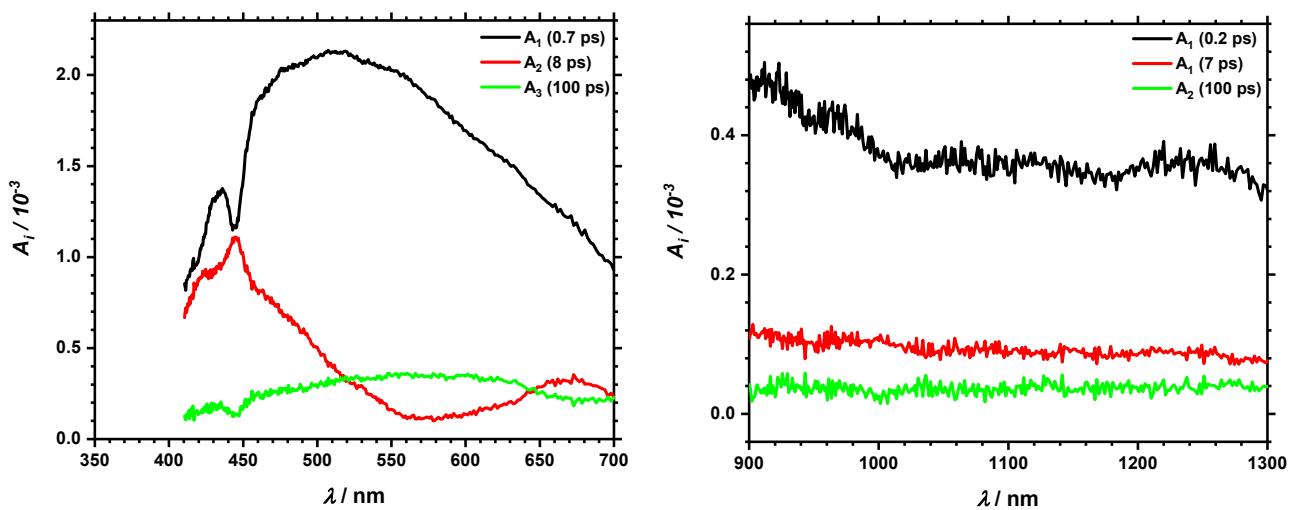


Figure S7: Decay associated spectra (DAS) for given time constants from fits of the experimental data after excitation with 400/388 nm and probe in Vis (left) and NIR (right). Global fit near the pump wavelength is not possible due to artifacts caused by scattered light.

[23] M. Klinger, C. Schenk, F. Henke, A. Clayborne, A. Schnepf and A. N. Unterreiner, *Chemical Communications*, 2015, **51**, 12278-12281.

NMR investigations

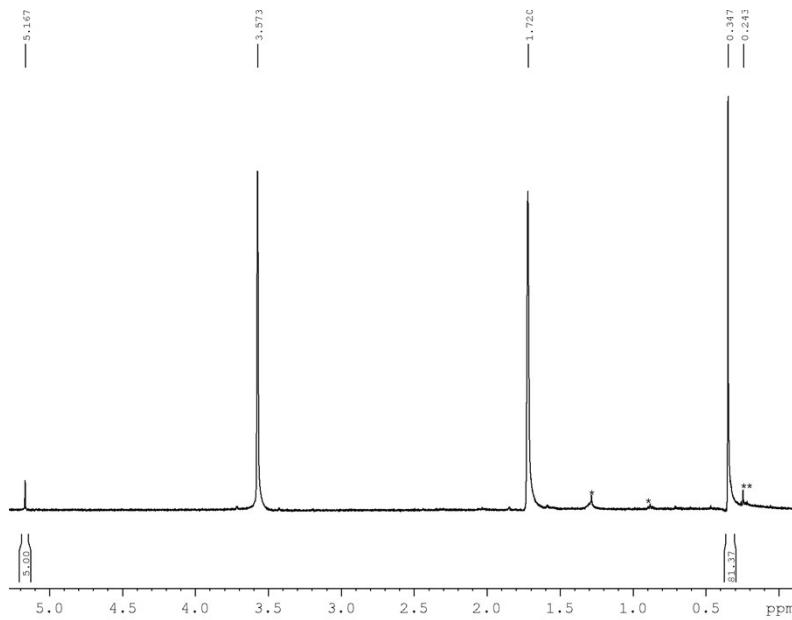


Figure S8: ¹H-NMR spectrum of $[FeCp(CO)_2]Ge_9(Hyp)_3$ at room temperature. Peaks marked * are pentane residue from crystallization, ** is leftover $KGe_9(Hyp)_3$.

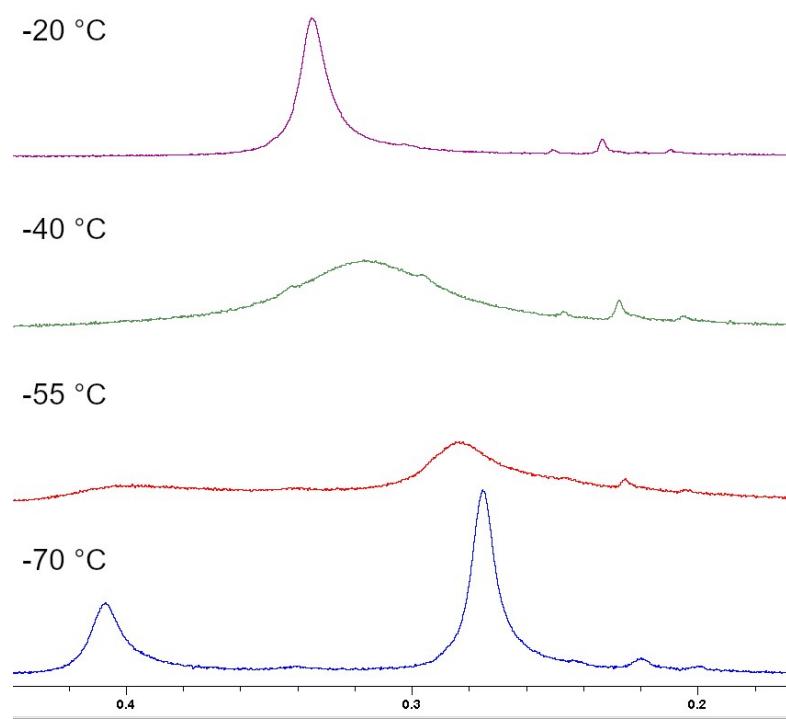


Figure S9: VT-¹H-NMR spectra of $[FeCp(CO)_2]Ge_9(Hyp)_3$.

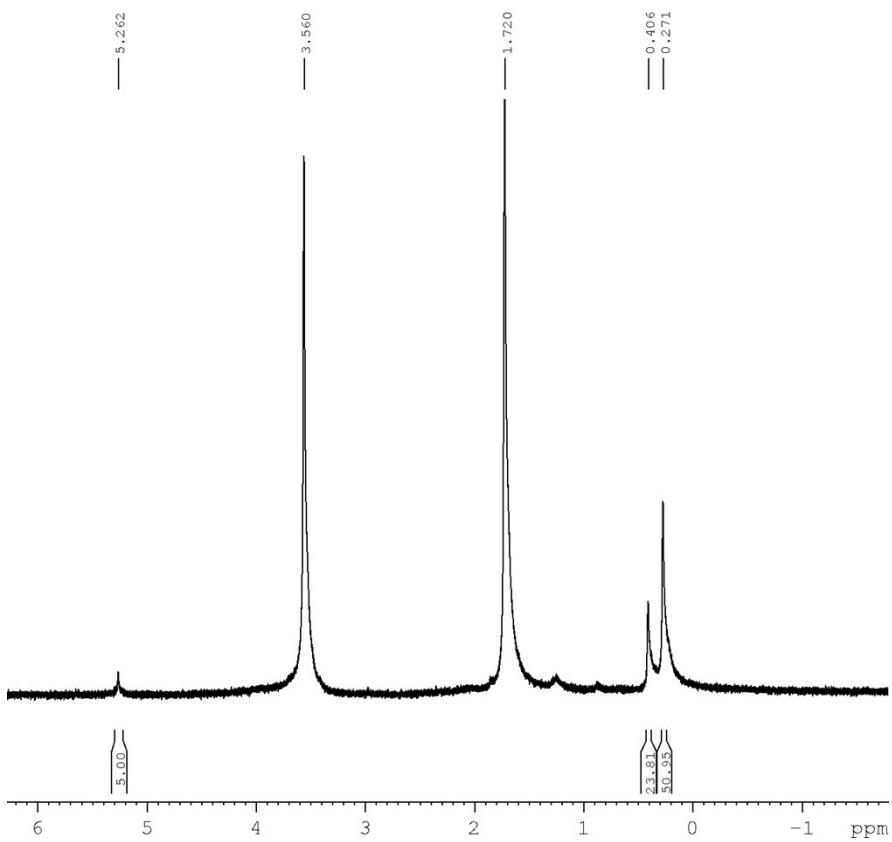


Figure S10: ^1H -NMR spectrum of $[\text{FeCp}(\text{CO})_2]\text{Ge}_9(\text{Hyp})_3$ at -80°C

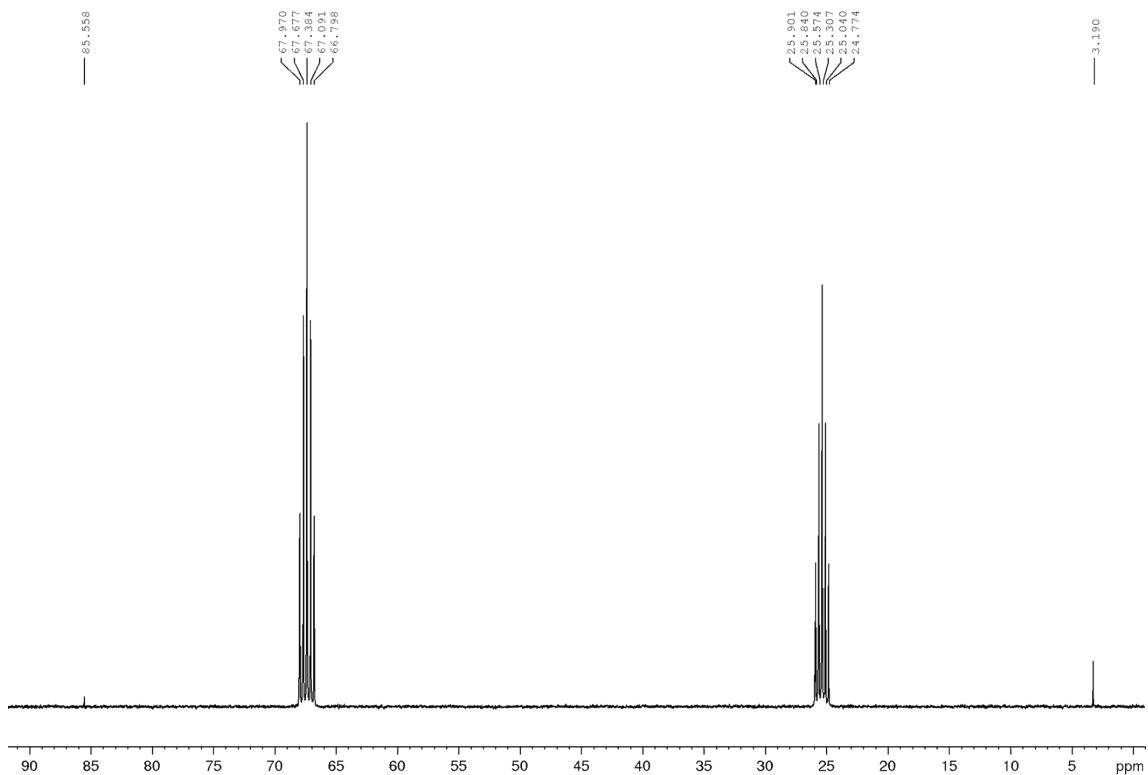


Figure S11: $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of $[\text{FeCp}(\text{CO})_2]\text{Ge}_9(\text{Hyp})_3$ at room temperature.

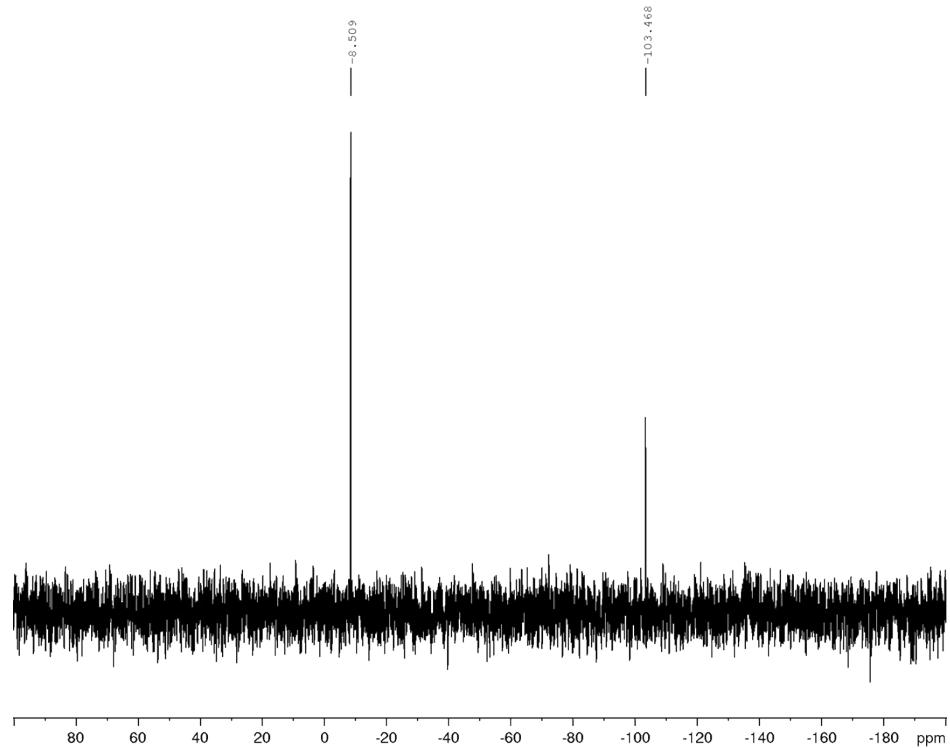


Figure S12: $^{29}\text{Si}\{\text{H}\}$ -dept-45-NMR spectrum of $[\text{FeCp}(\text{CO})_2]\text{Ge}_9(\text{Hyp})_3$ at room temperature.

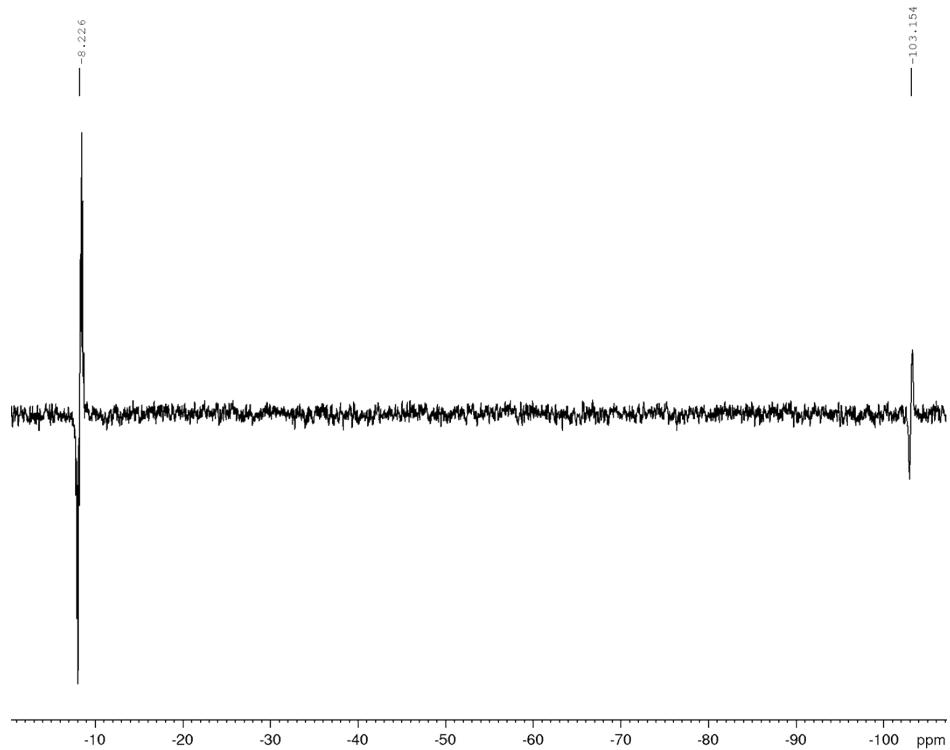


Figure S13: ^{29}Si incept-nd-NMR spectrum of $[\text{FeCp}(\text{CO})_2]\text{Ge}_9(\text{Hyp})_3$ at room temperature.

IR spectrum

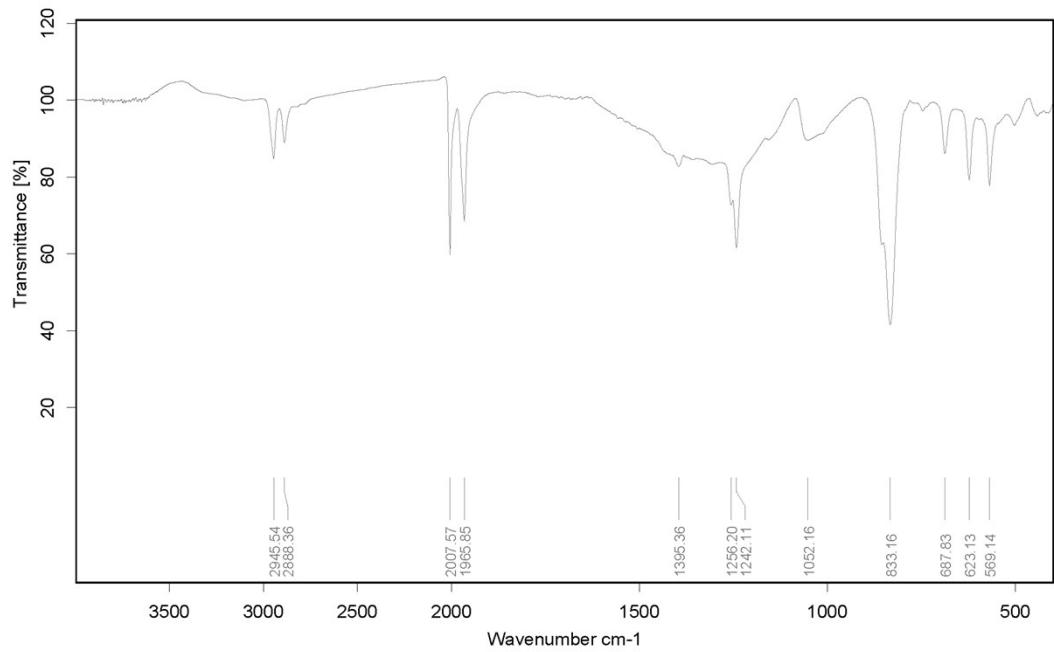


Figure S14: IR spectrum in KBr of $\text{FeCp}(\text{CO})_2\text{Ge}_9(\text{Hyp})_3$.