Supporting Information

A Molecular Model for the Ge(100) Buckled Dimer

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1 Experimental Section

1.1 General Considerations

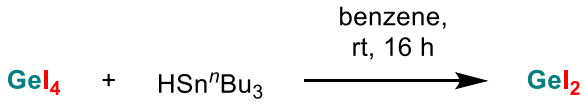
All used reagents and solvents were purchased from commercial sources. Unless otherwise noted, all manipulations were carried out under a dry nitrogen or argon atmosphere. Solvents were degassed prior to use with three freeze-pump-thaw cycles and were stored in sealed Schlenk ampoules over activated molecular sieve (3 or 4 Å, respectively) under a dry argon atmosphere. Liquid reactants were degassed for at least 10 minutes with a constant stream of dry argon through the fluid phase and were dried by storage over activated molecular sieve (3 or 4 Å, respectively). Solid reagents were dried and purified if necessary either by the application of vacuum and elevated temperature, or by sublimation under reduced pressure at elevated temperature. All reactions on preparative scale were carried out in flame-dried standard laboratory glassware under a dry argon atmosphere using Schlenk line techniques. Syringes, magnetic stirring bars, and needles were dried and/or flushed with argon prior to use. Reaction on the NMR sample scale were done in dry J. Young NMR tubes. Compounds sensitive to ambient conditions were handled and stored in a Sylatech glove box filled with dry nitrogen gas. Removal of solvents *in vacuo* was performed using a Schlenk line. Literature-known compounds H_4Cx^{Me} and H_4Cx^{Et},[1] K_4Cx^{Me} and K_4Cx^{Et} (adapted),[2] GeI_4 and $Cx^{Et}Ge(thf)_2$,[3] $GeCl_2$(1,4-dioxane)[4] and $NaB(C_6F_5)_4$[5] were synthesized following published procedures. GeO_2, HI (57 % aqueous), $GeCl_4$, HSn^nBu_3, PPh_2Ph, PPh_2Cl, NH_3 (1 M in dioxane), $Ni(COD)_2$, were purchased from commercial source and used as received. PPh_4Cl, piperidine-1-carbonitrile, sulfur, selenium, dimethyl disulfide, phenylacetylene and triethylphosphine oxide were purchased from a commercial source and dried and in case of liquids degassed by bubbling argon through the solution by 5 minutes before usage. Nuclear magnetic resonance (NMR) spectra were collected with a Bruker BZH 200/52, a Bruker DPX 200, a Bruker Avance II 400, or a Bruker Avance III 600 spectrometer at 298 K unless otherwise noted. Measurements with the Bruker Avance spectrometers were carried out by the NMR facility of the Institute of Inorganic Chemistry of the University of Heidelberg. Chemical shifts δ are given in parts per million (ppm) relative to the tetramethylsilane resonance. ^{1}H NMR data is reported as follows: chemical shift δ [ppm], multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sept = septet, m = multiplet), scalar spin-spin coupling constant [Hz] as $^XJ_{AB}$ (X = number of chemical bonds between coupled nuclei; A, B = coupled nuclei), integration value, signal assignment. $^{13}C\{^1H\}$ NMR data is reported as follows: chemical shift δ [ppm], multiplicity (only for $^XJ_{CP}$, d = doublet), type of carbon atom (CH_3, CH_2, CH, C_q), signal assignment. The protons of the aromatic pyrrole rings of the calix[4]pyrrolato ligand are denoted “β-H”, the respective carbon atoms “β-C”. The quaternary carbon atoms of the aromatic pyrrole rings in the ligand are named “C_q-pyrrole”. The atoms of the ligand’s Ethyl groups are called “CH_2-Ethyl, -CH_2-” or “CH_3-Ethyl, -CH_3” respectively and the quaternary carbon atoms to which they are attached “α-C”.

The elemental analyses for the determination of C-, H- and N-content [%] were performed by the staff of the Microanalytical Laboratory of the Institutes of Chemistry at Heidelberg University on an elemental analyzer (*vario EL* or *vario MICRO cube*, *Elementar Analysensysteme* GmbH).

High resolution mass spectrometry (HR-MS) experiments were performed by the Mass Spectrometry Facility of the Institute of Organic Chemistry of the University of Heidelberg on mass spectrometers (*JEOL AccuTOF GCx for EI pos.*, *Bruker ApexQe hybrid 9.4 T FT-ICR for* ESI).

1.2 Synthesis and Characterization

1.2.1 Synthesis of Germanium(II)iodide

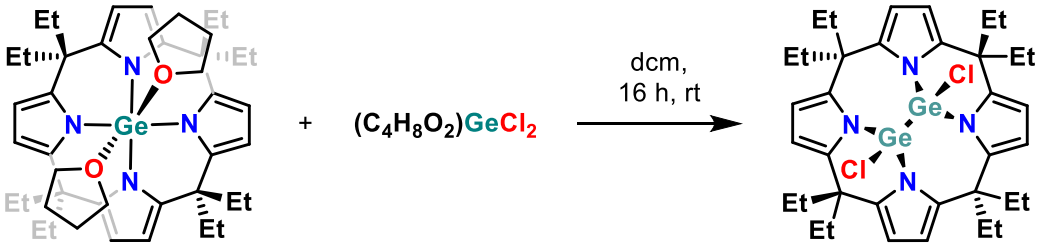


Reactants			*Products*	
Formula	GeI_4	$C_{12}H_{28}Sn$	Formula	GeI_2
MW	580,25	291,07	MW	326,44
Limiting?	***Yes***	No	Equivalents	
Equivalents		***1,08***	%Completion	
Sample Mass	***5,16g***	2,79g	Expected Mass	2,90g
%Weight			Expected Moles	8,89mmol
Molarity			Measured Mass	***2,25g***
Density		***1,08g/mL***	Purity	
Volume		2,58mL	Product Mass	2,25g
Reactant Moles	8,89mmol	9,60mmol	Product Moles	6,89mmol
Reactant Mass	5,16g	2,79g	%Yield	77,57%

The synthesis of germanium(II)iodide was adapted from a synthesis of $GeCl_2$(dioxane) reported by Roskamp.[4] In a Schlenk tube germanium(IV)iodide was dissolved in dichloromethane (400 mL) and HSn^nBu_3 was added to the solution and immediate gas evolution and precipitation of a yellow solid was observed. The mixture was stirred for 16 h at room temperature. Afterwards, ¼ of the solvent of the suspension was evaporated. The suspension was filtrated; the solid residue was washed with hexane (4 x 30.0 mL), sublimed to remove residual HI/GeI_4 ($5*10^{-2}$, 80 °C).

Note: Additional drying at elevated temperatures might be necessary for complete removal of HI. Purity of synthesized germanium(II)iodide was confirmed by clean reaction with $Cx^{Et}Ge(thf)_2$ *(see reaction below).*

1.2.2 Synthesis of *meso*-Octaethylcalix[4]pyrrolato-1,2-dichloro-digermane $Cx^{Et}Ge_2Cl_2$



Reactants			*Products*	
Formula	$C_{44}H_{64}GeN_4O_2$	$C_4H_8Cl_2GeO_2$	Formula	$C_{36}H_{48}Cl_2Ge_2N_4$
MW	753,65	231,64	MW	752,97
Limiting?	***Yes***	No	Equivalents	
Equivalents	***1,00***	***1,00***	%Completion	
Sample Mass	***400,00mg***	122,94mg	Expected Mass	399,64mg
%Weight			Expected Moles	530,75µmol
Molarity			Measured Mass	***347,00mg***
Density			Purity	
Volume			Product Mass	347,00mg
Reactant Moles	530,75µmol	530,75µmol	Product Moles	460,84µmol
Reactant Mass	400,00mg	122,94mg	%Yield	86,83%

$Cx^{Et}Ge(thf)_2$ and $GeCl_2$(1,4-dioxane) were dissolved in dichloromethane (7.00 mL) and the mixture was stirred for 16 h at room temperature. The solvent of the solution was evaporated. To remove residual dioxane, the solid residue was redissolved in toluene (10.0 mL) and the solvent was again evaporated and the solid residue was dried *in vacuo* overnight to give the title compound as an orange powder.

Final purification was performed by recrystallization. Therefore, the solid residue was dissolved in tetrahydrofuran (5.00 mL) and filtrated. Slow evaporation of the solvent of the filtrate at room temperature gave yellow-ish crystals which were washed with cold pentane (2 x 2.00 mL) and crushed yielding a yellow powder which was dried *in vacuo* for 16 h to give the title compound as a fine yellow powder.

SCXRD: Single crystals for the SCXRD analysis were obtained by storing a concentrated dichloromethane solution at –35 °C.

Elemental Analysis for **$Cx^{Et}Ge_2Cl_2$**: Calculated for **$Cx^{Et}Ge_2Cl_2$**: C: 57.43, H: 6.49, N: 7.44. Found: C: 57.17, H: 6.28, N: 7.27.

^{1}H-NMR (600 MHz, 298 K, benzene-d_6) δ = 6.17 (d, *J* = 3.54 Hz, 2H, β-C*H*), 5.91 (d, *J* = 3.47 Hz, 2H, β-C*H*), 2.57 (bs, 2H, ethyl-CH_2), 2.31 (bs, 2H, ethyl-CH_2), 2.09 (q, 2H, *J* = 7.34 Hz, ethyl-CH_2), 1.82 (q, 2H, ethyl-CH_2), 0.99 (t, *J* = 6.96 Hz, 3H, methyl-CH_3), 0.92 (t, *J* = 7.62 Hz, 3H, methyl-CH_3), 0.69 (t, *J* = 7.34 Hz, 3H, methyl-CH_3), 0.53 (t, *J* = 7.34 Hz, 3H, methyl-CH_3) ppm.

$^{13}C\{^{1}H\}$ NMR (151 MHz, 298 K, benzene-d_6) δ = 142.6 (C_q, α-*C*), 140.1 (C_q, α-*C*), 110.2 (β-*C*H), 109.5 (β-*C*H), 44.9 (C_q, *meso*-C), 44.7 (C_q, *meso*-C), 38.2 (*C*H_2-ethyl), 32.0 (*C*H_2-ethyl), 28.6 (*C*H_2-ethyl), 27.6 (*C*H_2-ethyl), 9.3 (*C*H_3-methyl), 9.2 (*C*H_3-methyl), 9.0 (*C*H_3-methyl), 8.6 (*C*H_3-methyl) ppm.

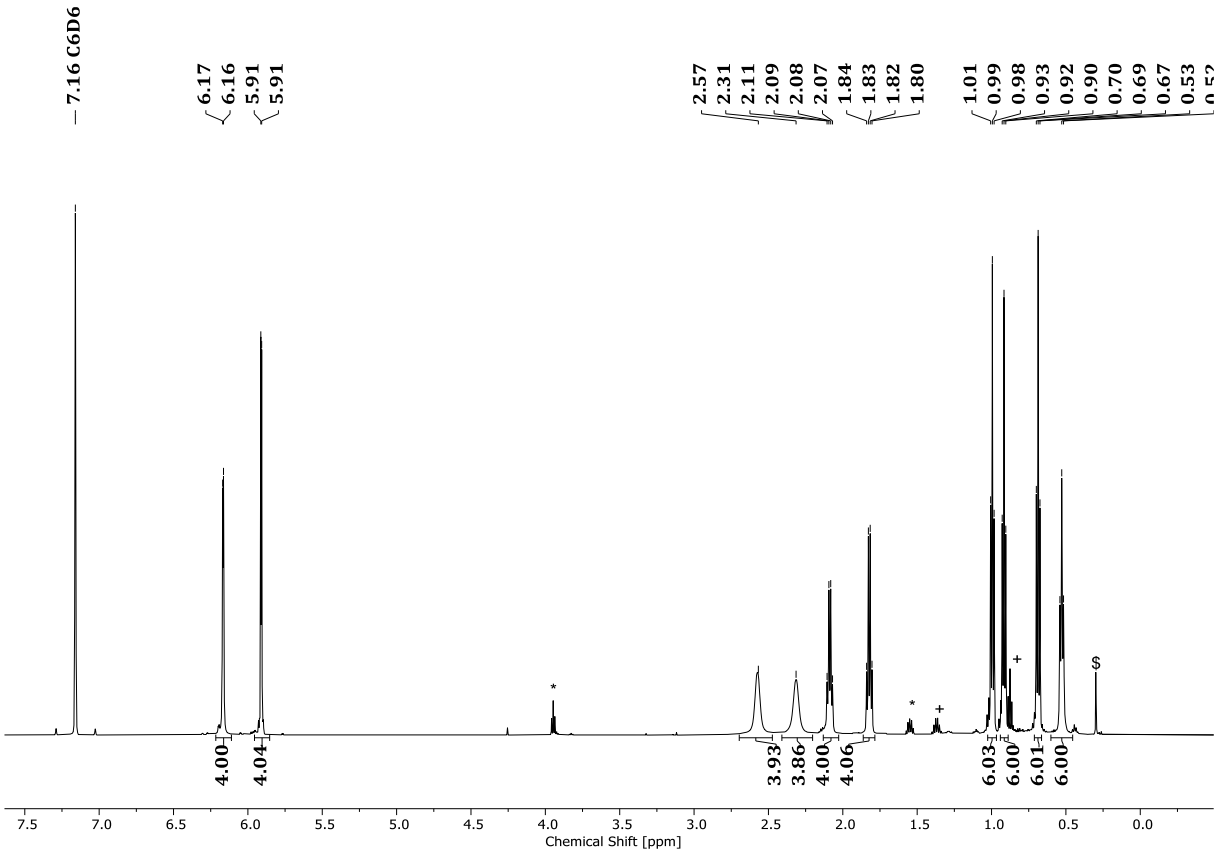


Figure S 1-1. ^{1}H NMR (600 MHz, 298 K, benzene-*d6*) spectrum of **$Cx^{Et}Ge_2Cl_2$**. * = Diethyl ether (stemming from solvent), + = residual pentane, $ silicon grease.

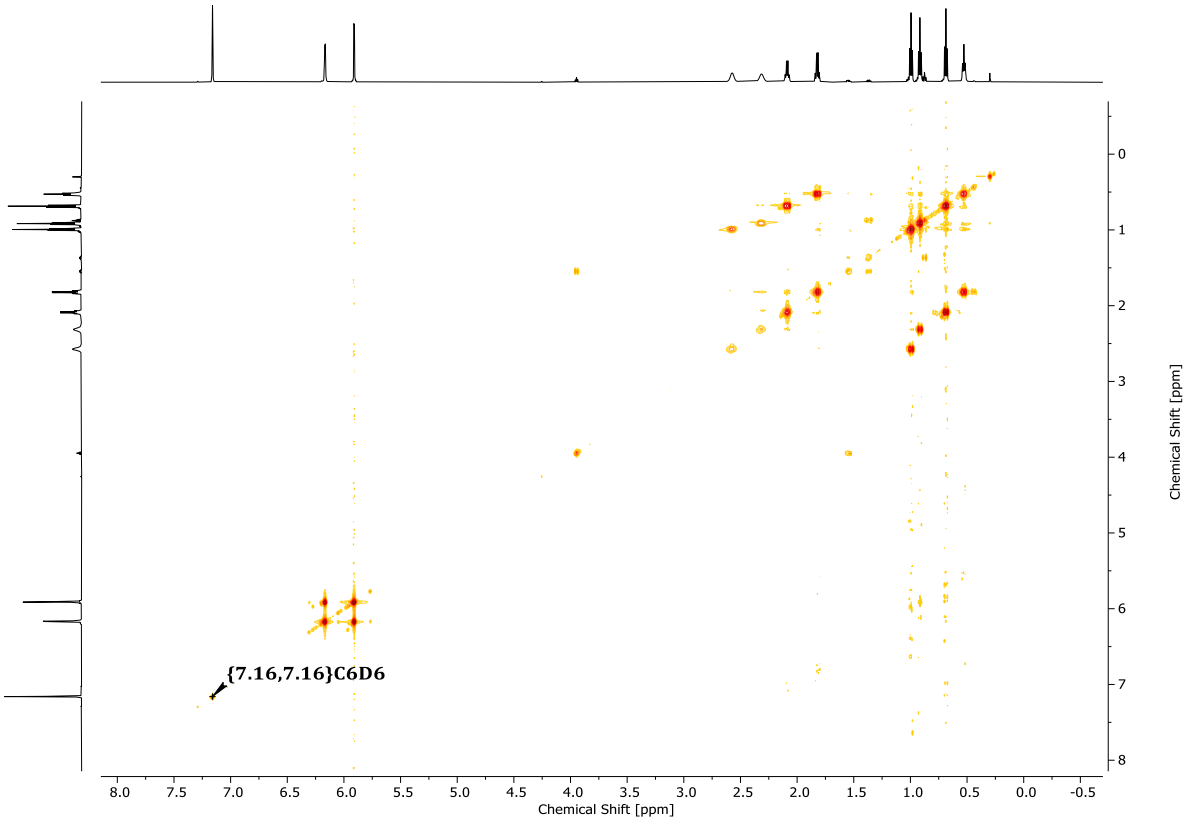


Figure S 1-2. ^{1}H-^{1}H COSY NMR (600 MHz, 298 K, benzene-*d6*) spectrum of **Cx^{Et}Ge$_2$Cl$_2$**.

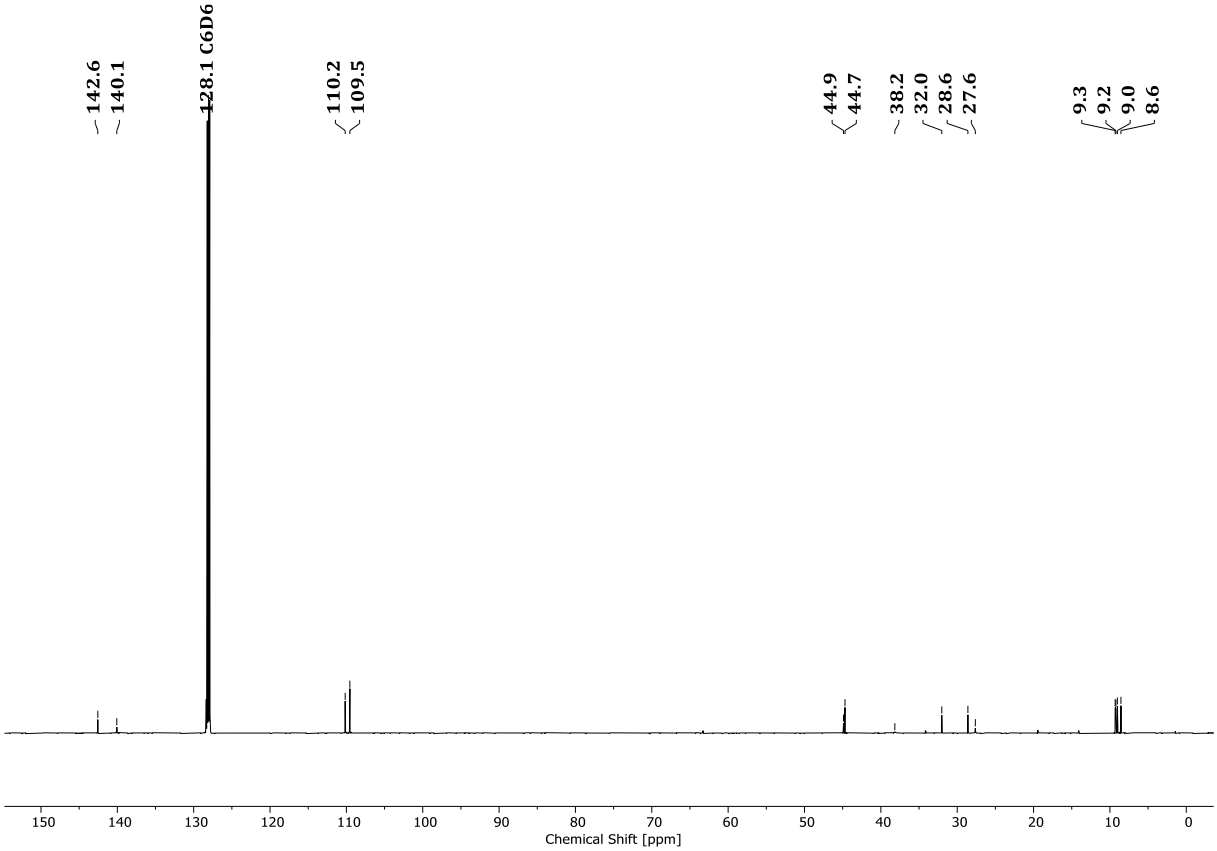


Figure S 1-3. ^{13}C{^{1}H} NMR (151 MHz, 298 K, benzene-*d6*) spectrum of **Cx^{Et}Ge$_2$Cl$_2$**.

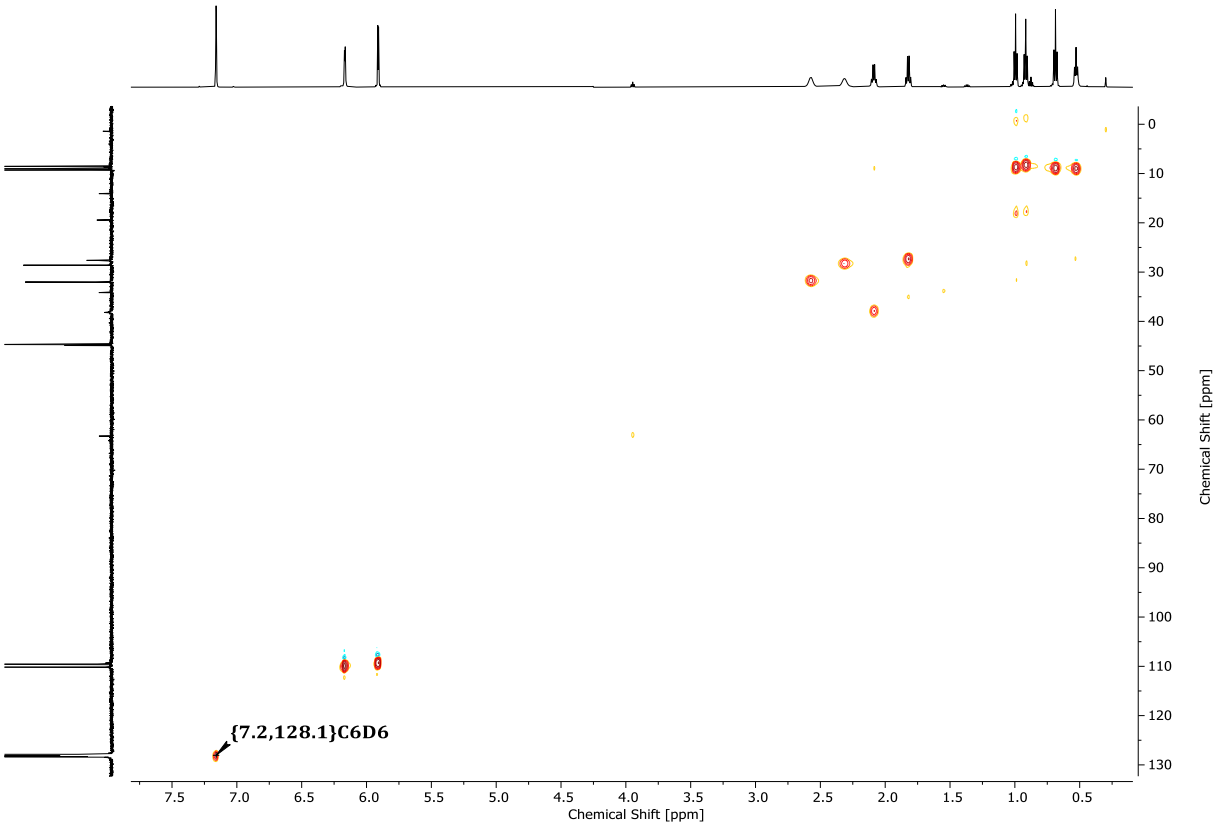
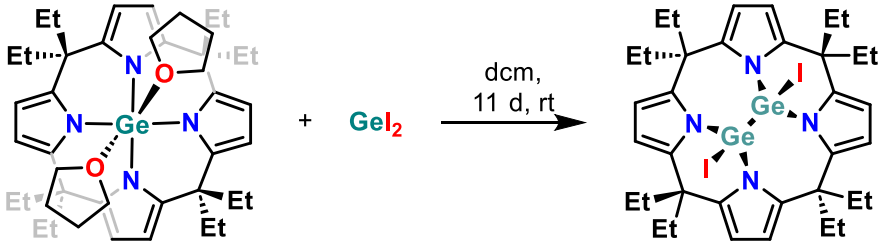


Figure S 1-4. ^{1}H-^{13}C HSQC NMR (600 MHz, 298 K, benzene-*d6*) spectrum of **$Cx^{Et}Ge_2Cl_2$**.

1.2.3 Synthesis of *meso*-Octaethylcalix[4]pyrrolato-1,2-diiodo-digermane $Cx^{Et}Ge_2I_2$



Reactants			*Products*	
Formula	$C_{44}H_{64}GeN_4O_2$	GeI_2	Formula	$C_{36}H_{48}Ge_2I_2N_4$
MW	753,65	326,44	MW	935,88
Limiting?	***Yes***	No	Equivalents	
Equivalents	***1,00***	***1,00***	%Completion	
Sample Mass	***434,00mg***	187,98mg	Expected Mass	538.94mg
%Weight			Expected Moles	575.86µmol
Molarity			Measured Mass	***430.00mg***
Density			Purity	
Volume			Product Mass	430.00mg
Reactant Moles	575,86µmol	575,86µmol	Product Moles	459.46µmol
Reactant Mass	434,00mg	187,98mg	%Yield	79.79%

[$Cx^{Et}Ge(thf)_2$] and germanium(II)iodide were suspended in dichloromethane (3.00 mL). The mixture was stirred for 11 days until all of the germanium(II)diiodide was consumed. The solvent of the

solution was evaporated, the solid residue was washed with pentane (8.00 mL) and afterwards dried in vacuo for 16 h to receive a brown-ish powder.

Final purification was performed by recrystallization. Therefore, the solid residue was dissolved in tetrahydrofuran (5.00 mL) and filtrated. Slow evaporation of the solvent of the filtrate at room temperature gave yellow-ish crystals which were washed with cold pentane (2 x 2.00 mL) and crushed yielding a yellow powder which was dried *in vacuo* for 4 h to give the title compound as a fine yellow powder.

Note: The long reaction time is most likely caused by the poor solubility of germanium(II)iodide and can be shortened by using an excess of germanium(II)iodide, which can be separated by filtration after the completeness.

SCXRD: Single crystals for the SCXRD analysis were obtained by slow evaporation of the solvent of a concentrated tetrahydrofuran solution at –35 °C.

Elemental Analysis for **$Cx^{Et}Ge_2I_2$**: Calculated for **$Cx^{Et}Ge_2I_2$**: C: 46.20, H: 5.17, N: 5.99. Found: C: 45.97, H: 5.43, N: 5.58.

^{1}H-NMR (600 MHz, 298 K, tetrahydrofuran-d_8) δ = 6.08 (d, *J* = 3.51 Hz, 2H, β-C*H*), 5.98 (d, *J* = 3.55 Hz, 2H, β-C*H*), 2.38 (m, 2H, ethyl-CH_2), 2.31 (m, 2H, ethyl-CH_2), 2.09 (m, 2H, ethyl-CH_2), 2.07 (m, 2H, ethyl-CH_2), 1.03 (t, *J* = 7.24 Hz, 3H, methyl-CH_3), 0.98 (t, *J* = 6.96 Hz, 3H, methyl-CH_3), 0.81 (m, 3H, methyl-CH_3), 0.66 (t, *J* = 7.37 Hz, 3H, methyl-CH_3) ppm.

^{13}C{^{1}H} NMR (151 MHz, 298 K, tetrahydrofuran-d_8) δ = 143.4 (C_q, α-*C*), 140.5 (C_q, α-*C*), 110.6 (β-*C*H), 109.7 (β-*C*H), 45.8 (C_q, *meso*-C), 45.4 (C_q, *meso*-C), 38.1 (*C*H_2-ethyl)*, 33.0 (*C*H_2-ethyl), 29.7 (*C*H_2-ethyl)*, 29.0 (*C*H_2-ethyl), 11.1 (*C*H_3-methyl), 10.3 (*C*H_3-methyl), 9.6 (*C*H_3-methyl), 9.1 (*C*H_3-methyl) ppm.

**Determined by ^{1}H-^{13}C-HSQC.*

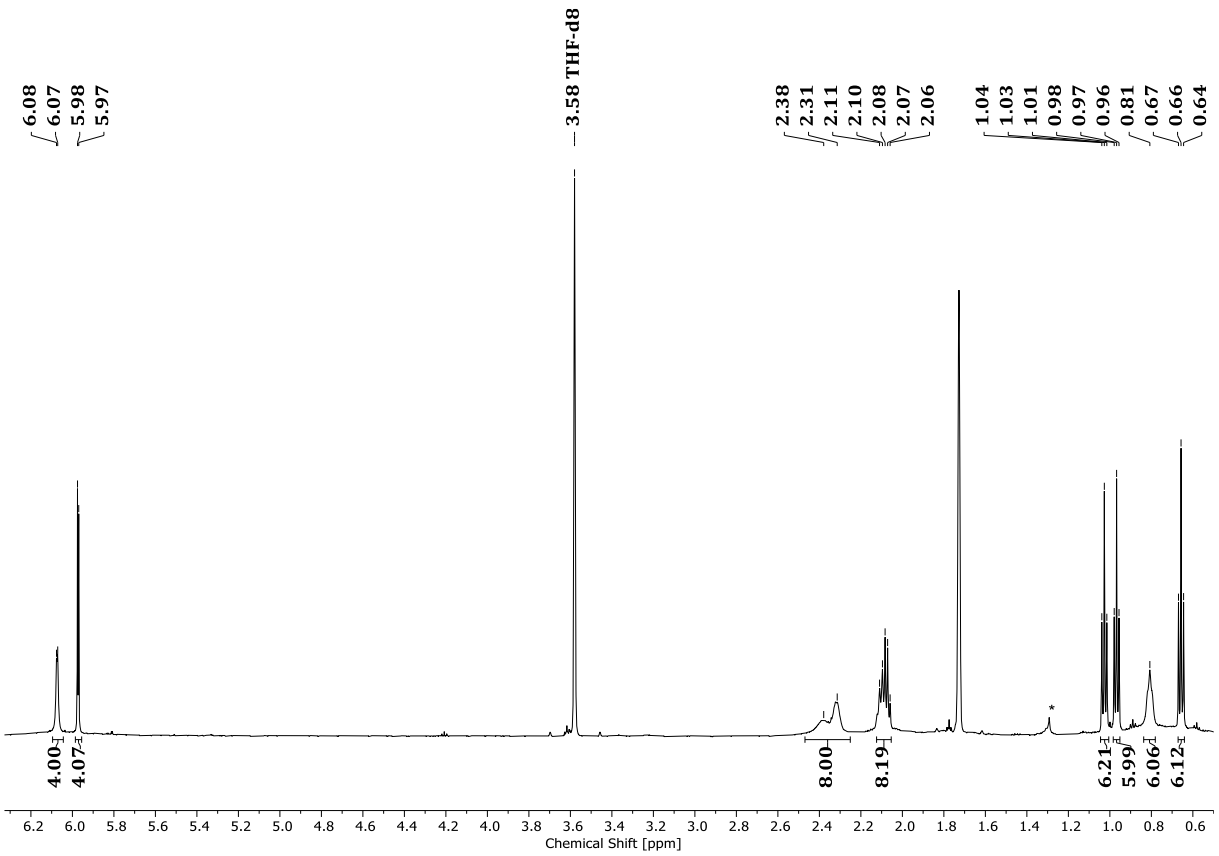


Figure S 1-5. ^{1}H NMR (600 MHz, 298 K, tetrahydrofuran-*d8*) spectrum of **Cx^{Et}Ge$_2$I$_2$**. * = Pentane.

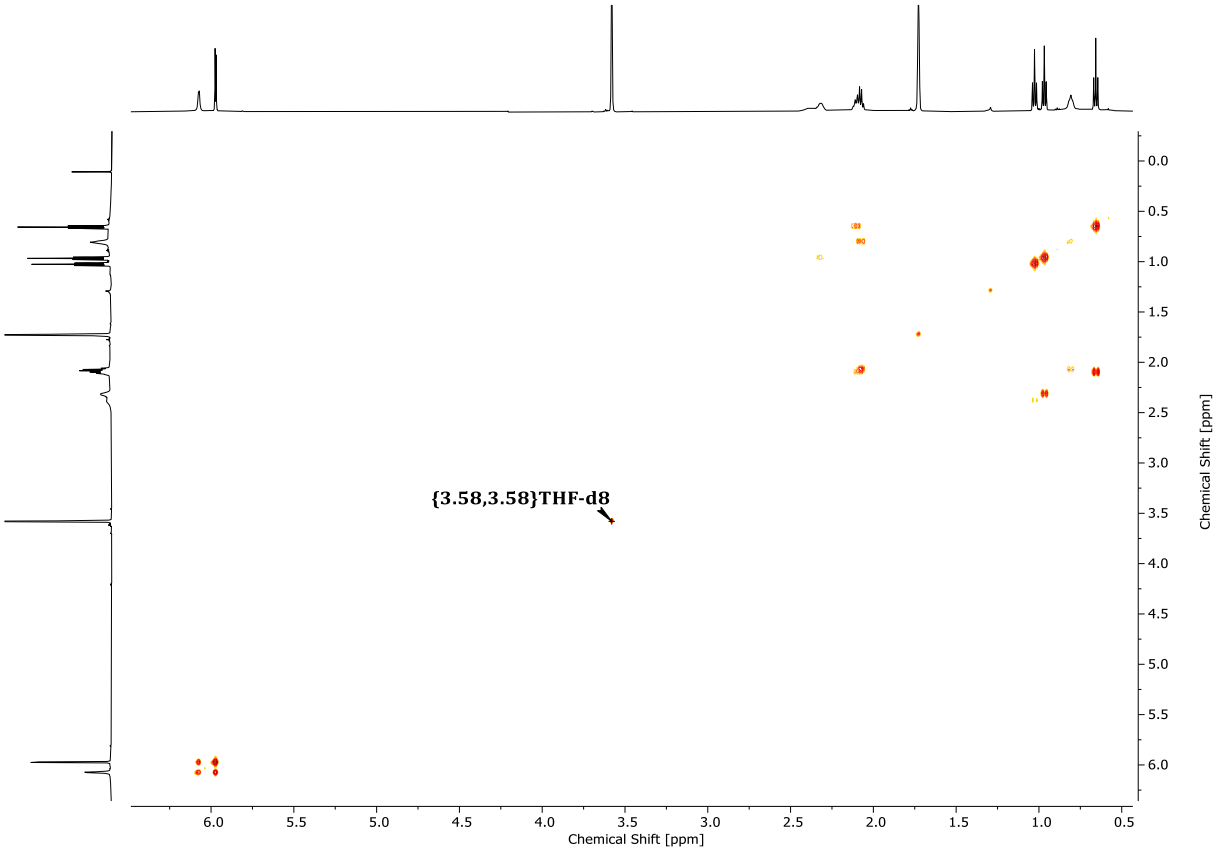


Figure S 1-6. ^{1}H-^{1}H COSY NMR (600 MHz, 298 K, tetrahydrofuran-*d8*) spectrum of **Cx^{Et}Ge$_2$I$_2$**.

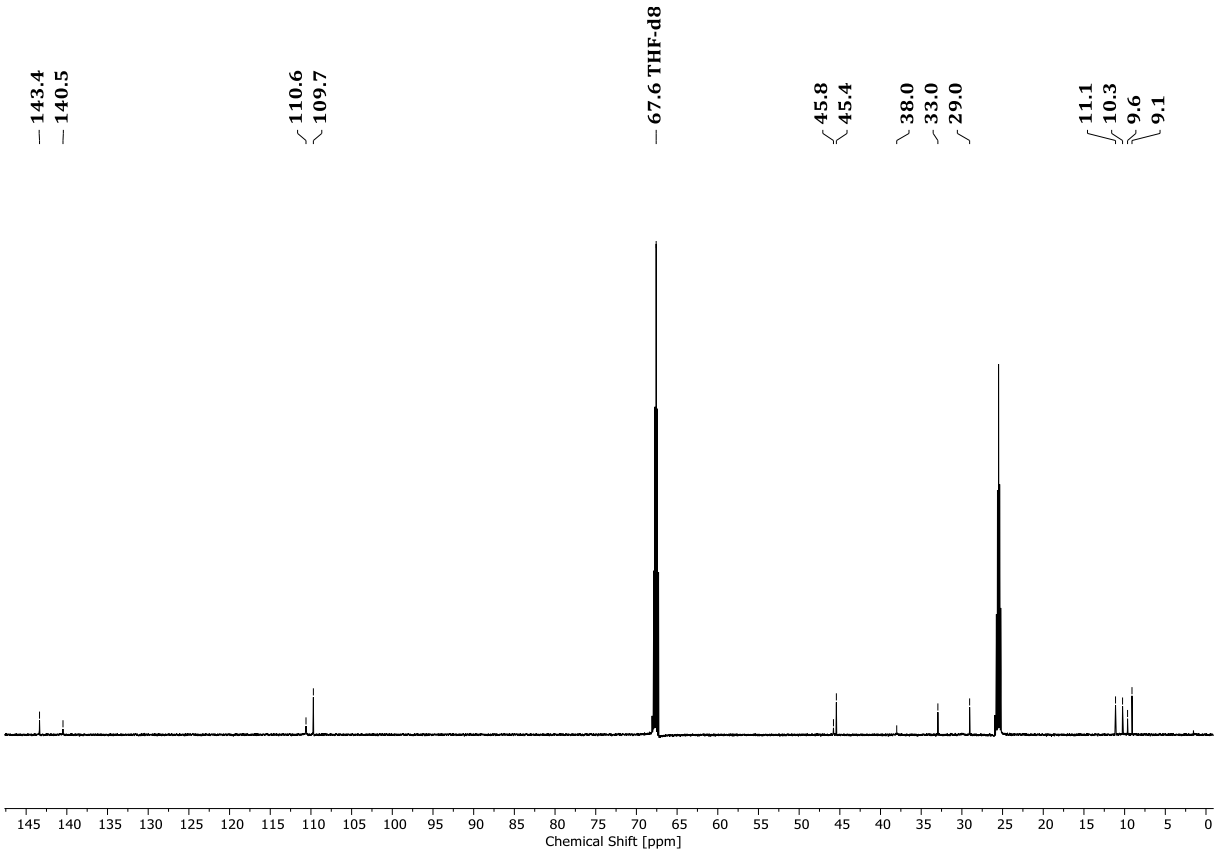


Figure S 1-7. $^{13}C\{^{1}H\}$ NMR (151 MHz, 298 K, tetrahydrofuran-*d8*) spectrum of **$Cx^{Et}Ge_2I_2$.**

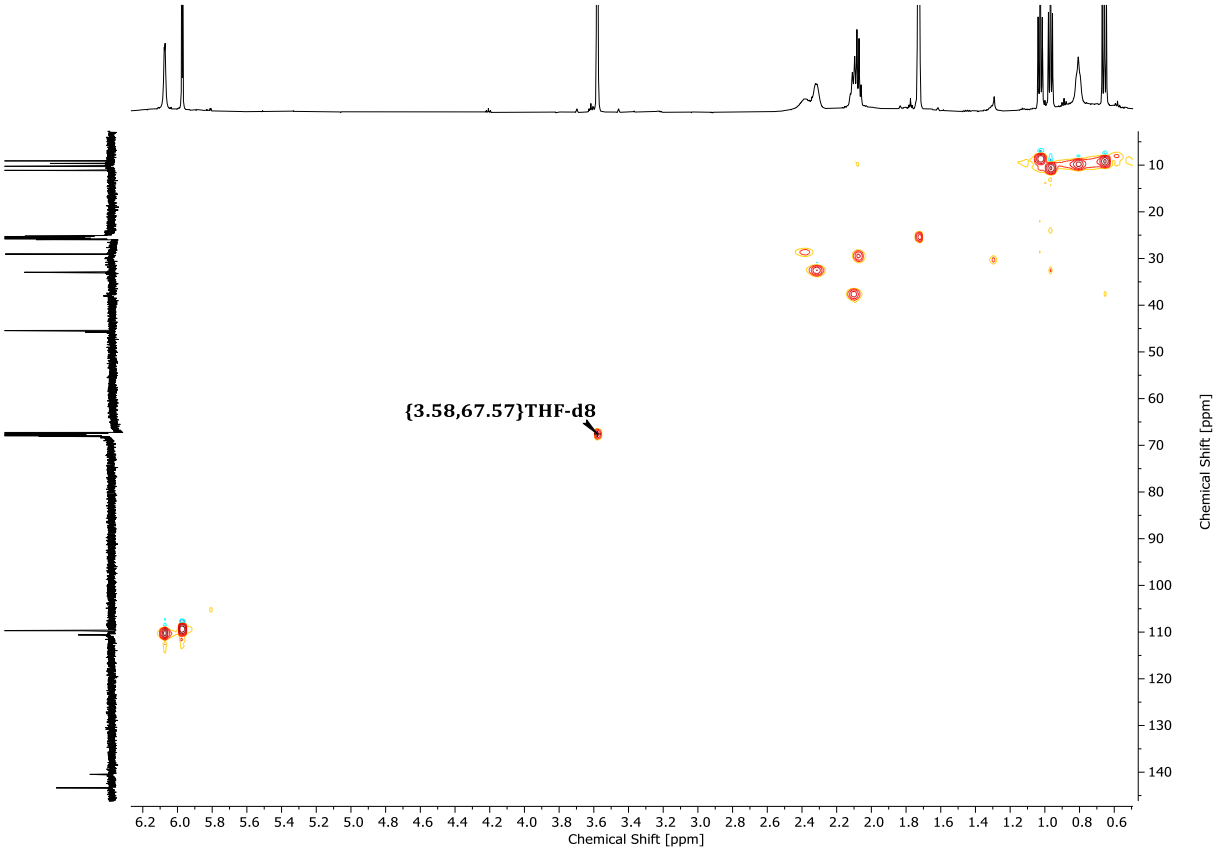
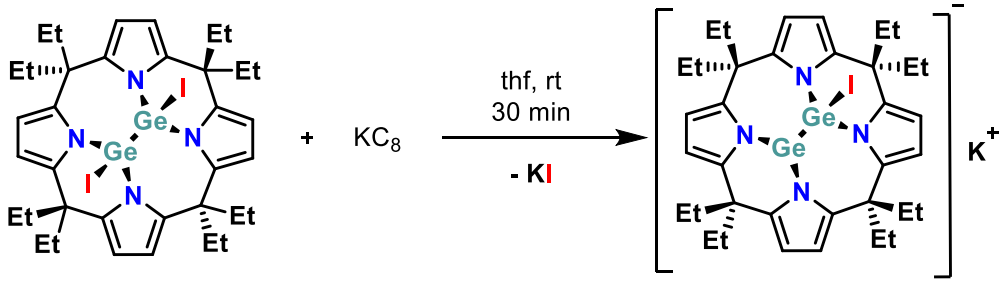


Figure S 1-8. ^{1}H-^{13}C HSQC NMR (600 MHz, 298 K, tetrahydrofuran-*d8*) spectrum of **$Cx^{Et}Ge_2I_2$.**

1.2.4 Reduction of *meso*-Octaethylcalix[4]pyrrolato-1,2-diiodo-digermane $Cx^{Et}Ge_2I_2$



Reactants			*Products*	
Formula	$C_{36}H_{48}Ge_2I_2N_4$	C_8K	Formula	$C_{36}H_{48}Ge_2IKN_4$
MW	935.88	135.19	MW	848.07
Limiting?	***Yes***	No	Equivalents	
Equivalents	***1.00***	***4.00***	%Completion	
Sample Mass	***5.00mg***	2.89mg	Expected Mass	4.53mg
%Weight			Expected Moles	5.34µmol
Molarity			Measured Mass	
Density			Purity	
Volume			Product Mass	
Reactant Moles	5.34µmol	21.37µmol	Product Moles	
Reactant Mass	5.00mg	2.89mg	%Yield	

In a J. Young NMR tube, **[$Cx^{Et}Ge_2I_2$]** and potassium graphite were suspended in tetrahydrofuran-*d8* (0.45 mL) and the reaction mixture was stirred for 30 minutes at room temperature. The suspension was filtrated. ^{1}H NMR spectroscopy confirmed the formation of a new, less symmetrical species, which was identified by ESI(−)-MS as **K[$Cx^{Et}Ge_2I$]** and after the addition of 18-crown-6 (0.90 eq., 1.27 mg) crystallized as **K@18-crown-6[$Cx^{Et}Ge_2I$]**. A yield was not determined, since the compound was not further used.

SCXRD: Single crystals for the SCXRD analysis were obtained by gas vapor diffusion of pentane into a concentrated tetrahydrofuran solution at –35 °C.

ESI(–)-MS: Calculated for **[$Cx^{E}Ge_2I$]$^-$**: 809.1362. Found: 809.1357 (tetrahydrofuran).

^{1}H-NMR of **K[$Cx^{Et}Ge_2I$]** (600 MHz, 298 K, tetrahydrofuran-*d8*): δ = 6.00 (d, *J* = 3.2 Hz, 2H, β-C*H*), 5.90 – 5.89 (m, 4H, β-C*H*), 5.83 (d, *J* = 4.1 Hz, 2H, β-C*H*), 2.64 – 2.56 (m, 2H, CH_2-ethyl), 2.49 – 2.46 (m, 2H, CH_2-ethyl), 2.35 – 2.31 (m, 4H, CH_2-ethyl), 2.09 – 1.99 (m, 6H, CH_2-ethyl), 1.91 (q, *J* = 6.1 Hz, 2H, CH_2-ethyl), 1.06 (t, *J* = 7.3 Hz, 6H, CH_3-methyl), 0.99 (t, *J* = 7.0 Hz, 6H, CH_3-methyl), 0.91 (t, *J* = 7.2 Hz, 3H, CH_3-methyl), 0.64 (t, *J* = 7.2 Hz, 3H, CH_3-methyl), 1.06 (t, *J* = 7.5 Hz, 3H, CH_3-methyl) ppm.

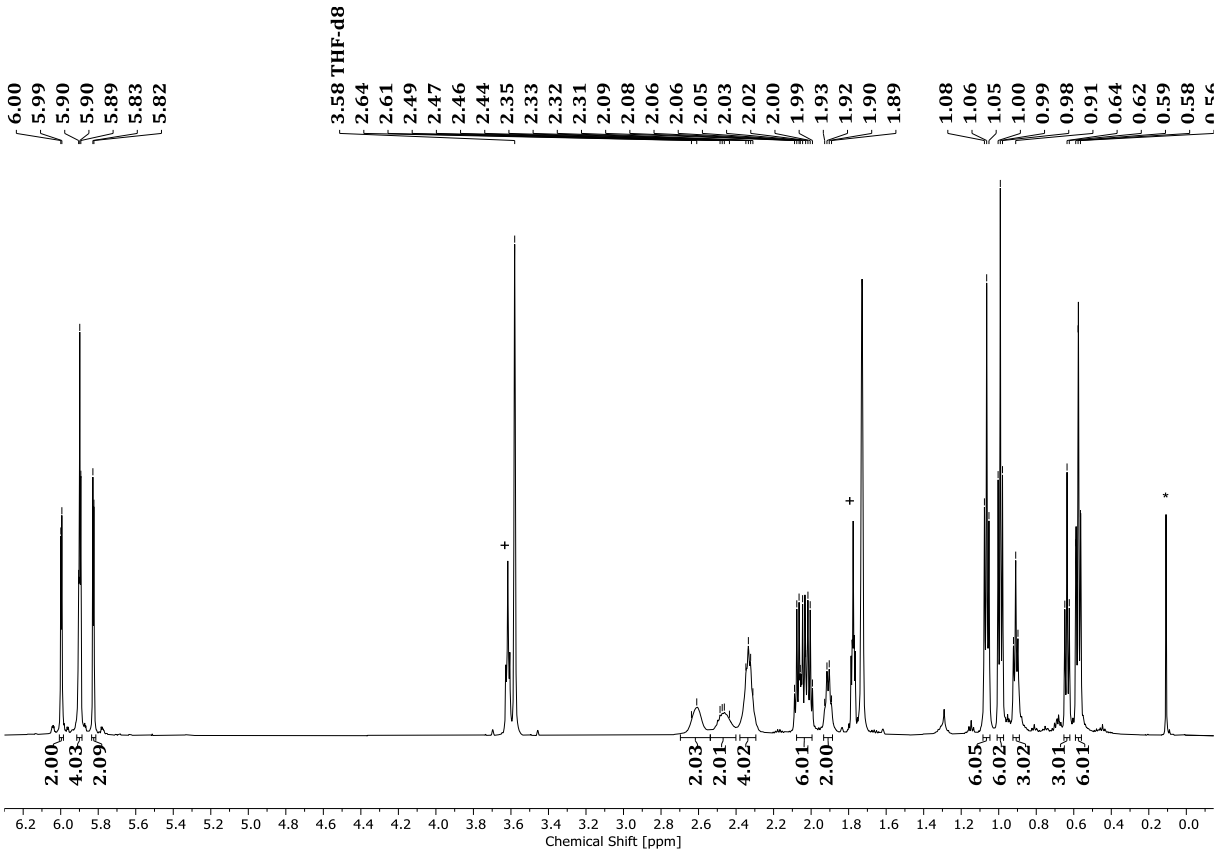
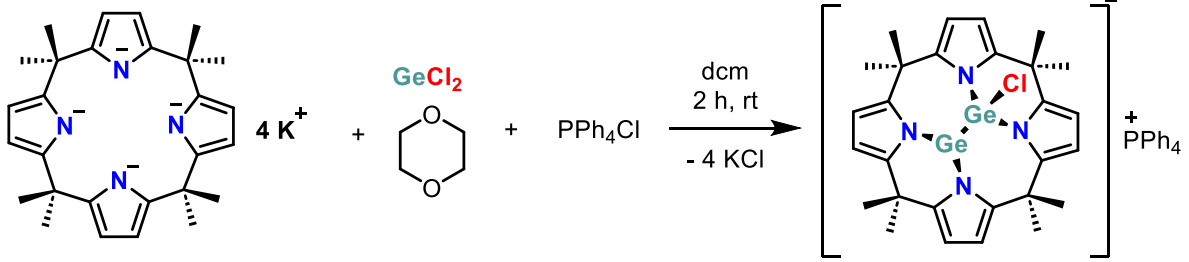


Figure S 1-9. ^{1}H NMR (600 MHz, 298 K, tetrahydrofuran-*d8*) spectrum of **K[Cx^{Et}Ge$_2$I].** + = Tetrahydrofuran, * silicon grease.

1.2.5 Synthesis of Tetraphenylphosphonium *meso*-Octamethylcalix[4]pyrrolato-1-chlorodigermanate PPh_4[Cx^{Me}Ge$_2$Cl]



Reactants				*Products*	
Formula	$C_{28}H_{32}K_4N_4$	$C_4H_8Cl_2GeO_2$	$C_{24}H_{20}ClP$	Formula	$C_{52}H_{52}ClGe_2N_4P$
MW	580.99	231.64	374.85	MW	944.70
Limiting?	***Yes***	No	No	Equivalents	
Equivalents	***1.00***	***2.00***	***0.80***	%Completion	***80.00%***
Sample Mass	***1.00g***	797.39mg	516.15mg	Expected Mass	1.30g
%Weight				Expected Moles	1.38mmol
Molarity				Measured Mass	***1.06g***
Density				Purity	
Volume				Product Mass	1.06g
Reactant Moles	1.72mmol	3.44mmol	1.38mmol	Product Moles	1.12mmol
Reactant Mass	1.00g	797.39mg	516.15mg	%Yield	81.49%

[K]$_4$[Cx^{Me}] and $GeCl_2$(1,4-dioxane) were suspended in dichloromethane (10.0 mL), and the resulting mixture was stirred at rt for 1 h. Next, PPh_4Cl was added and the reaction mixture was stirred at rt

for an additional hour. Subsequent filtration was followed by removal of the filtrate's solvent under reduced pressure. The solid residue was dried *in vacuo* overnight. The dried solid was suspended in benzene (5.00 mL), filtrated and the filtrate was washed with benzene (2 x 5.00 mL) before being dried *in vacuo* for 16 hours to obtain the title compound as a colourless solid.

Note: Only 0.80 eq. of PPh_4Cl were added to prevent an excess of PPh_4^+ in the final product. To remove 1,4-dioxane it might help to suspend the crude product in small amounts of toluene and remove the solvent under reduced pressure several times.

SCXRD: Single crystals for the SCXRD analysis were obtained by gas phase diffusion of pentane into a concentrated dichloromethane solution at −35 °C.

Elemental Analysis for **$[PPh_4][Cx^{Me}Ge_2Cl]$ x 0.20 eq. CH_2Cl_2**: Calculated for **$[PPh_4][Cx^{Me}Ge_2Cl]$**: C: 64.97, H: 5.80, N: 5.48. Found: C: 65.14, H: 5.97, N: 5.72.

ESI(–)-MS: Calculated for **$[Cx^{Me}Ge_2Cl]^-$**: 605.07. Measured: 605.10 (dichloromethane).

^{1}H-NMR (600 MHz, 298 K, dichloromethane-*d2*): δ = 7.72 – 7.66 (m, 4H, *p*-PPh_4), 7.60 – 7.54 (m, 8H, *m*-PPh_4), 7.52 – 7.44 (m, 8H, *o*-PPh_4), 5.86 (d, *J* = 3.2 Hz, 2H, β-C*H*), 5.79 (d, *J* = 3.2 Hz, 2H, β-C*H*), 5.75 (d, *J* = 2.3 Hz, 2H, β-C*H*), 5.67 (d, *J* = 4.1 Hz, 2H, β-C*H*), 2.07 (s, 6H, CH_3-methyl), 1.82 (s, 6H, CH_3-methyl), 1.58 (s, 3H, CH_3-methyl), 1.57 (s, 3H, CH_3-methyl), 1.56 (s, 3H, CH_3-methyl), 1.43 (s, 3H, CH_3-methyl) ppm.

^{13}C{^{1}H} NMR (151 MHz, 298 K, dichloromethane-*d2*): δ = 145.8 (C_q, α-*C*), 145.3 (C_q, α-*C*), 142.4 (C_q, α-*C*), 142.3 (C_q, α-*C*), 136.1 (d, $^3J(^{31}P,^{13}C)$ = 3.0 Hz, *p*-PPh_4), 134.7 (d, $^3J(^{31}P,^{13}C)$ = 10.2 Hz, *m*-PPh_4), 130.8 (d, $^3J(^{31}P,^{13}C)$ = 12.9 Hz, *o*-PPh_4), 117.7 (d, $^3J(^{31}P,^{13}C)$ = 89.7 Hz, C_q,PPh_4), 104.5 (*C*H, β-C), 104.2 (*C*H, β-C), 103.7 (*C*H, β-C), 101.7 (*C*H, β-C), 37.4 (2C, C_q, *meso*-C), 36.7 (C_q, *meso*-C), 36.4 (*C*H_3-methyl), 36.3 (C_q, *meso*-C), 34.7 (*C*H_3-methyl), 31.7 (*C*H_3-methyl), 31.2 (*C*H_3-methyl), 28.6 (*C*H_3-methyl), 27.2 (*C*H_3-methyl) ppm.

^{31}P NMR: (121 MHz, dichloromethane-*d2*) δ = 23.1 (PPh_4^+).

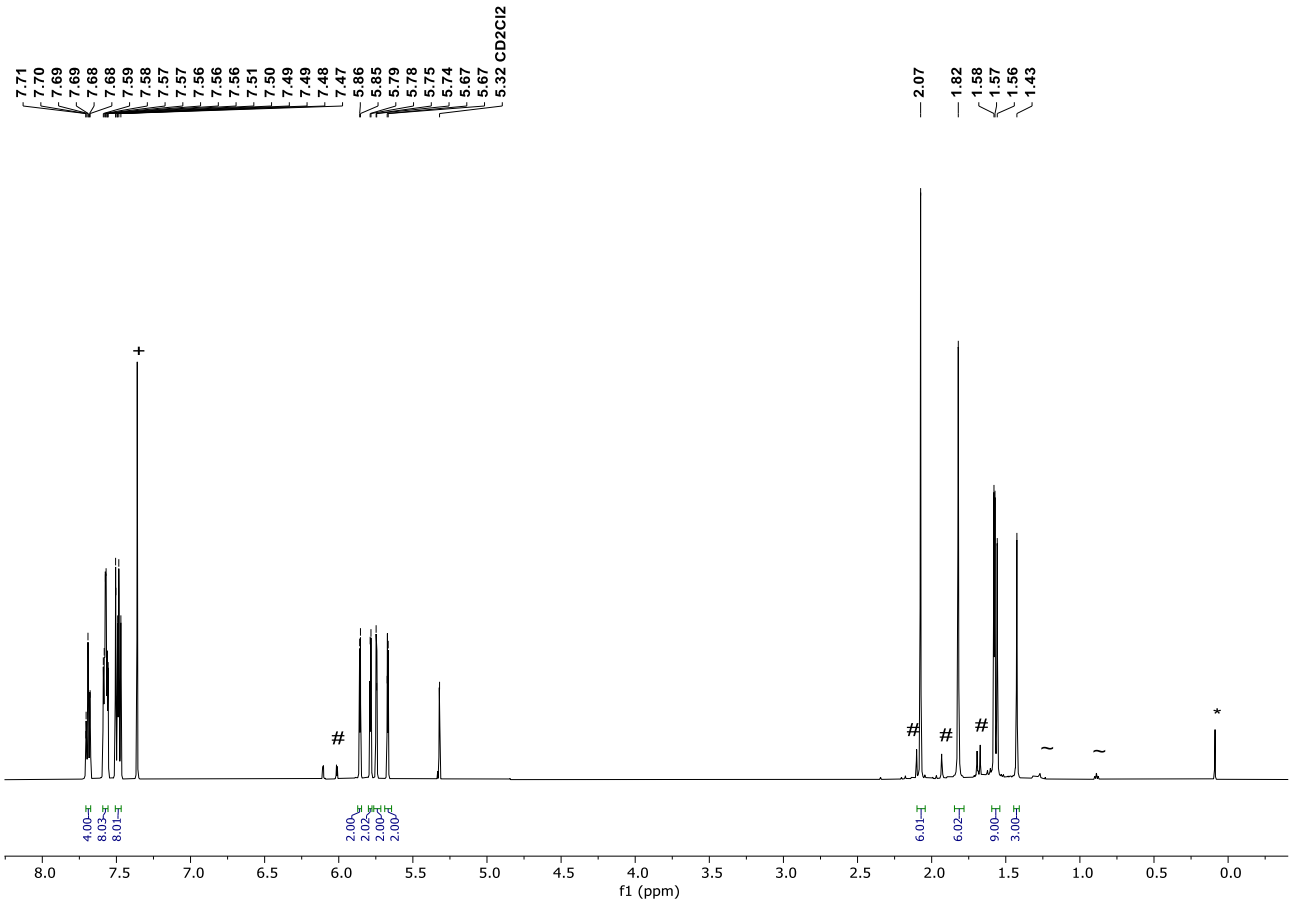


Figure S 1-10. ^{1}H NMR (600 MHz, 298 K, dichloromethane-*d2*) spectrum of **$PPh_4[Cx^{Me}Ge_2Cl]$.** + = Benzene, * = silicon grease, ~ pentane (stemming from the solvent), # $Cx^{Me}Ge_2Cl_2$.

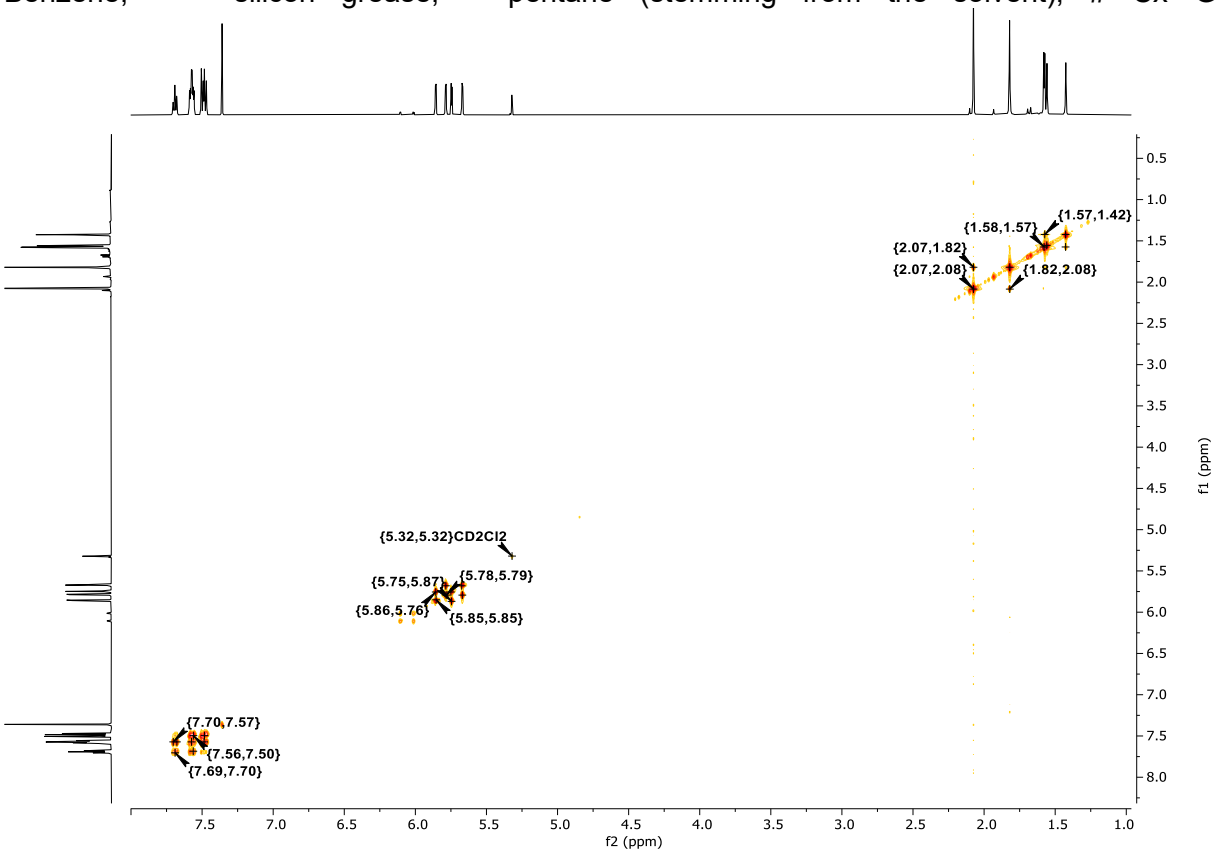


Figure S 1-11. ^{1}H-^{1}H COSY NMR (600 MHz, 298 K, dichloromethane-*d2*) spectrum of **$PPh_4[Cx^{Me}Ge_2Cl]$.**

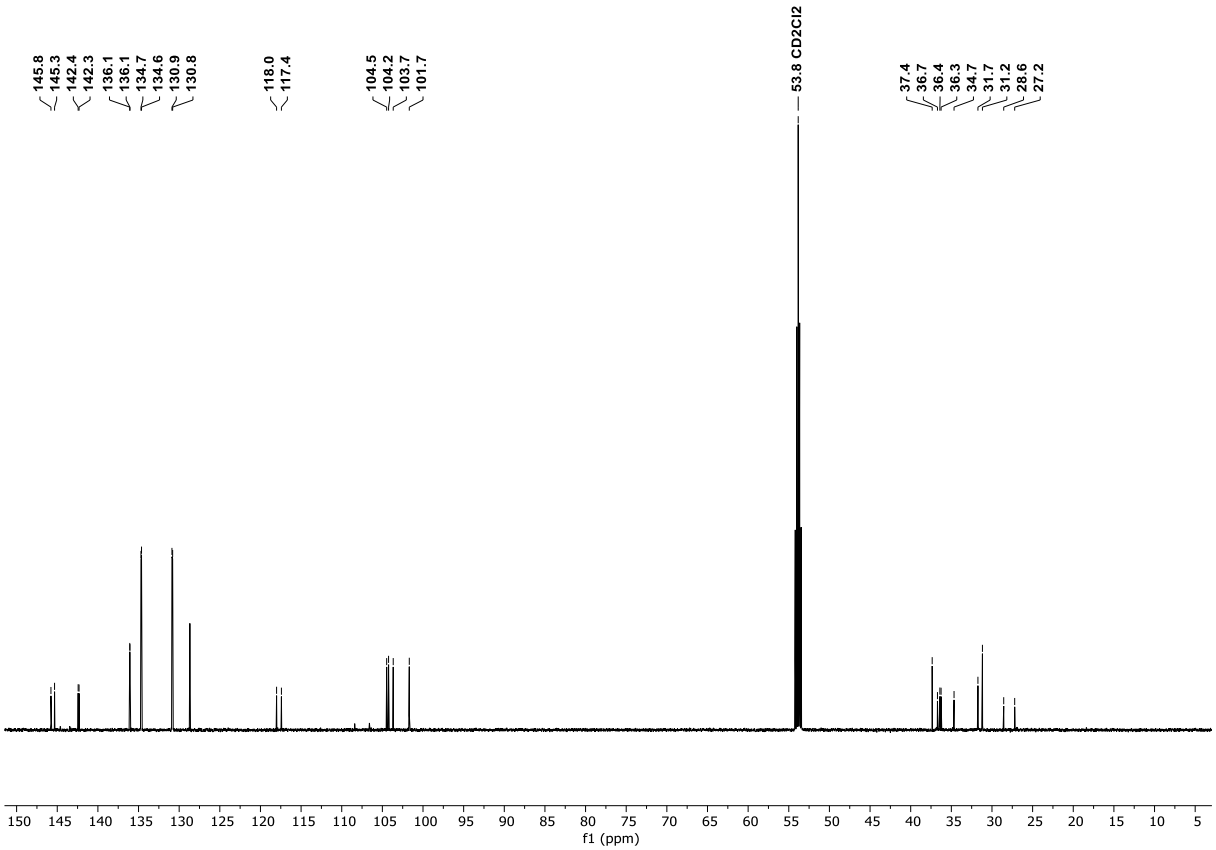


Figure S 1-12. $^{13}C\{^{1}H\}$ NMR (151 MHz, 298 K, dichloromethane-*d2*) spectrum of **$PPh_4[Cx^{Me}Ge_2Cl]$**. + = silicon grease.

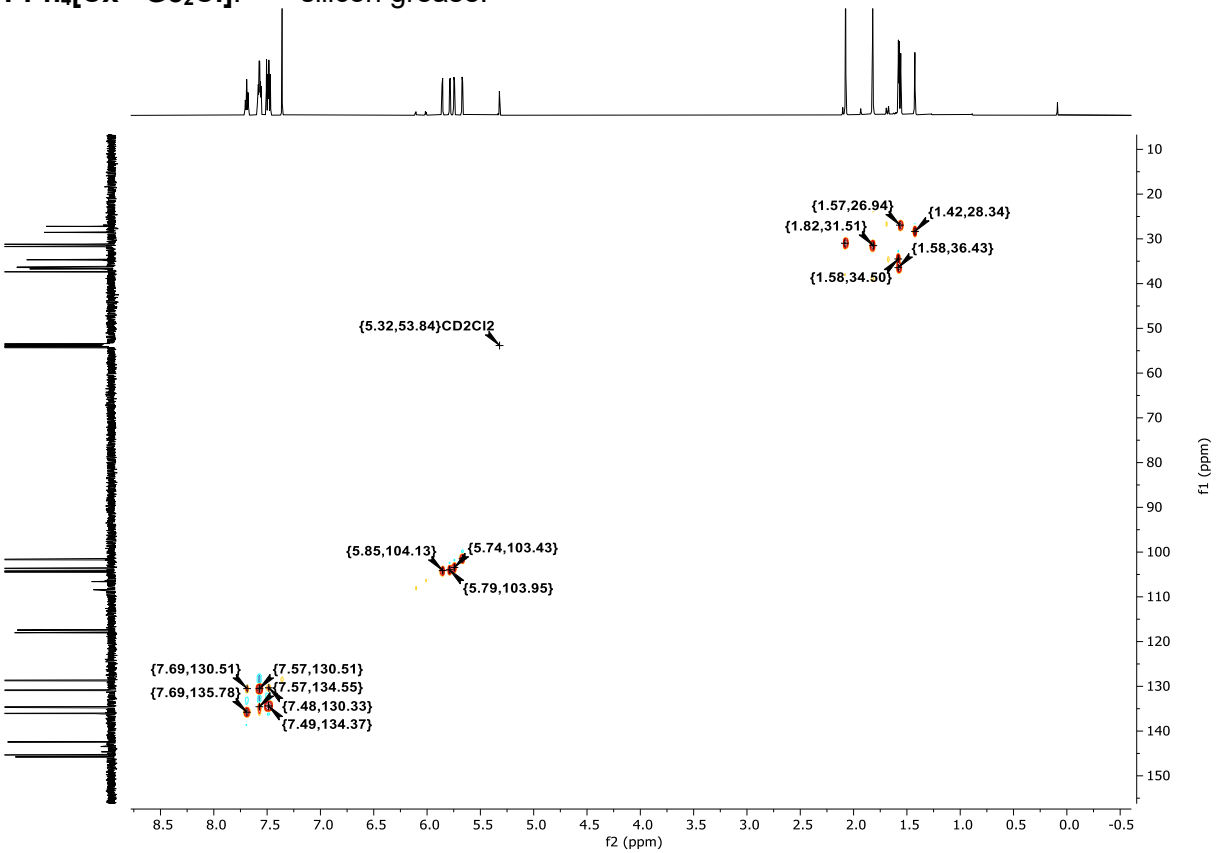


Figure S 1-13. ^{1}H-^{13}C HSQC NMR (600 MHz, 298 K, dichloromethane-*d2*) spectrum of **$PPh_4[Cx^{Me}Ge_2Cl]$.**

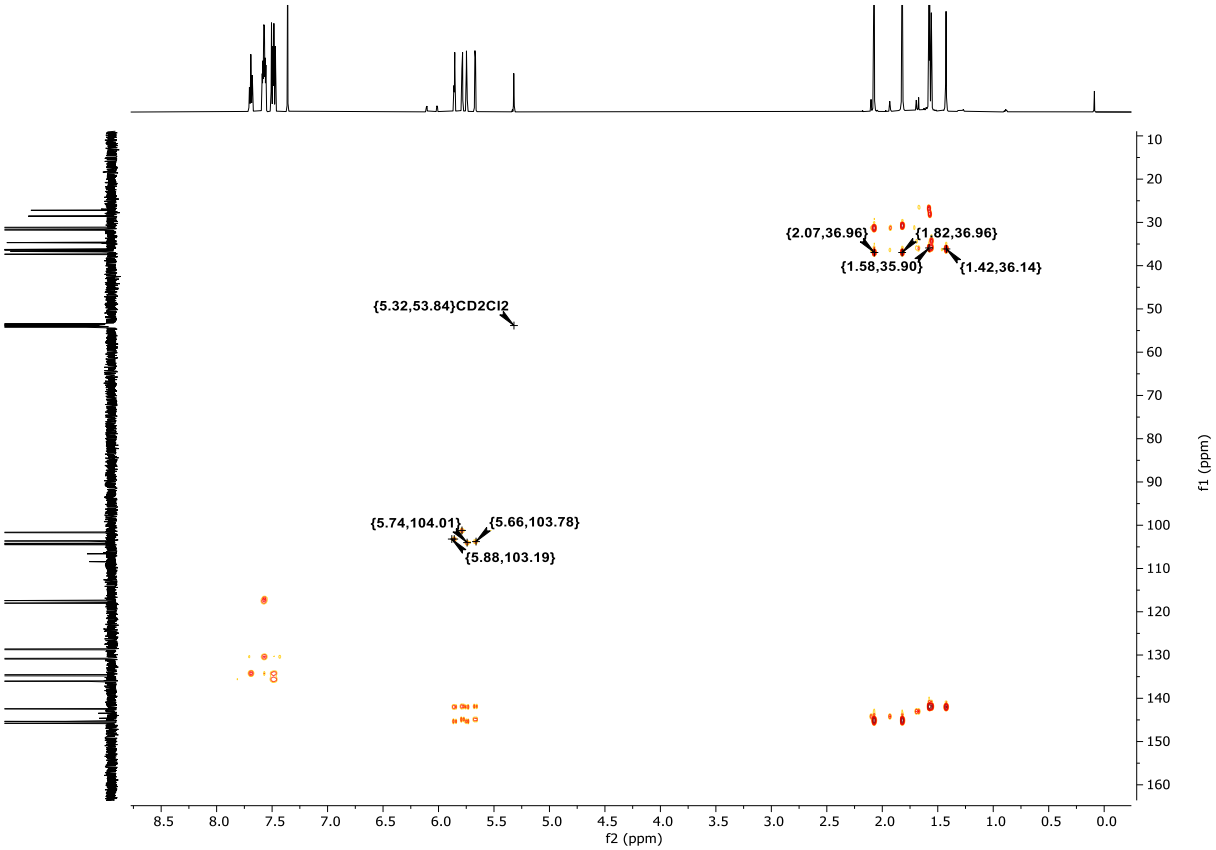


Figure S 1-14. ^{1}H-^{13}C HMBC NMR (600 MHz, 298 K, dichloromethane-*d2*) spectrum of **PPh$_4$[Cx^{Me}Ge$_2$Cl].**

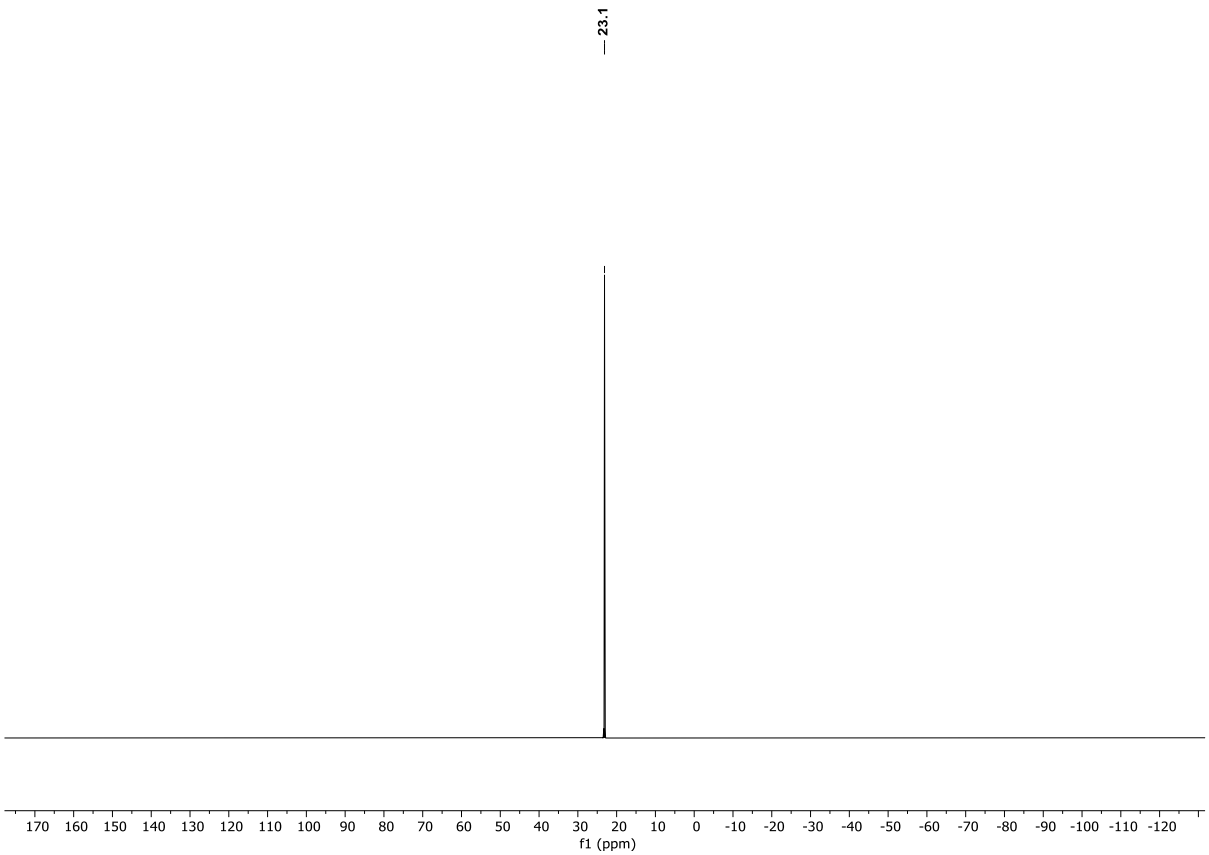
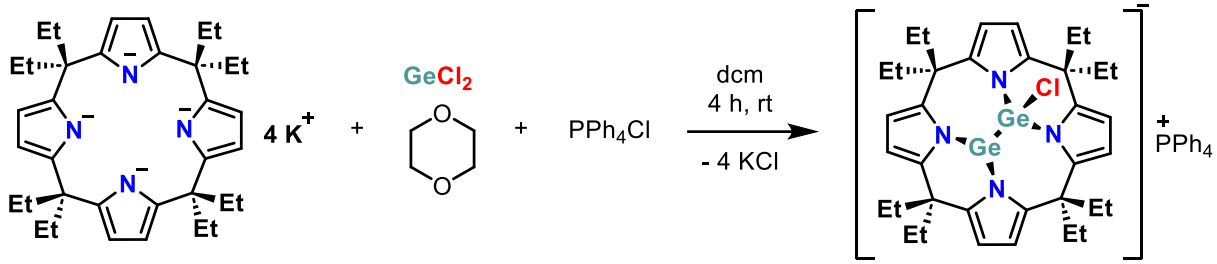


Figure S 1-15. ^{31}P{^{1}H} NMR (121 MHz, 298 K, dichloromethane-*d2*) spectrum of **PPh$_4$[Cx^{Me}Ge$_2$Cl].**

1.2.6 Synthesis of Tetraphenylphosphonium *meso*-Octaethylcalix[4]pyrrolato-1-chlorodigermanate $PPh_4[Cx^{Et}Ge_2Cl]$



Reactants				*Products*	
Formula	$C_{36}H_{48}K_4N_4$	$C_4H_8Cl_2GeO_2$	$C_{24}H_{20}ClP$	Formula	$C_{60}H_{68}ClGe_2N_4P$
MW	693.20	231.64	374.85	MW	1056.92
Limiting?	***Yes***	No	No	Equivalents	
Equivalents	***1.00***	***2.00***	***0.90***	%Completion	***90.00%***
Sample Mass	***4.00g***	2.67g	1.95g	Expected Mass	5.49g
%Weight				Expected Moles	5.19mmol
Molarity				Measured Mass	***4.63g***
Density				Purity	
Volume				Product Mass	4.63g
Reactant Moles	5.77mmol	11.54mmol	5.19mmol	Product Moles	4.38mmol
Reactant Mass	4.00g	2.67g	1.95g	%Yield	84.35%

$[K]_4[Cx^{Et}]$ and $GeCl_2$(1,4-dioxane) were suspended in dichloromethane (30 mL), and the resulting mixture was stirred at rt for 2 h. Next, PPh_4Cl was added and the reaction mixture was stirred at rt for additional 2 h. Subsequent filtration was followed by removal of the filtrate's solvent under reduced pressure. The dried solid was suspended in toluene (40.0 mL) and stirred at rt for 1 h before the addition of pentane (80.0 mL). The resulting suspension was filtrated and the residue was dried for 2 hours *in vacuo*. Afterwards, the solid was dried via solvent lyophilization using benzene to obtain the title compound as an off-white solid.

Note: Only 0.90 eq. of PPh_4Cl were added to prevent an excess of PPh_4^+ in the final product. To remove 1,4-dioxane it might help to suspend the crude product in small amounts of toluene and remove the solvent under reduced pressure several times.

SCXRD: Single crystals for the SCXRD analysis were obtained by gas phase diffusion of pentane into a concentrated dichloromethane solution at −35 °C.

Elemental Analysis for **$PPh_4[Cx^{Et}Ge_2Cl]$**: Calculated for **$PPh_4[Cx^{Et}Ge_2Cl]$**: C: 68.19, H: 6.49, N: 5.30. Found: C: 68.32, H: 6.39, N: 5.15.

ESI(–)-MS: Calculated for **$[Cx^{Et}Ge_2Cl]^-$**: 717.1991. Found: 717.2008 (dichloromethane).

^{1}H-NMR (400 MHz, 298 K, dichloromethane-*d2*): δ = 7.70 - 7.67 (m, 4H, *p*-PPh_4), 7.59 –7.55 (m, 8H, *m*-PPh_4), 7.48 – 7.44 (m, 8H, *o*-PPh_4), 5.83 (d, ^{3}J = 3.21 Hz, 2H, β-C*H*), 5.76 (d, ^{3}J = 3.25 Hz, 2H, β-C*H*), 5.67 (d, ^{3}J = 3.37 Hz, 2H, β-C*H*), 5.62 (d, ^{3}J = 3.26 Hz, 2H, β-C*H*), 2.53 (s, 2H, CH_2-ethyl), 2.41 (m, 2H, CH_2-ethyl), 2.37 – 2.23 (m, 4H, CH_2-ethyl), 1.03 (t, ^{3}J = 7.37 Hz, 6H, CH_3-methyl), 0.90 (t, ^{3}J = 7.06 Hz, 6H, CH_3-methyl), 0.71 (s, 3H, CH_3-methyl), 0.57 (t, ^{3}J = 7.25 Hz, 3H, CH_3-methyl), 0.53 (t, ^{3}J = 7.37 Hz, 3H, CH_3-methyl), 0.40 (t, ^{3}J = 7.17 Hz, 3H, CH_3-methyl) ppm.

^{13}C{^{1}H} NMR (151 MHz, 298 K, dichloromethane-*d2*): δ = 144.5 (C_q, α-*C*), 143.1 (C_q, α-*C*), 139.1 (C_q, α-*C*), 138.6 (C_q, α-*C*), 136.1 (d, $^{3}J(^{31}P,^{13}C)$ = 15.1 Hz, *p*-PPh_4), 134.7 (d, $^{3}J(^{31}P,^{13}C)$ = 15.1 Hz, *m*-PPh_4), 130.9 (d, $^{3}J(^{31}P,^{13}C)$ = 15.1 Hz, *o*-PPh_4), 117.7 (d, $^{3}J(^{31}P,^{13}C)$ = 90.6 Hz, C_q,PPh_4), 105.9 (*C*H, β-C), 105.7 (*C*H, β-C), 105.3 (*C*H, β-C), 104.3 (*C*H, β-C), 45.0 (C_q, *meso*-C), 44.9 (C_q, *meso*-C), 44.4 (2C, C_q, *meso*-C), 43.3 (C_q, *meso*-C)*, 39.3 (*C*H_2-ethyl), 29.9 (*C*H_2-ethyl), 29.9 (*C*H_2-ethyl, shoulder), 28.7 (*C*H_2-ethyl), 28.5 (*C*H_2-ethyl), 27.5 (*C*H_2-ethyl), 26.0 (*C*H_2-ethyl), 10.4 (*C*H_3-methyl), 9.9 (*C*H_3-methyl), 9.6 (*C*H_3-methyl), 9.5 (*C*H_3-methyl), 9.4 (*C*H_3-methyl), 9.4 (*C*H_3-methyl) ppm.

^{31}P NMR: (121 MHz, dichloromethane-*d2*) δ = 23.1 (PPh_4^+).

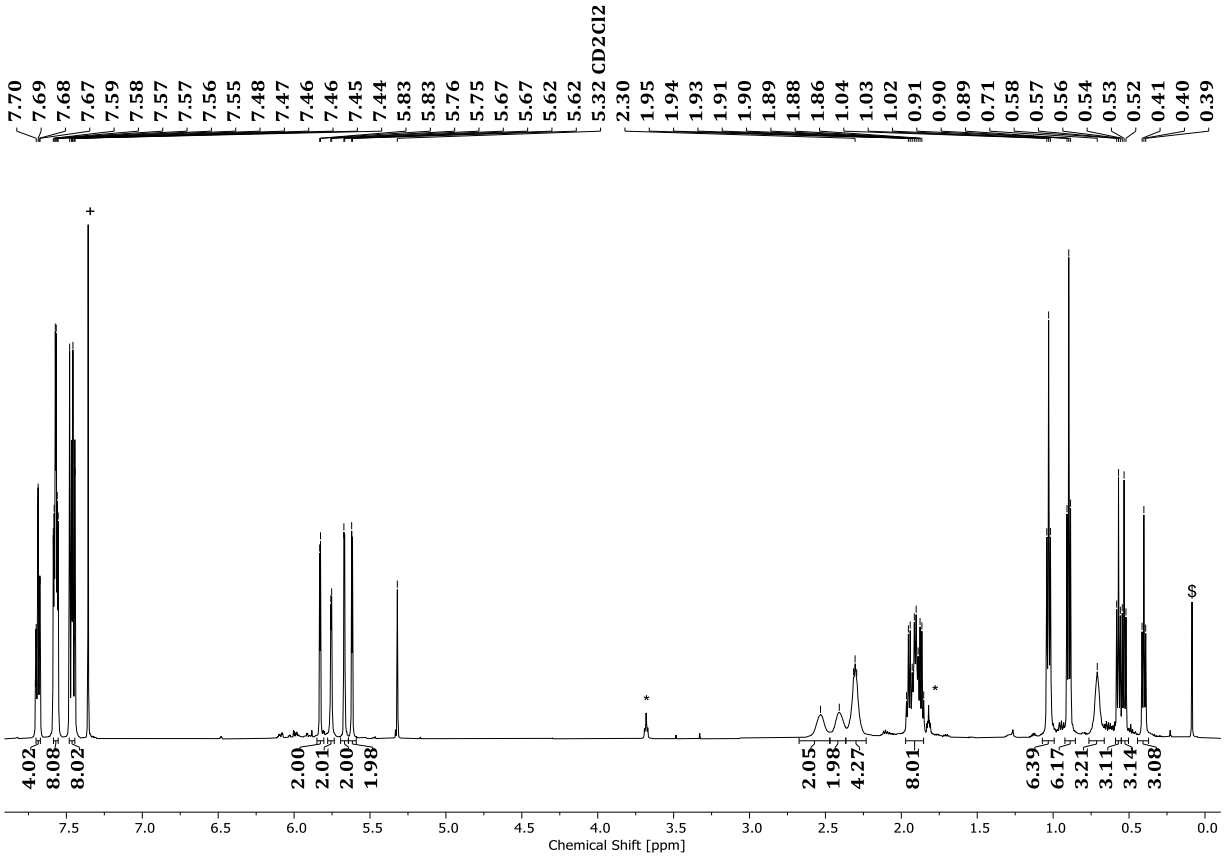


Figure S 1-16. ^{1}H NMR (600 MHz, 298 K, dichloromethane-*d2*) spectrum of **PPh_4[$Cx^{Et}Ge_2Cl$]**. * = Tetrahydrofuran, + = benzene, $ = silicon grease.

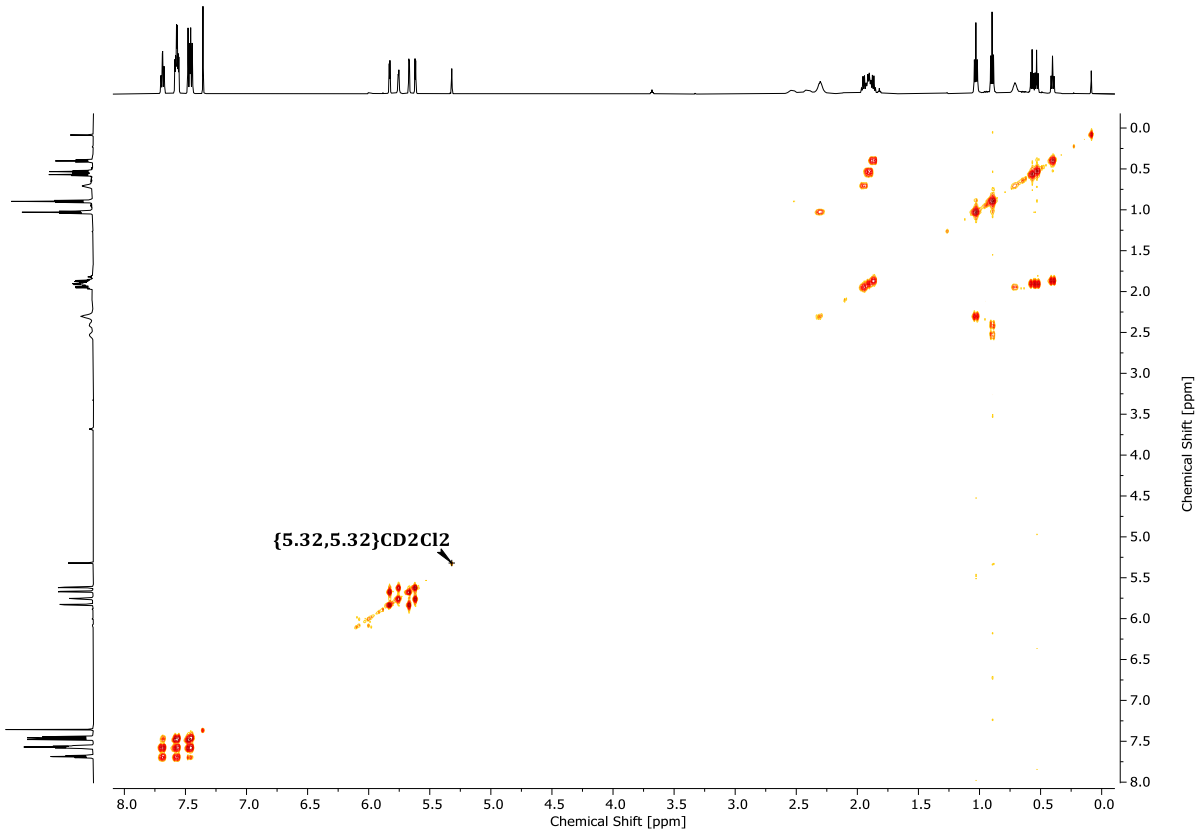


Figure S 1-17. ^{1}H-^{1}H COSYNMR (600 MHz, 298 K, dichloromethane-*d2*) spectrum of **$PPh_4[Cx^{Et}Ge_2Cl]$.**

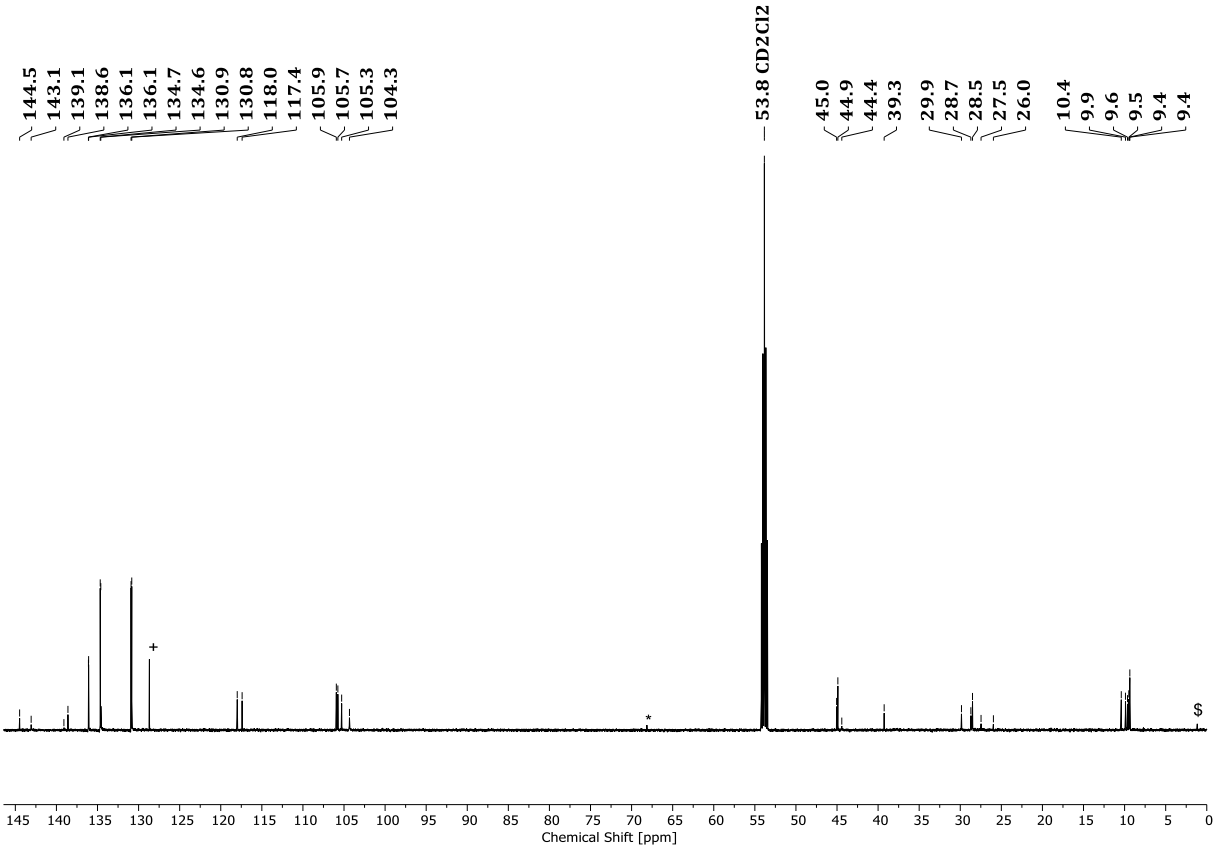


Figure S 1-18. ^{13}C{^{1}H} NMR (151 MHz, 298 K, dichloromethane-*d2*) spectrum **of $PPh_4[Cx^{Et}Ge_2Cl]$.** * = Tetrahydrofuran, + = benzene, $ = silicon grease.

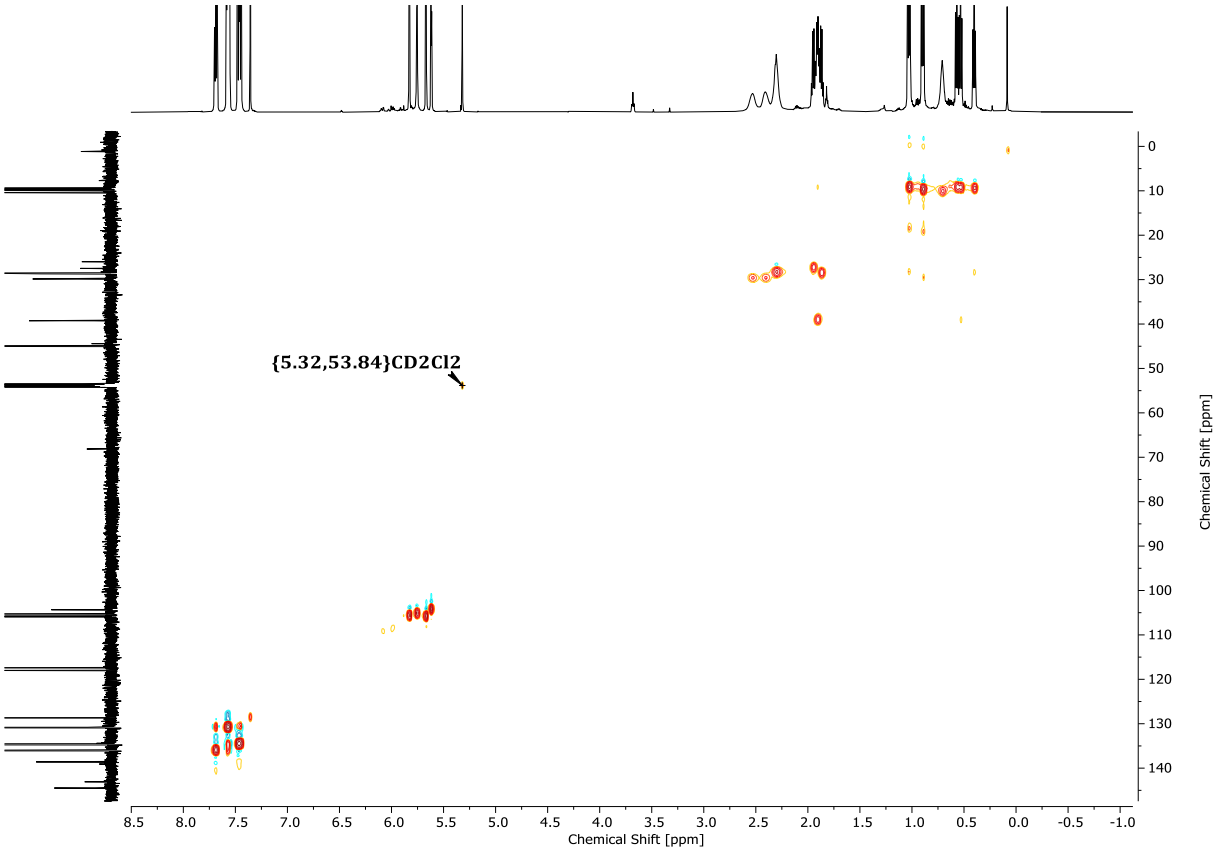


Figure S 1-19. ^{1}H-^{13}C HSQC NMR (600 MHz, 298 K, dichloromethane-*d2*) spectrum of **PPh$_4$[Cx^{E}-^{t}Ge$_2$Cl]**.

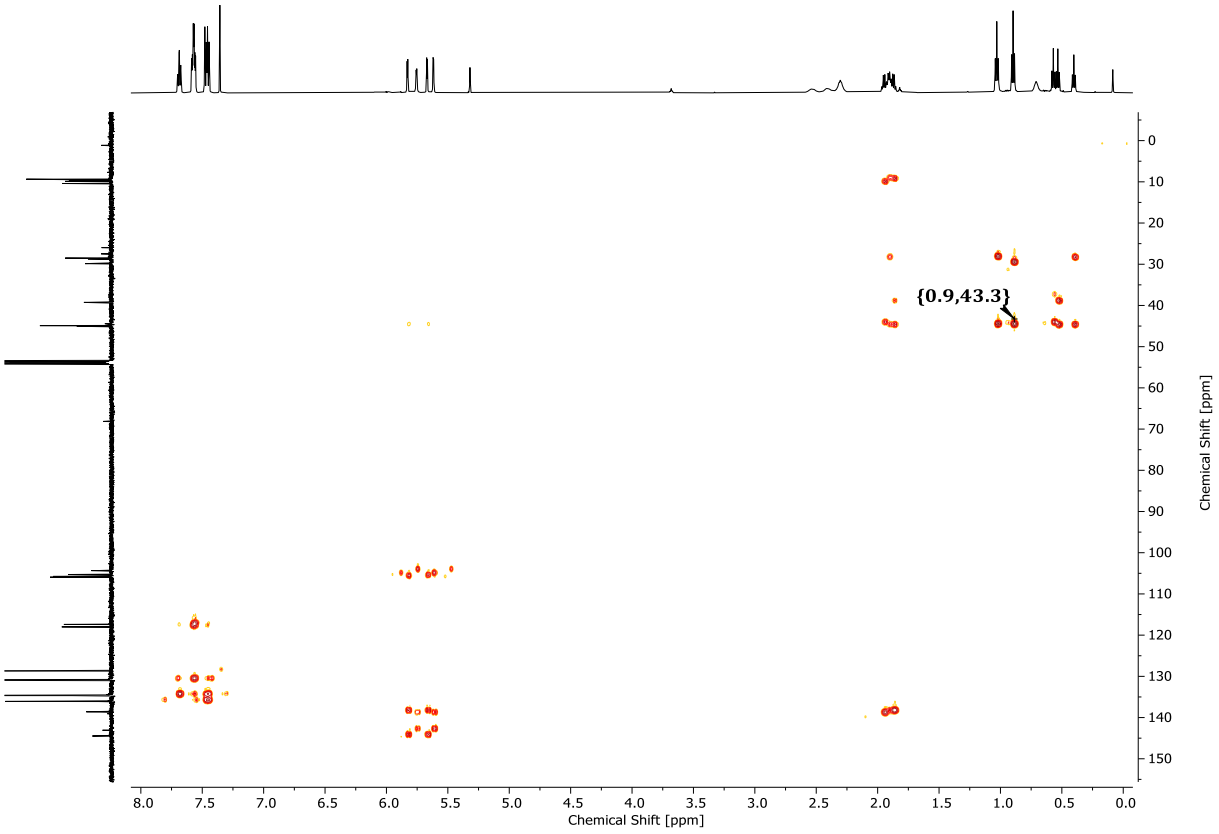


Figure S 1-20. ^{1}H-^{13}C HMBC NMR (600 MHz, 298 K, dichloromethane-*d2*) spectrum of **PPh$_4$[Cx^{E}-^{t}Ge$_2$Cl]**.

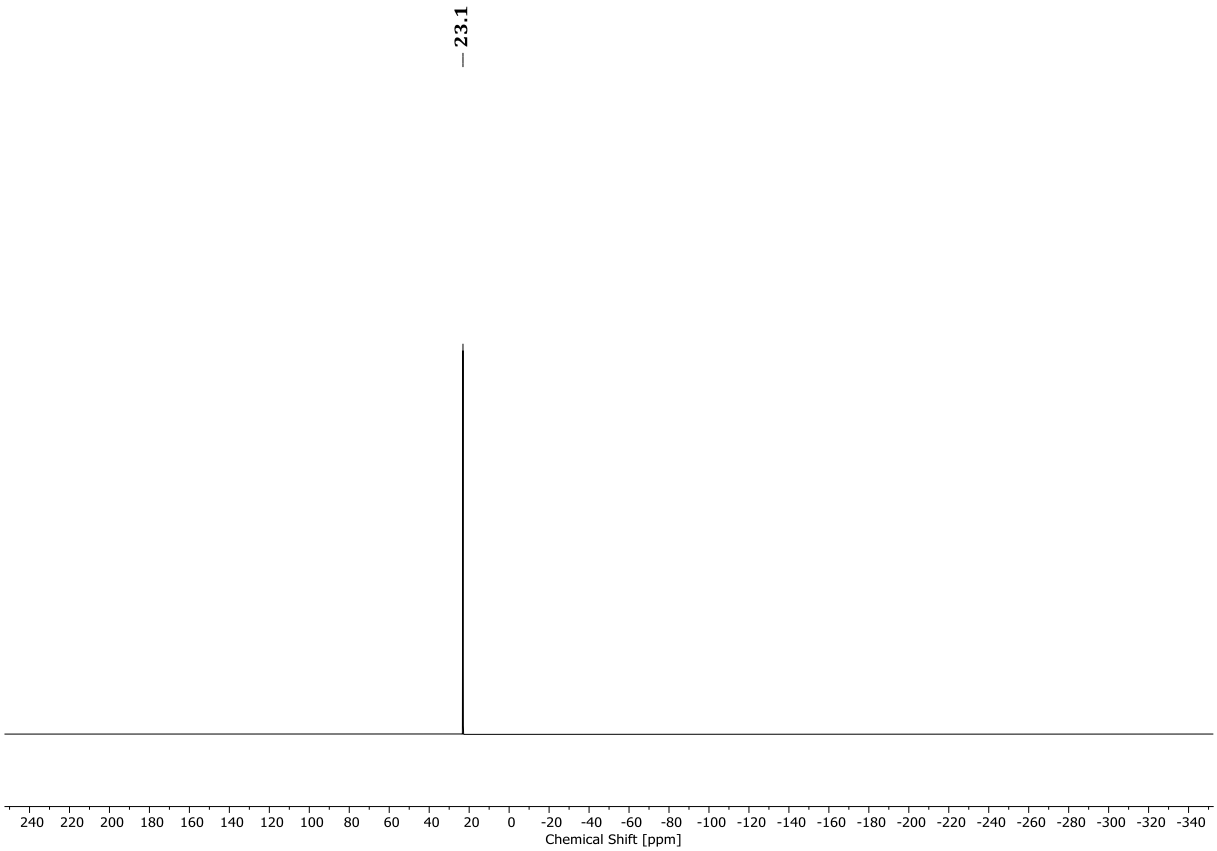
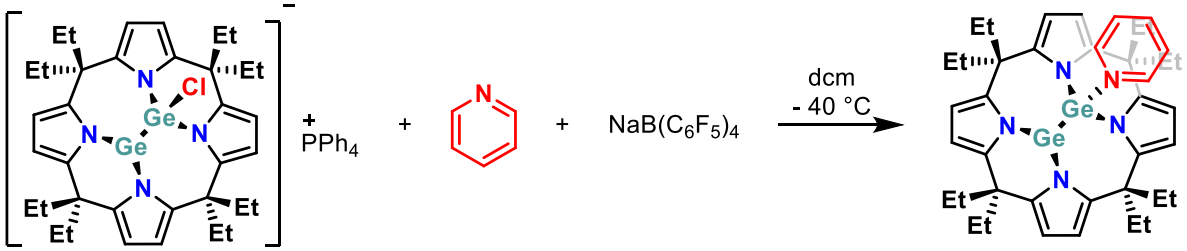


Figure S 1-21. $^{31}P\{^{1}H\}$ NMR (121 MHz, 298 K, dichloromethane-*d2*) spectrum of **$PPh_4[Cx^{Et}Ge_2Cl]$.**

1.2.7 Synthesis of *meso*-Octaethylcalix[4]pyrrolato-1-pyridine-digermene $Cx^{Et}Ge_2$(pyridine)



Reactants				*Products*	
Formula	**$C_{60}H_{68}ClGe_2N_4P$**	**C_5H_5N**	**$C_{24}BF_{20}Na$**	Formula	**$C_{41}H_{53}Ge_2N_5$**
MW	1056,92	79,10	702,03	MW	761,17
Limiting?	***Yes***	No	No	Equivalents	***1,00***
Equivalents	***1,00***	***5,00***	***1,00***	%Completion	
Sample Mass	***200,00mg***	74,84mg	132,85mg	Expected Mass	144,04mg
%Weight				Expected Moles	189,23µmol
Molarity				Measured Mass	***48,70mg***
Density		***982,00mg/mL***		Purity	
Volume		76,21mmL		Product Mass	48,70mg
Reactant Moles	189,23µmol	946,15µmol	189,23µmol	Product Moles	63,98µmol
Reactant Mass	200,00mg	74,84mg	132,85mg	%Yield	33,81%

$PPh_4[Cx^{Et}Ge_2Cl]$, $NaBArF_{20}$ and pyridine (py) were dissolved in dichloromethane (5.00 mL) at −35 °C. The mixture turned turbid due to the precipitation of NaCl. The mixture was stirred for 2 minutes. Pentane (30.0 mL) was added and the formed precipitate was removed *via* filtration. The

solvent of the filtrate was removed under reduced pressure and the solid residue was dried *in vacuo* to give the title compound **Cx^{Et}Ge$_2$(py)** as an off-white solid (120 mg, 109 µmol, 83 %). The crude product was recrystallized from a mixture of hexane (3.00 mL) and dichloromethane (a few drops) at room temperature to give yellow crystals. The crystals were ground and the fine powder was dried *in vacuo* for 16 h to the title compound **Cx^{Et}Ge$_2$(py)** as a yellow powder.

SCXRD: Single crystals suitable for SCXRD analysis were obtained from a concentrated solution in pentane at −35 °C.

Elemental Analysis for **Cx^{Et}Ge$_2$(py)**: Calculated for **Cx^{Et}Ge$_2$(py)** x 0.05 eq. silicon grease ($HSi(CH_3)_2(OH)$): C: 64.54, H: 7.04, N: 9.16. Found: C: 64.11, H: 7.19, N: 9.30.

^{1}H NMR (600 MHz, 298 K, dichloromethane-*d2*): δ = 7.38 (tt, *J* = 7.65, 1.50 Hz, 1H, *p*-py-C*H*), 6.70 – 6.65 (m, 2H, *m*-py-C*H*), 6.20 (d, ^3J = 3.18 Hz, 2H, β-C*H*), 5.92 (d, ^3J = 3.36 Hz, 2H, β-C*H*), 5.84 (d, ^3J = 3.22 Hz, 2H, β-C*H*), 5.48 (d, ^3J = 3.32 Hz, 2H, β-C*H*), 5.46 (d, *J* = 6.54 Hz, 2H, *o*-py-C*H*), 2.81 – 2.72 (m, 2H, CH_2-ethyl), 2.47 – 2.32 (m, 6H, CH_2-ethyl), 1.98 (q, *J* = 7.18 Hz, 2H, CH_2-ethyl), 1.88 (q, ^3J = 7.20 Hz, 2H, CH_2-ethyl), 1.82 (q, ^3J = 7.35 Hz, 2H, CH_2-ethyl), 1.54 (q, ^3J = 7.38 Hz, 2H, CH_2-ethyl), 0.99 (t, ^3J = 7.26 Hz, 6H, CH_3-methyl), 0.88 (t, ^3J = 7.13 Hz, 6H, CH_3-methyl), 0.77 (brs, 3H, CH_3-methyl), 0.63 (t, ^3J = 7.21 Hz, 3H, CH_3-methyl), 0.55 (t, ^3J = 7.39 Hz, 3H,CH_3-methyl), -0.09 (t, ^3J = 7.20 Hz, 3H, CH_3-methyl) ppm.

^{13}C {^{1}H} NMR (151 MHz, 298 K, dichloromethane-d_2) δ = 147.5 (*o*-py-*C*), 146.1 (C_q, α-*C*), 143.5 (C_q, α-*C*), 141.9 (C_q, α-*C*), 140.3 (C_q, α-*C*), 139.6 (*p*-py-*C*), 123.8 (*m*-py-*C*), 110.0 (*C*H, β-C), 109.9 (*C*H, β-C), 107.1 (*C*H, β-C), 105.0 (*C*H, β-C), 47.7 (C_q, *meso*-C), 46.7 (C_q, 2C, *meso*-C), 46.5 (C_q, *meso*-C), 44.3 (*C*H_2-ethyl), 35.3 (*C*H_2-ethyl, determined by ^{1}H-^{13}C-HSQC), 33.4 (*C*H_2-ethyl), 32.2 (*C*H_2-ethyl), 28.0 (*C*H_2-ethyl), 25.6 (*C*H_2-ethyl), 10.0 (*C*H_3-methyl), 9.9 (*C*H_3-methyl), 9.2 (*C*H_3-methyl), 9.1 (*C*H_3-methyl), 9.0 (*C*H_3-methyl), 8.7 (*C*H_3-methyl) ppm.

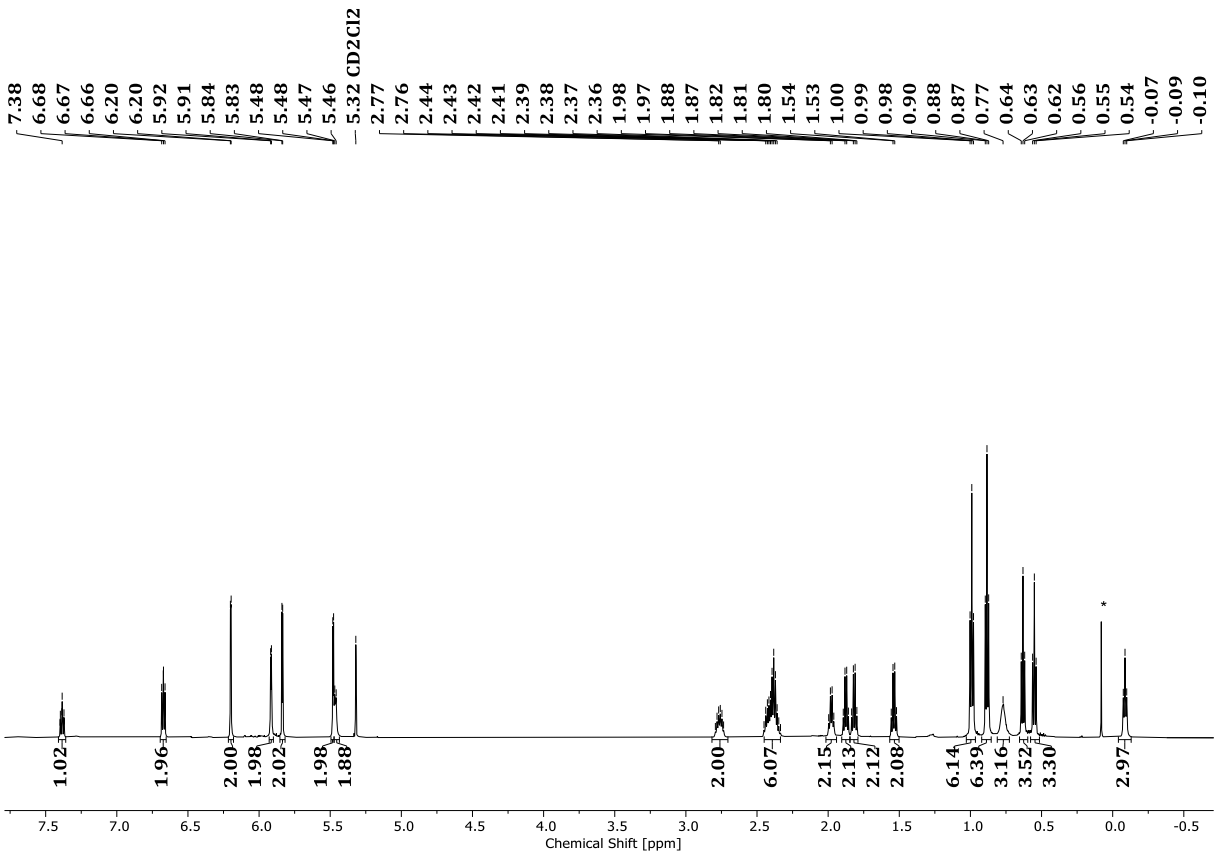


Figure S 1-22. ^{1}H NMR (600 MHz, 298 K, dichloromethane-*d2*) spectrum **of $Cx^{Et}Ge_2$(py).** * = Silicon grease.

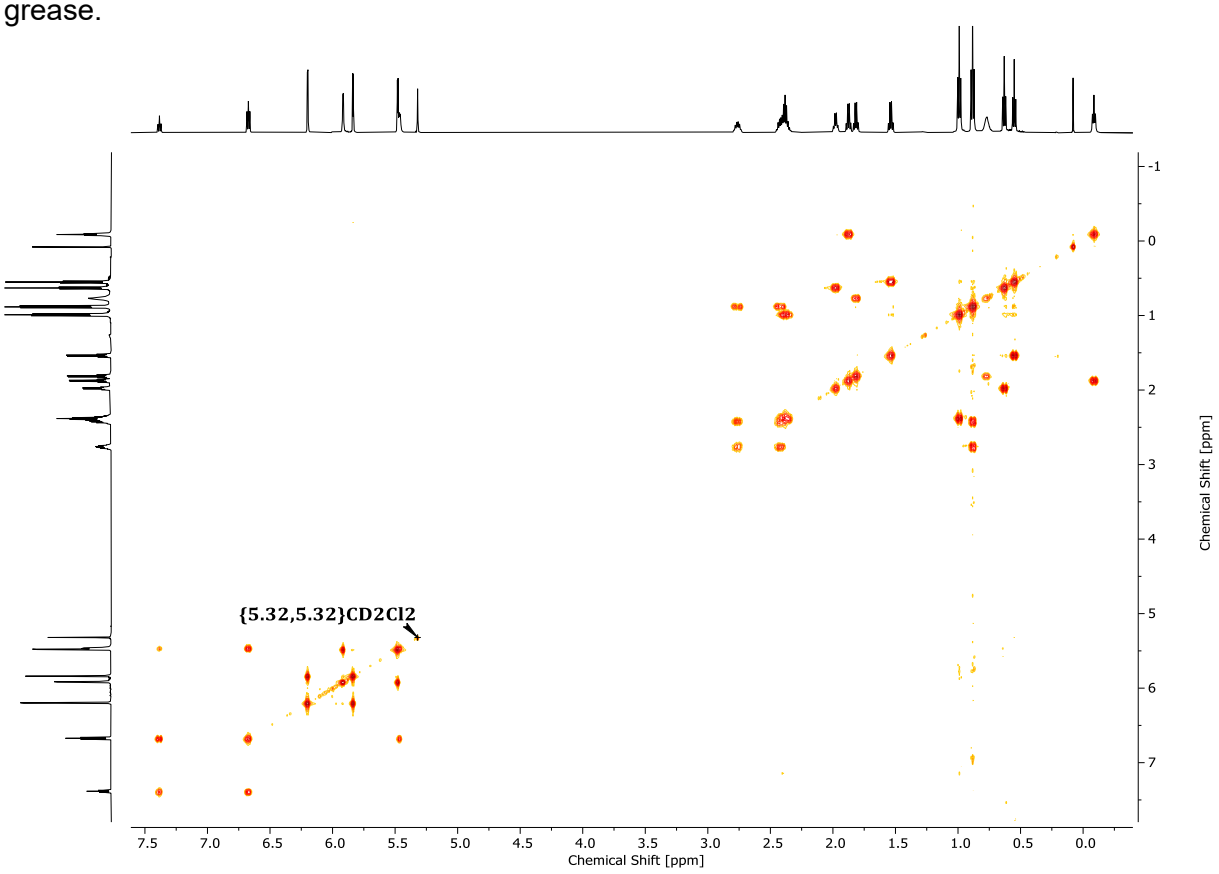


Figure S 1-23. ^{1}H-^{1}H COSY NMR (600 MHz, 298 K, dichloromethane-*d2*) spectrum of **$Cx^{Et}Ge_2$(py).**

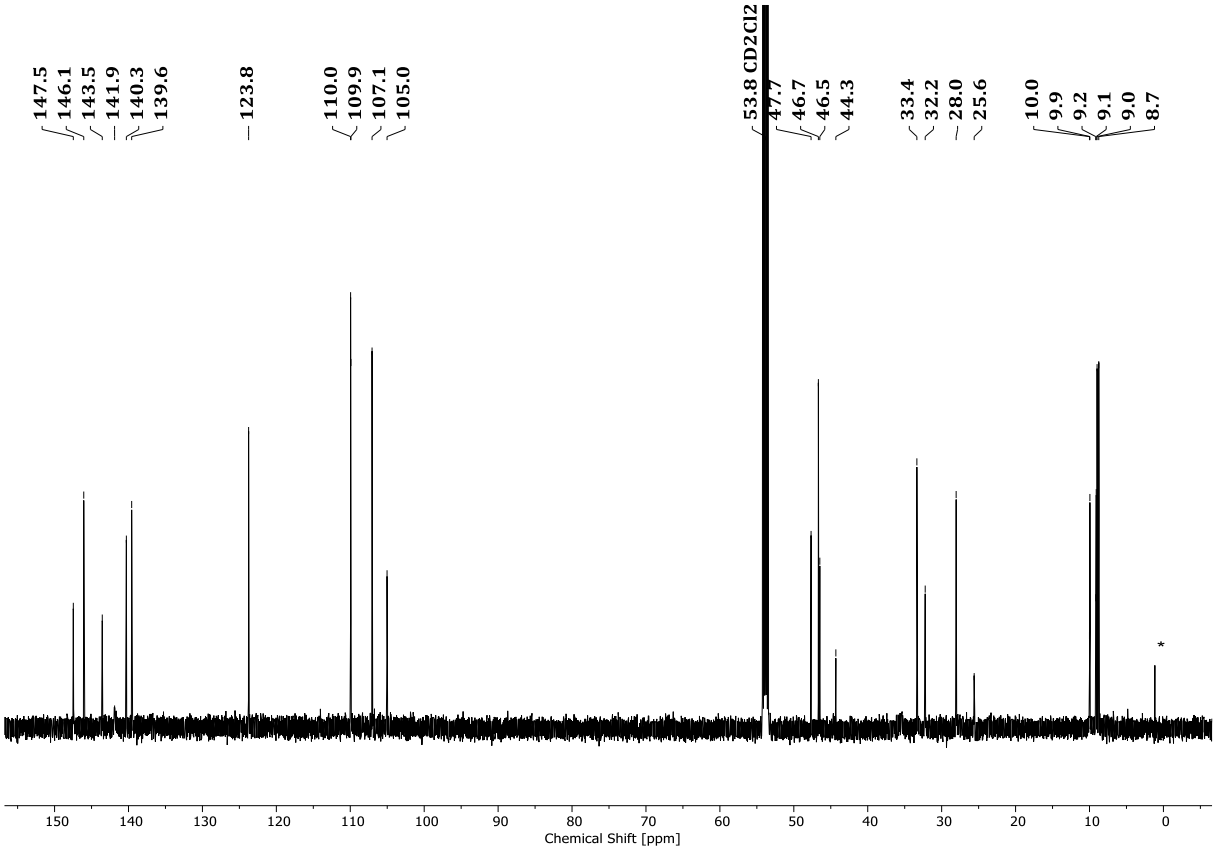


Figure S 1-24. $^{13}C\{^{1}H\}$ NMR (151 MHz, 298 K, dichloromethane-*d2*) spectrum of **$Cx^{Et}Ge_2$(py).** * = Silicon grease.

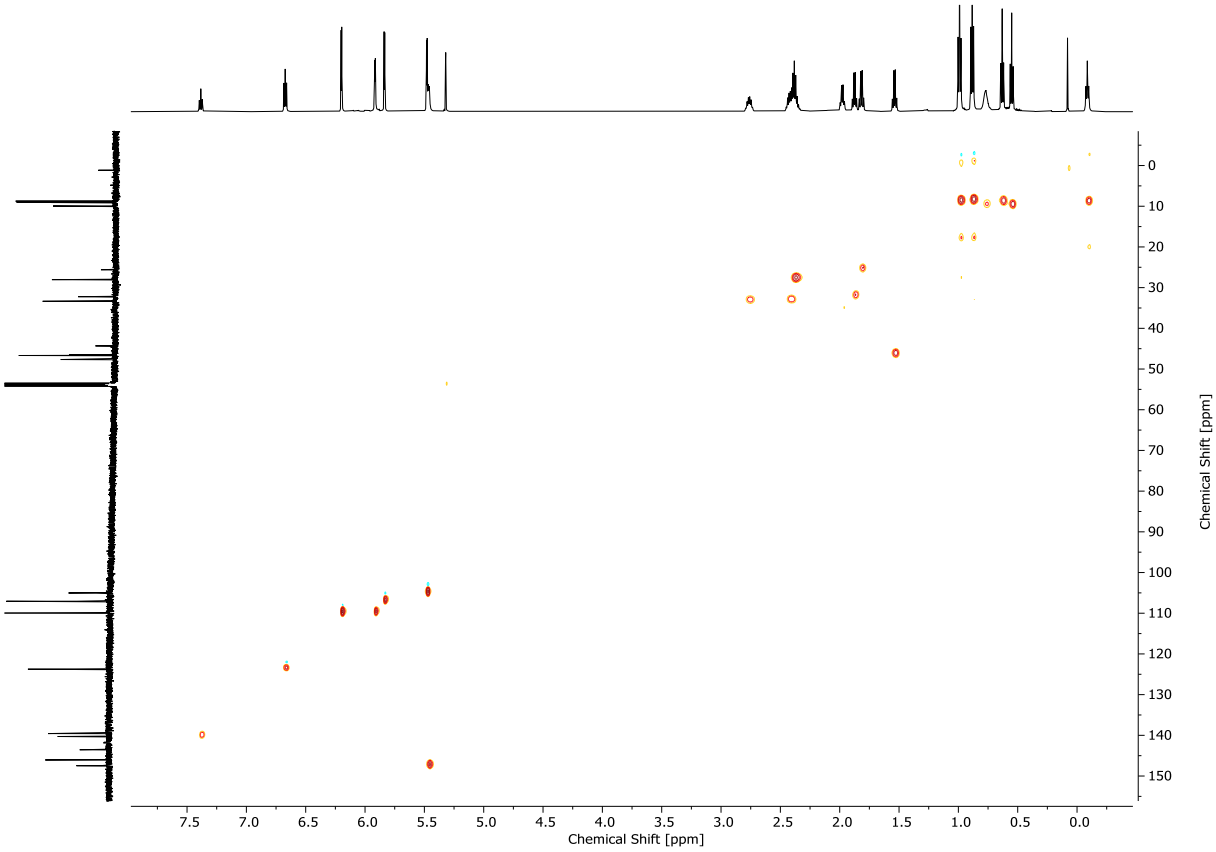


Figure S 1-25. ^{1}H-^{13}C HSQC NMR (600 MHz, 298 K, dichloromethane-*d2*) spectrum of **$Cx^{Et}Ge_2$(py).**

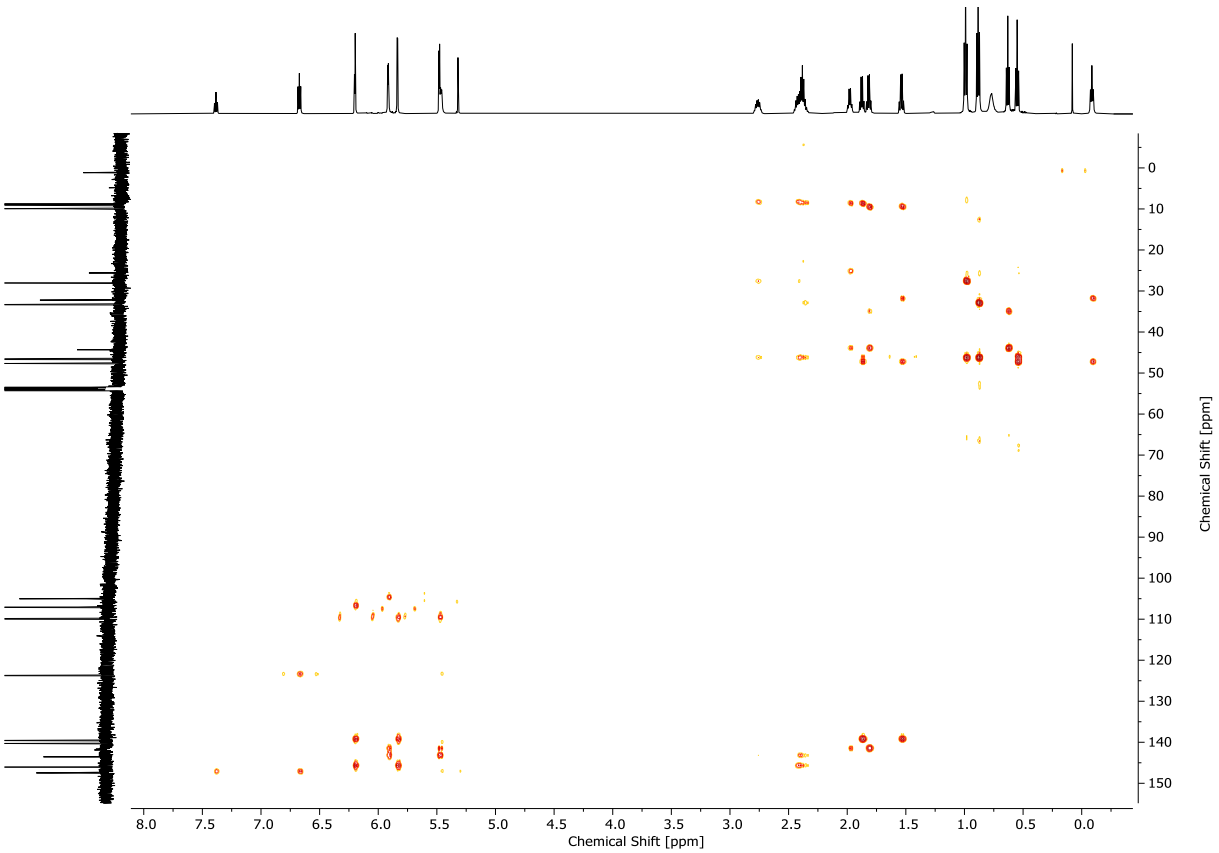
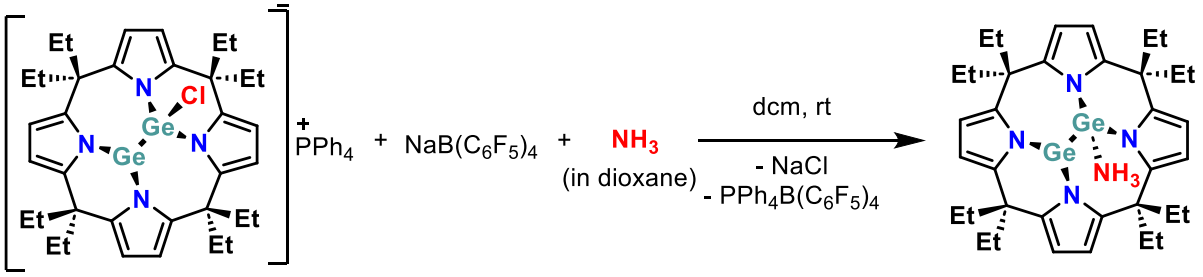


Figure S 1-26. ^{1}H-^{13}C HMBC NMR (600 MHz, 298 K, dichloromethane-*d2*) spectrum of **Cx^{Et}Ge$_2$(py).**

1.2.8 Synthesis of *meso*-Octaethylcalix[4]pyrrolato-1azane-digermene Cx^{Et}Ge$_2$(NH$_3$)



Reactants				*Products*	
Formula	**$C_{60}H_{68}ClGe_2N_4P$**	**$C_{24}BF_{20}Na$**	**H_3N**	Formula	**$C_{36}H_{51}Ge_2N_5$**
MW	1056.92	702.03	17.03	MW	699.10
Limiting?	***Yes***	No	No	Equivalents	
Equivalents	***1.00***	***1.00***	***2.00***	%Completion	
Sample Mass	***70.00mg***	46.50mg	2.26mg	Expected Mass	46.30mg
%Weight				Expected Moles	66.23µmol
Molarity			***400.00mM***	Measured Mass	***32.10mg***
Density				Purity	***66.00%***
Volume			331.15mmL	Product Mass	21.19mg
Reactant Moles	66.23µmol	66.23µmol	132.46µmol	Product Moles	30.30µmol
Reactant Mass	70.00mg	46.50mg	2.26mg	%Yield	45.76%

PPh$_4$Cx^{Et}Ge$_2$Cl, NaBArF$_{20}$ and NH$_3$ (0.40 M in dioxane) were dissolved in dichloromethane (1.00 mL). The mixture was stirred for 15 minutes, while turning turbid due to the precipitation of NaCl. The solvent of the reaction mixture was evaporated under reduced pressure and the residual solid was

dried for 16 hours. The solid was extracted with pentane (3 x 5.00 mL) and afterwards filtrated using a syringe filter. The solvent of the filtrate was evaporated under reduced pressure and the solid residue was dried for 2 hours *in vacuo* to yield the title compound as a colourless powder.

Note: Due to usage of non-dry NH_3-dioxane solution some hydrolysis occurred and $Cx^{Et}H_4$ (33.3 %) was formed which could not be removed by any purification method, but NMR and EA of the isolated products confirmed absence of other impurities.

SCXRD: Single crystals suitable for SCXRD analysis were obtained by cooling down a concentrated pentane solution while evaporation of the solvent under reduced pressure.

Elemental Analysis for **$Cx^{Et}Ge_2(NH_3)$**: Calculated for **$Cx^{Et}Ge_2(NH_3)$ x 0.33 $Cx^{Et}H_4$**: C: 66.53, H: 7.96 N: 10.11. Found: C: 63.19, H: 8.38, N: 10.21.

^{1}H NMR (600 MHz, 298 K, benzene-*d6*): δ = 6.27 (d, ^3J = 3.3 Hz, 2H, β-C*H*), 6.06 (d, ^3J = 3.3 Hz, 2H, β-C*H*), 5.98 (d, ^3J = 3.3 Hz, 2H, β-C*H*), 5.95 (d, ^3J = 3.3 Hz, 2H, β-C*H*), 2.73 (dq, ^3J = 13.6, 7.2 Hz, 2H, CH_2-ethyl), 2.56 (q, ^3J = 7.2 Hz, 2H, CH_2-ethyl), 2.44 – 2.37 (m, 2H, CH_2-ethyl), 2.28 – 2.17 (m, 6H, CH_2-ethyl), 1.98 (q, ^3J = 7.2 Hz, 2H, CH_2-ethyl), 1.80 – 1.75 (m, 2H, CH_2-ethyl, covered by 8H of $Cx^{Et}H_4$-CH_2-ethyl), 1.16 (t, ^3J = 7.4 Hz, 3H, CH_3-methyl), 0.93 (t, ^3J = 7.2 Hz, 3H, CH_3-methyl), 0.84 – 0.76 (m, 12H, CH_3-methyl), 0.66 (t, ^3J = 7.1 Hz, 3H, CH_3-methyl, covered by 12H of $Cx^{Et}H_4$-CH_3-methyl), 0.51 (t, ^3J = 7.1 Hz, 3H, CH_3-methyl), 0.47 – 0.45 (m, 3H, CH_3-methyl) ppm.

^{13}C {^{1}H} NMR (151 MHz, 298 K, benzene-*d6*) δ = 148.0 (C_q, α-*C*), 145.2 (C_q, α-*C*), 143.8 (C_q, α-*C*), 137.8 (C_q, α-*C*), 108.8 (*C*H, β-C), 108.3 (*C*H, β-C), 106.6 (*C*H, β-C), 105.2 (*C*H, β-C), 55.6 (C_q, *meso*-C), 47.7 (C_q, *meso*-C), 45.8 (*C*H_2-ethyl), 44.8 (C_q, *meso*-C), 44.4 (C_q, *meso*-C), 43.1 (*C*H_2-ethyl), 41.1 (C_q, *meso*-C), 36.1 (*C*H_2-ethyl), 32.3 (*C*H_2-ethyl), 29.1 (*C*H_2-ethyl), 24.9 (*C*H_2-ethyl), 10.9 (*C*H_3-methyl), 10.1 (*C*H_3-methyl), 9.3 (*C*H_3-methyl), 9.2 (*C*H_3-methyl), 8.4 (*C*H_3-methyl), 8.3 (*C*H_3-methyl) ppm.

IR-ATR: v = 3442 (s), 3342 (w), 3147 (w), 3101 (w), 2964(s), 2933 (s), 2876 (s) cm^{-1}.

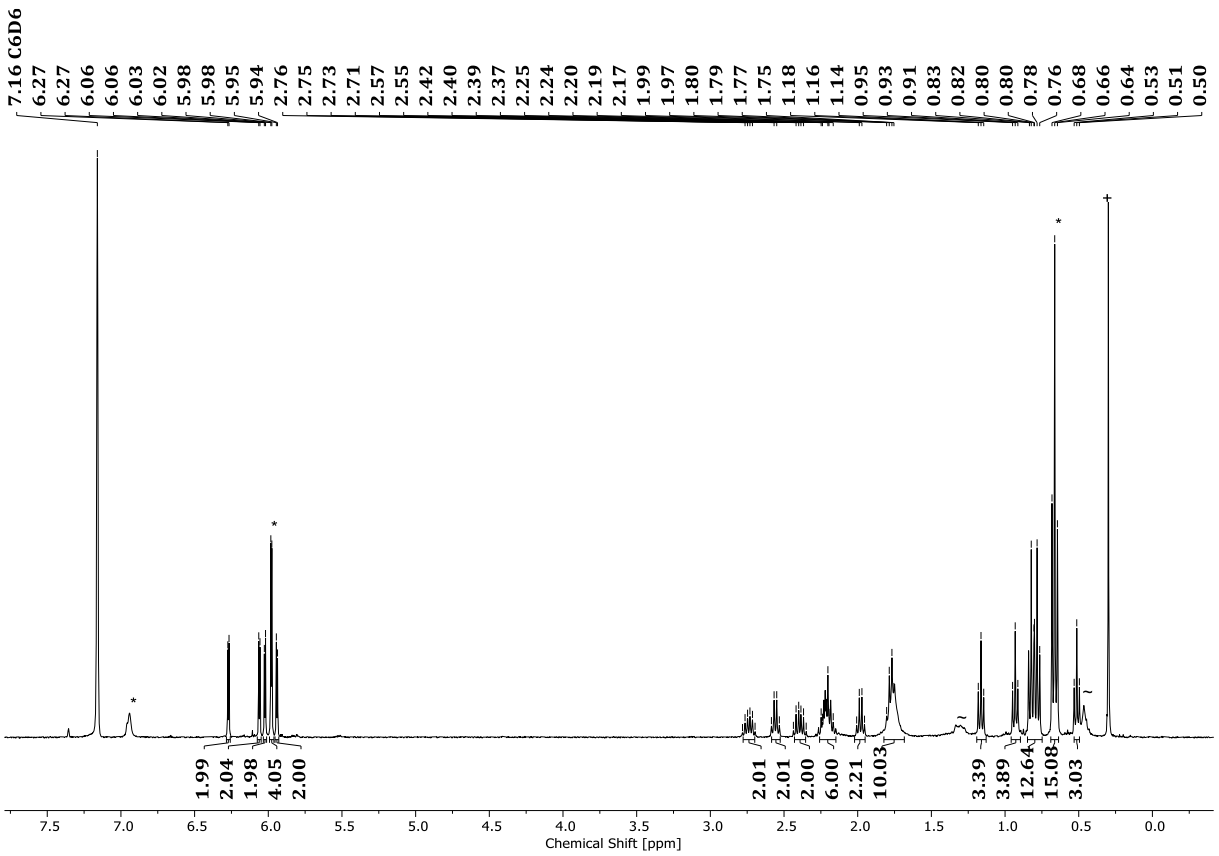


Figure S 1-27. ^{1}H NMR (600 MHz, 298 K, benzene-*d6*) spectrum of **$Cx^{Et}Ge_2(NH_3)$.** * = $Cx^{Et}H_4$, ~ = pentane, + = silicon grease.

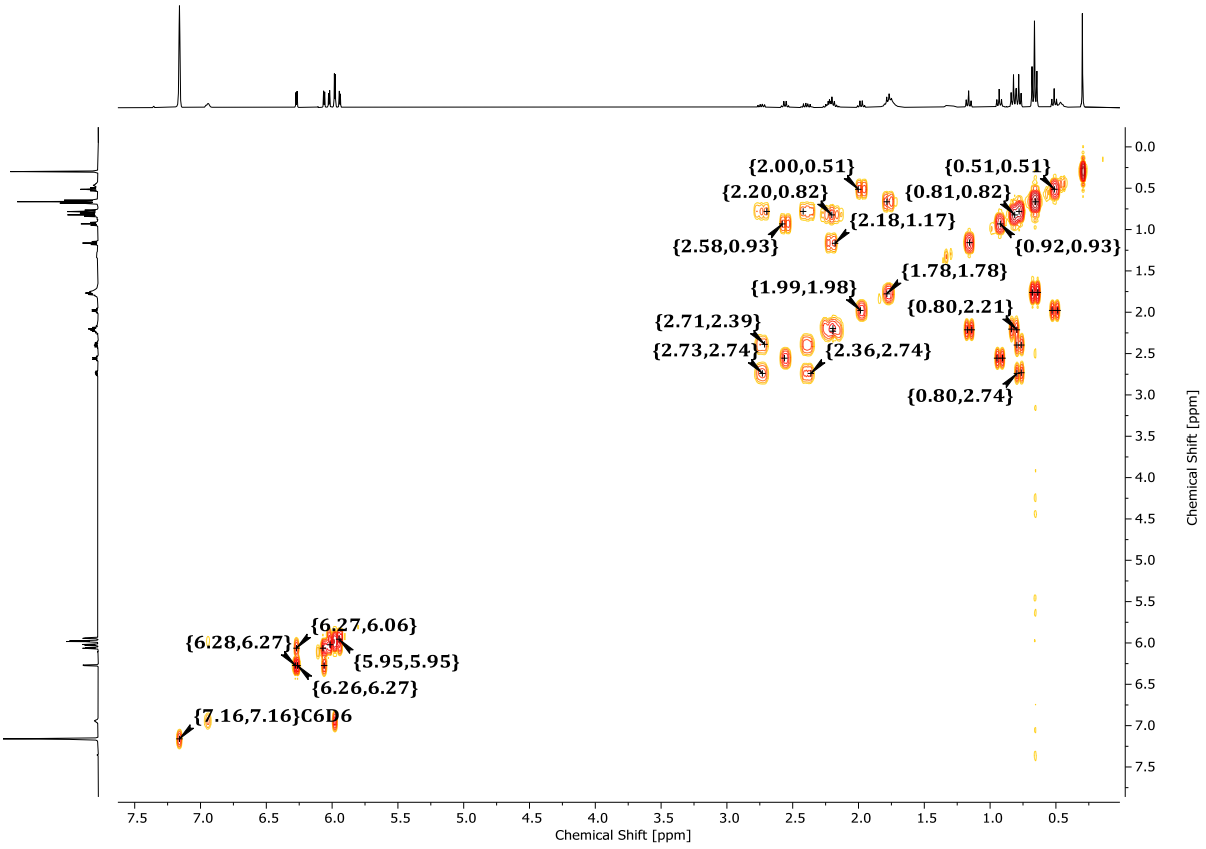


Figure S 1-28. ^{1}H-^{1}H COSY NMR (600 MHz, 298 K, benzene-*d6*) spectrum of **$Cx^{Et}Ge_2(NH_3)$.**

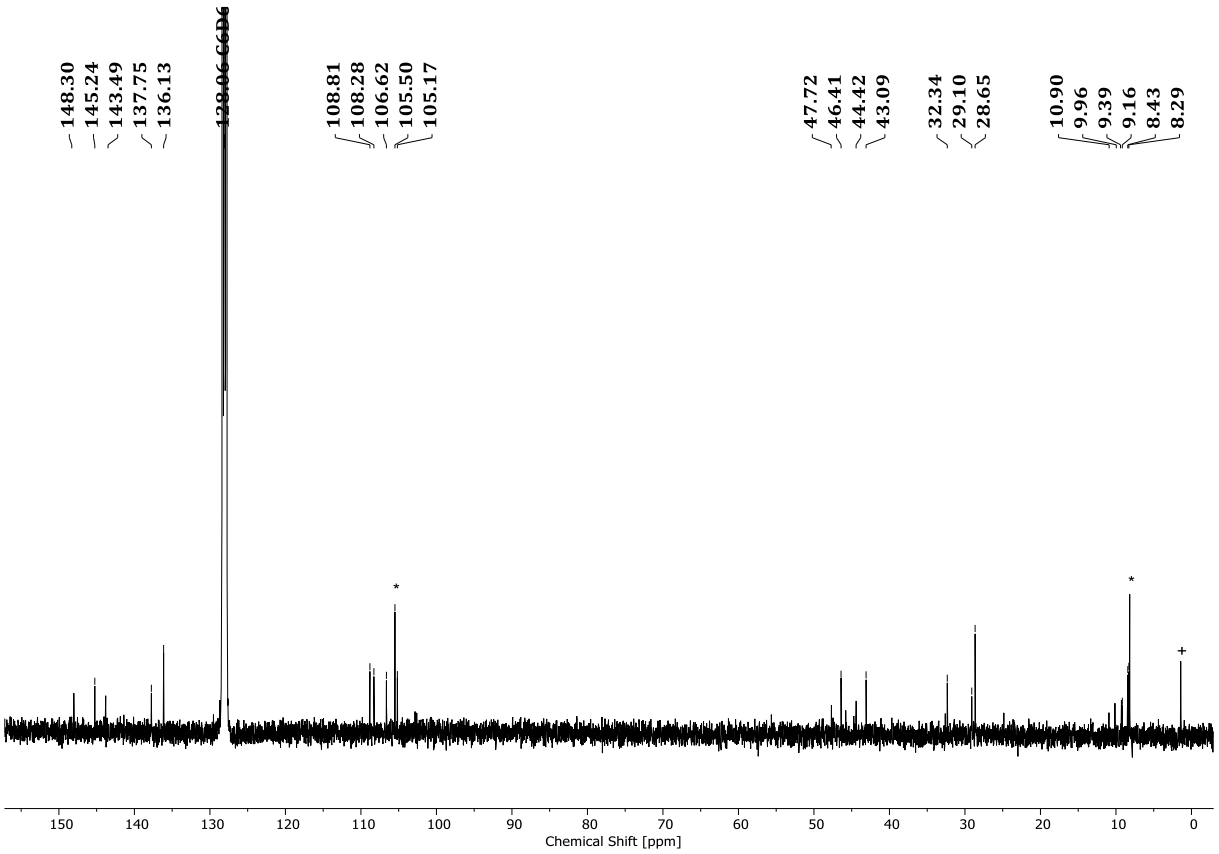


Figure S 1-29. $^{13}C\{^{1}H\}$ NMR (151 MHz, 298 K, benzene-*d6*) spectrum of **$Cx^{Et}Ge_2(NH_3)$.** * = $Cx^{Et}H_4$, + = silicon grease.

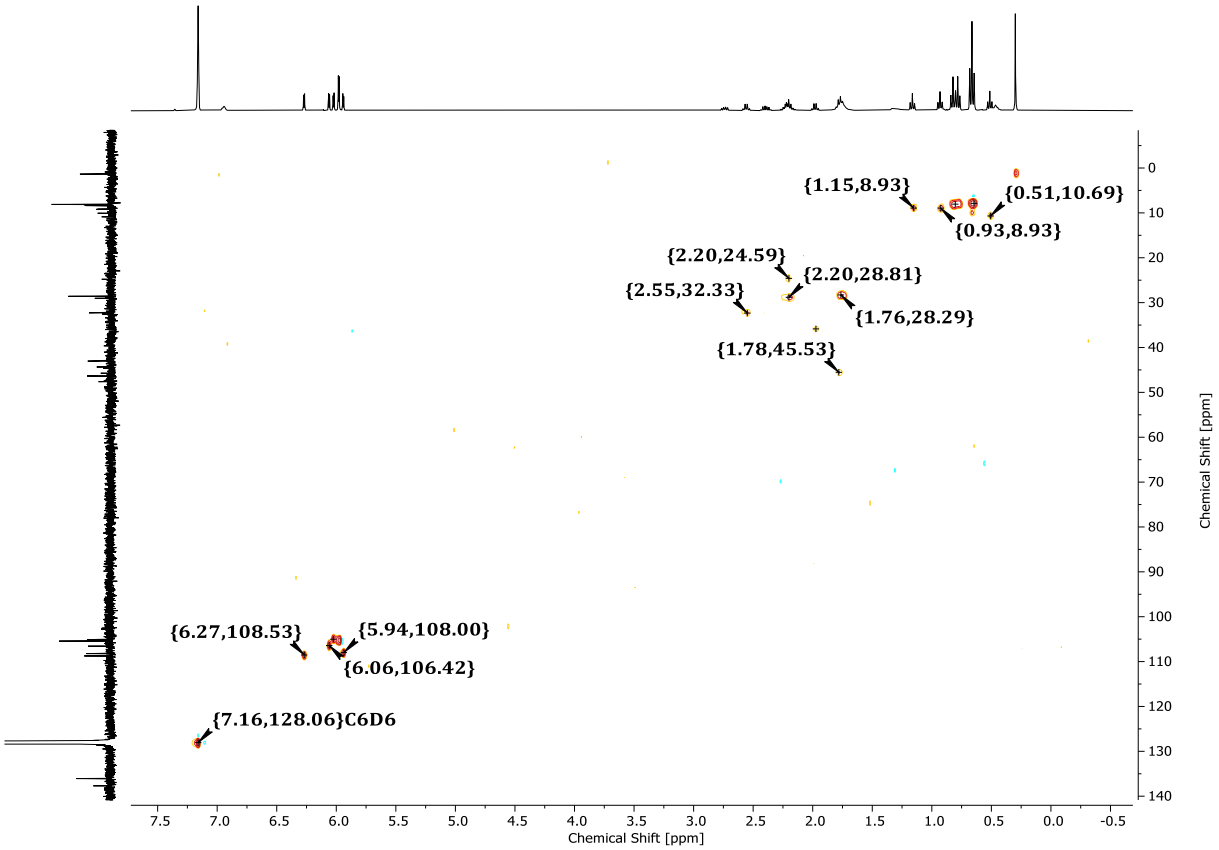


Figure S 1-30. ^{1}H-^{13}C HSQC NMR (600 MHz, 298 K, benzene-*d6*) spectrum of **$Cx^{Et}Ge_2(NH_3)$.**

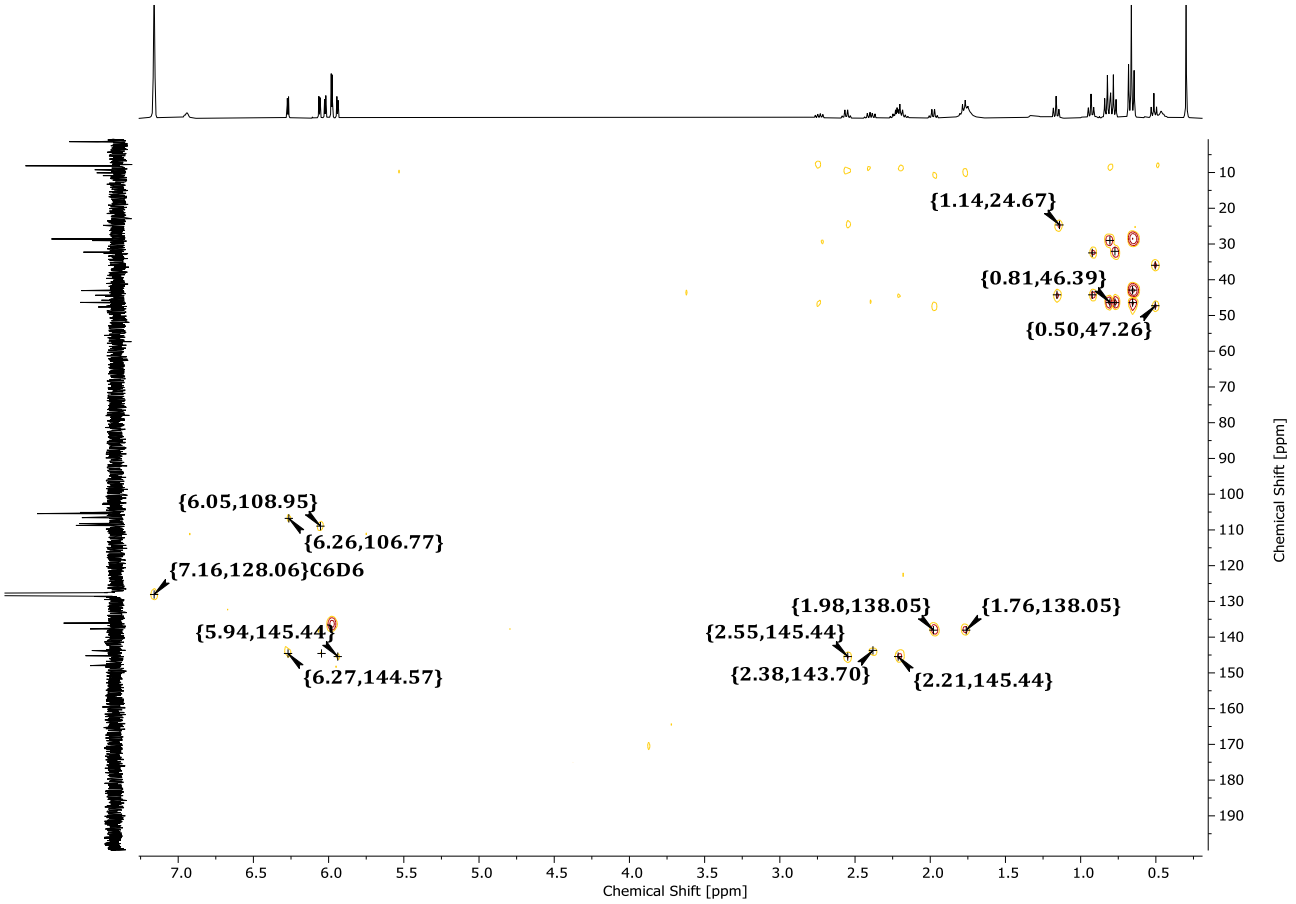
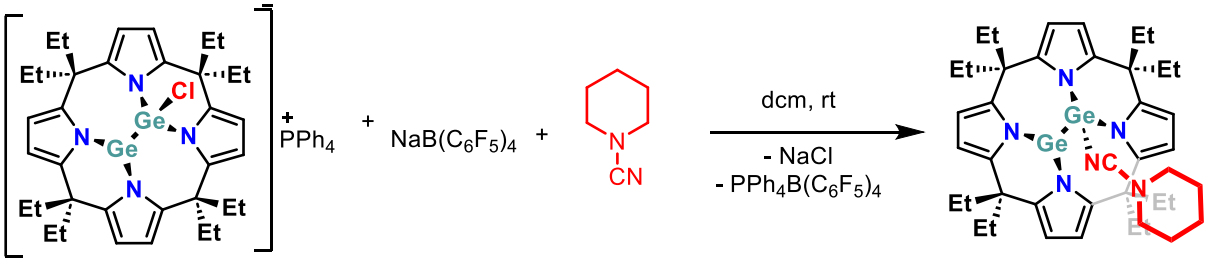


Figure S 1-31. ^{1}H-^{13}C HMBC NMR (600 MHz, 298 K, benzene-*d6*) spectrum of **Cx^{Et}Ge$_2$(NH$_3$).**

1.2.9 Synthesis of *meso*-Octaethylcalix[4]pyrrolato-1-piperidine-1-carbonitrile-digermane Cx^{Et}Ge$_2$(NC-pip)



Reactants				*Products*	
Formula	**$C_{60}H_{68}ClGe_2N_4P$**	**$C_{24}BF_{20}Na$**	**$C_6H_{10}N_2$**	Formula	**$C_{42}H_{58}Ge_2N_6$**
MW	1056.92	702.03	110.16	MW	792.23
Limiting?	***Yes***	No	No	Equivalents	
Equivalents	***1.00***	***1.00***	***1.02***	%Completion	
Sample Mass	***40.00mg***	26.57mg	4.25mg	Expected Mass	29.98mg
%Weight				Expected Moles	37.85µmol
Molarity				Measured Mass	***15.00mg***
Density			***950.00mg/mL***	Purity	
Volume			4.48mmL	Product Mass	15.00mg
Reactant Moles	37.85µmol	37.85µmol	38.60µmol	Product Moles	18.93µmol
Reactant Mass	40.00mg	26.57mg	4.25mg	%Yield	50.03%

PPh$_4$[Cx^{Et}Ge$_2$Cl], NaBArF$_{20}$ and the nitrile were dissolved in dichloromethane (1.00 mL). The mixture was stirred for 15 minutes, while turning turbid due to the precipitation of NaCl. The solvent

of the reaction mixture was evaporated under reduced pressure and the residual solid was dried for 2 hours. The solid was extracted with pentane (5.00 mL) and afterwards filtrated using a syringe filter. The volume of the filtrate was reduced to approx. 1 mL, while a clear solution was maintained and stored afterwards at −35 °C for 7 days to yield colourless crystals. The crystals were collected, crushed and dried *in vacuo* for 10 minutes to yield the title compound as a colourless powder.

SCXRD: Single crystals suitable for SCXRD analysis were obtained by storing a concentrated pentane solution at −35 °C.

Elemental Analysis for **$Cx^{Et}Ge_2$(NC-pip)**: Calculated for **$Cx^{Et}Ge_2$(NC-pip)**: C: 63.68, H: 7.38, N: 10.61. Found: C: 63.53, H: 7.40, N: 10.39.

^{1}H NMR (600 MHz, 298 K, dichloromethane-*d2*): δ = 6.32 (d, ^3J = 3.2 Hz, 2H, β-C*H*), 6.13 (d, ^3J = 3.2 Hz, 2H, β-C*H*), 6.09 (d, ^3J = 3.2 Hz, 2H, β-C*H*), 6.00 (d, ^3J = 3.2 Hz, 2H, β-C*H*), 2.96 (m, 2H, CH_2-ethyl), 2.65 (q, *J* = 7.2 Hz, 2H, CH_2-ethyl), 2.57 (m, 2H, CH_2-ethyl), 2.41 (m, 2H, CH_2-ethyl), 2.38 (m, 2H, CH_2-ethyl), 2.31 (q, *J* = 7.4 Hz, 2H, CH_2-ethyl), 2.20 (t, *J* = 5.6 Hz, 4H, pip-NCH_2CH_2CH_2), 2.16 (q, *J* = 7.2 Hz, 2H, CH_2-ethyl), 1.90 (q, *J* = 7.1 Hz, 2H, CH_2-ethyl), 1.33 (t, *J* = 7.4 Hz, 3H, CH_3-methyl), 1.01 (m, 9H, CH_3-methyl), 0.91 (t, *J* = 7.1 Hz, 6H, CH_3-methyl), 0.88 (t, *J* = 7.1 Hz, 6H, CH_3-methyl), 0.64 – 0.59 (m, 4H, pip-NCH_2CH_2CH_2), 0.55 (d, *J* = 6.1 Hz, 2H, pip-NCH_2CH_2CH_2) ppm.

^{13}C{^{1}H} NMR (151 MHz, 298 K, dichloromethane-d_2) δ = 145.9 (C_q, α-*C*), 144.9 (C_q, α-*C*), 143.6 (C_q, α-*C*), 139.1 (C_q, α-*C*), 128.4 (C_q, *C*N) 108.6 (*C*H, β-C), 108.2 (*C*H, β-C), 106.3 (*C*H, β-C), 104.2 (*C*H, β-C), 49.9 (*C*H_2-ethyl), 49.3 (CH_2, pip-N*C*H_2), 47.6 (C_q, *meso*-C), 46.3 (C_q, *meso*-C), 45.5 (*C*H_2-ethyl), 44.3 (C_q, *meso*-C), 35.4 (*C*H_2-ethyl), 34.4 (C_q, *meso*-C), 34.1 (*C*H_2-ethyl), 32.8 (*C*H_2-ethyl), 29.0 (*C*H_2-ethyl), 28.6 (*C*H_2-ethyl), 25.6 (*C*H_2-ethyl), 24.4 (*C*H_3-methyl), 23.6 (*C*H_3-methyl), 22.9 (CH_2, pip-NCH_2*C*H_2CH_2), 21.8 (CH_2, pip-NCH_2CH_2*C*H_2), 10.5 (*C*H_3-methyl), 10.4 (*C*H_3-methyl), 9.4 (*C*H_3-methyl), 8.9 (*C*H_3-methyl), 8.6 (*C*H_3-methyl), 8.2 (*C*H_3-methyl) ppm.

IR-ATR: v = 2262 (s, CN v) cm^{-1}.

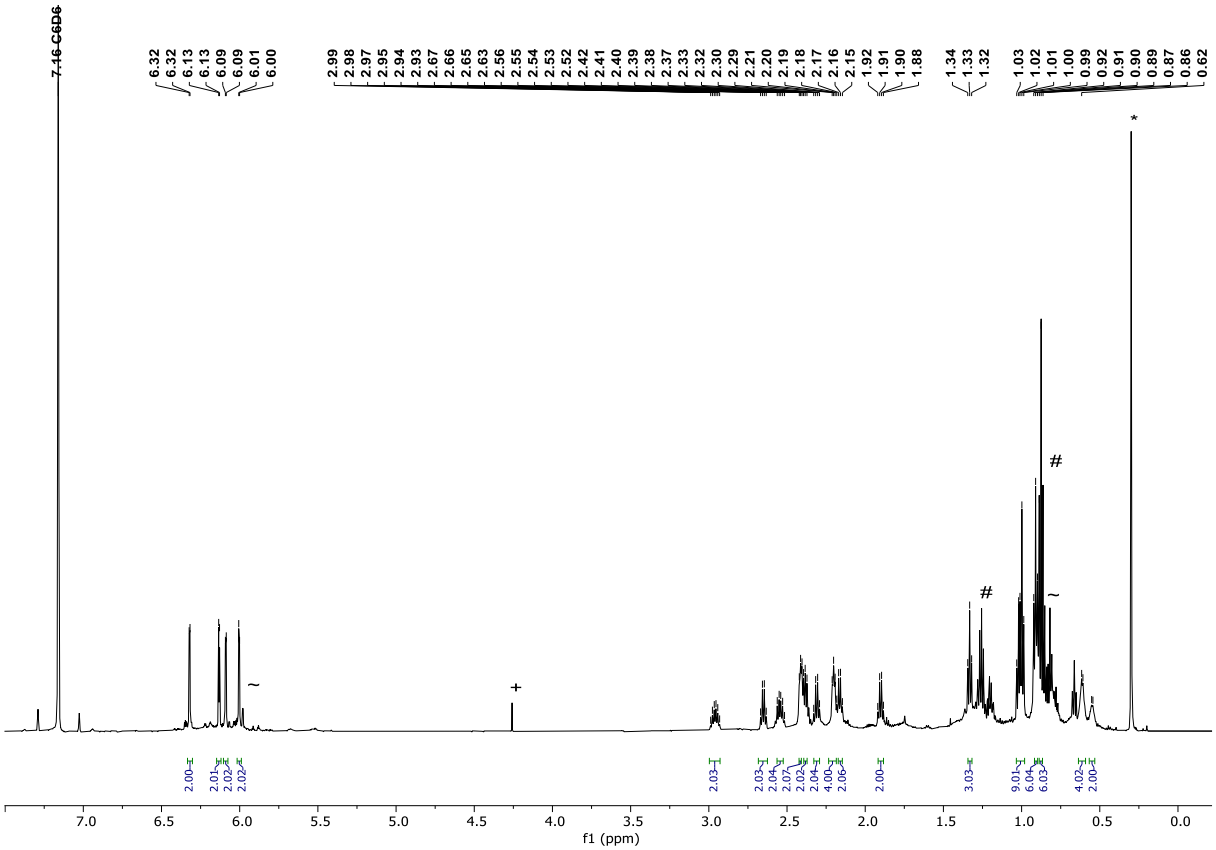


Figure S 1-32. ^{1}H NMR (600 MHz, 298 K, benzene-*d6*) spectrum of **Cx^{Et}Ge$_2$(NC-pip).** ~ = Cx^{Et}H$_4$, # = pentane, + = dichloromethane, * = silicon grease.

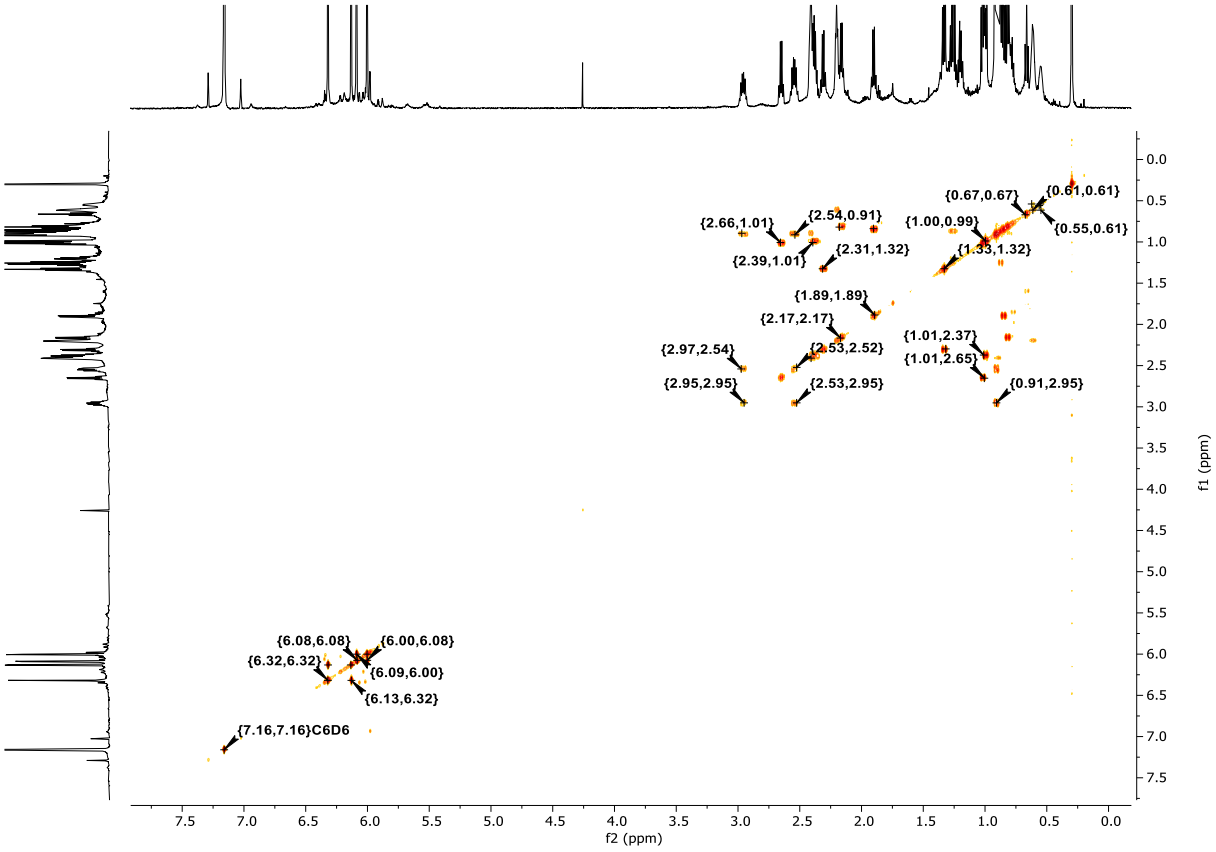


Figure S 1-33. ^{1}H-^{1}H COSY NMR (600 MHz, 298 K, benzene-*d6*) spectrum of **Cx^{Et}Ge$_2$(NC-pip).**

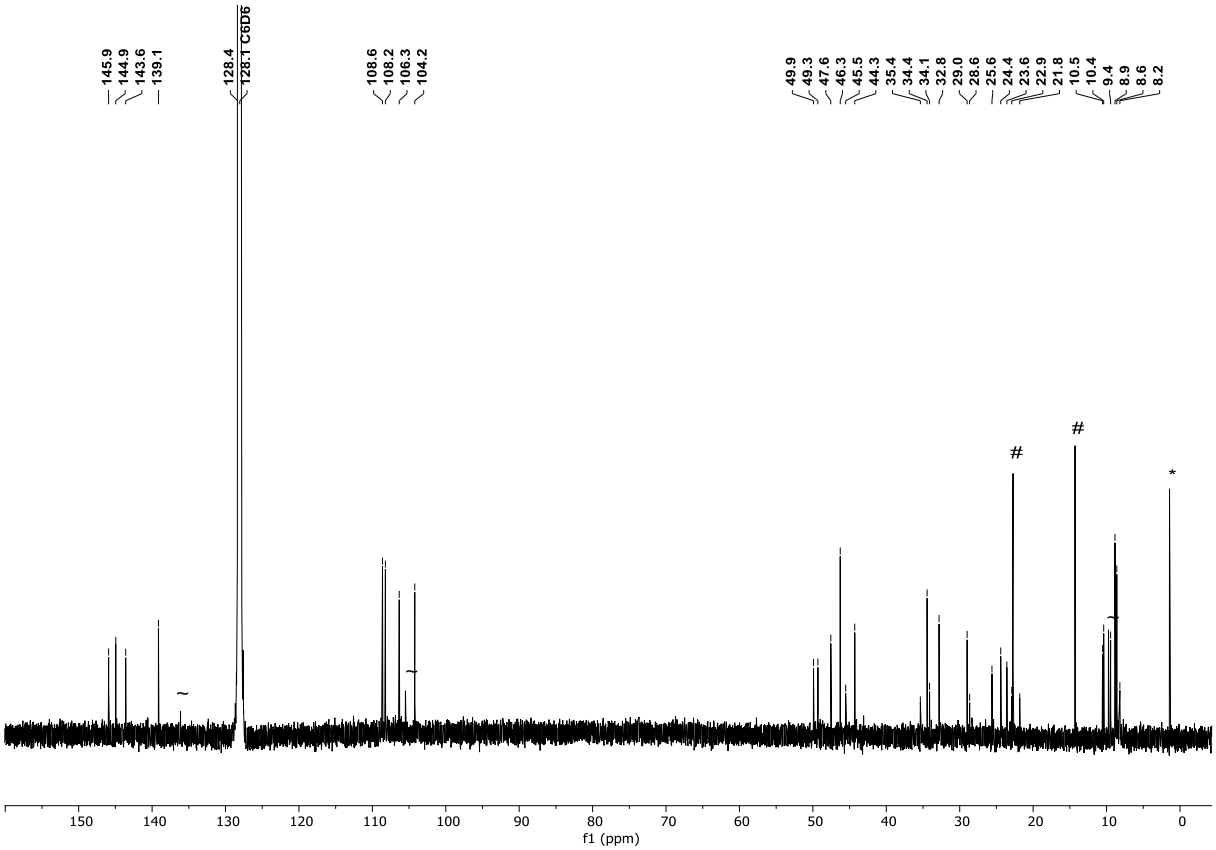


Figure S 1-34. $^{13}C\{^{1}H\}$ NMR (151 MHz, 298 K, benzene-*d6*) spectrum of **$Cx^{Et}Ge_2$(NC-pip)**. ~ = $Cx^{Et}H_4$, # = pentane, * = silicon grease.

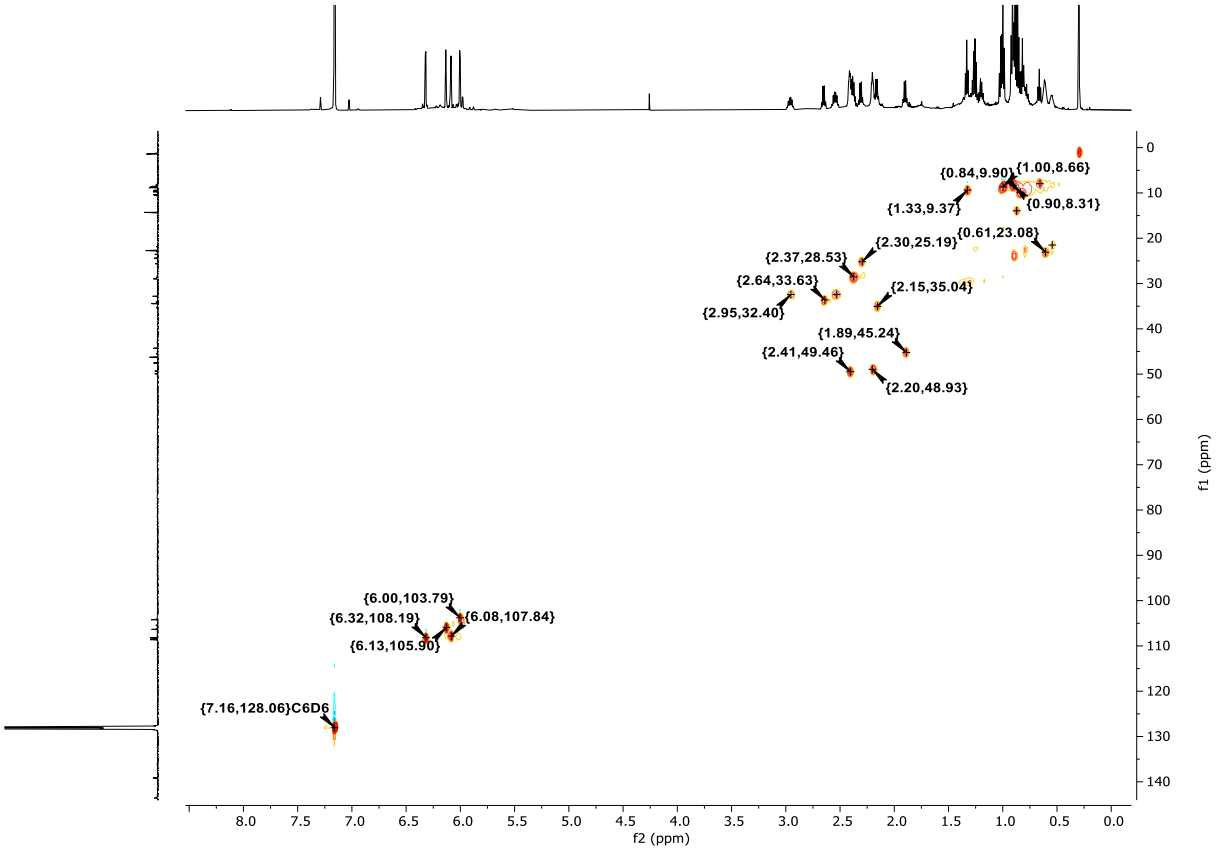


Figure S 1-35. ^{1}H-^{13}C HSQC NMR (600 MHz, 298 K, benzene-*d6*) spectrum of **$Cx^{Et}Ge_2$(NC-pip).**

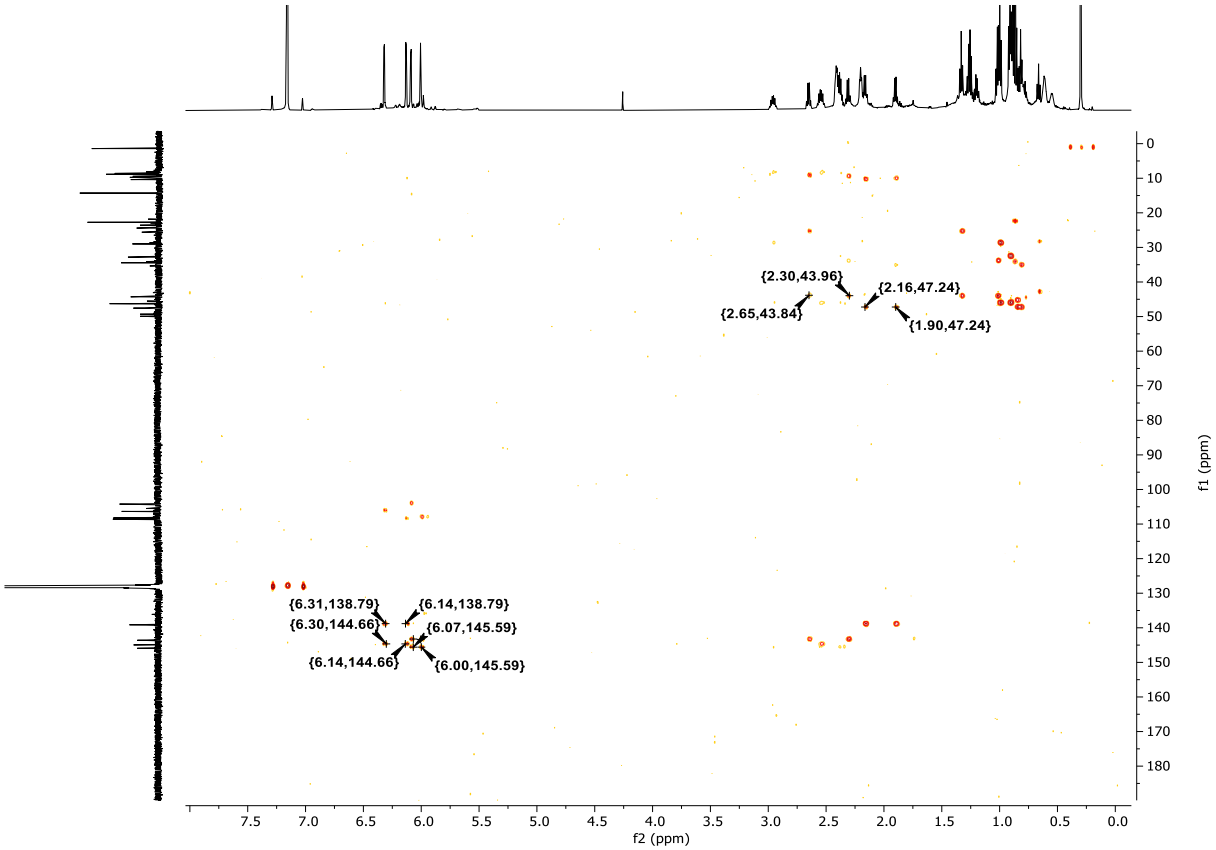
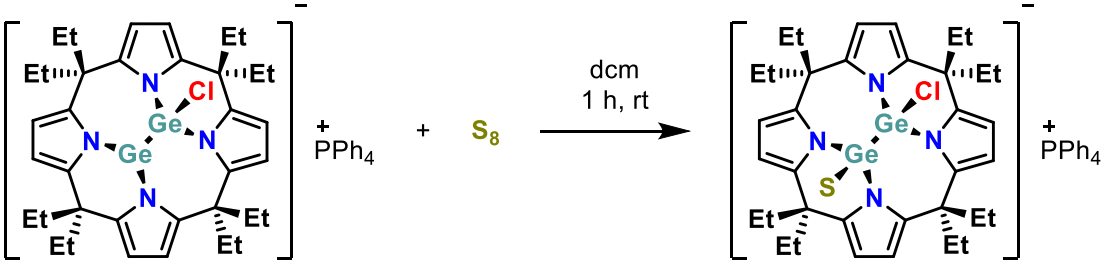


Figure S 1-36. ^{1}H-^{13}C HMBC NMR (600 MHz, 298 K, benzene-*d6*) spectrum of **$Cx^{Et}Ge_2$(NC-pip).**

1.2.10 Synthesis of Tetraphenylphosphonium *meso*-Octaethylcalix[4]pyrrolato-2-chlorodigermane-1-thiolate $PPh_4[Cx^{Et}Ge_2ClS]$



Reactants			*Products*	
Formula	$C_{60}H_{68}ClGe_2N_4P$	S_8	Formula	$C_{60}H_{68}ClGe_2N_4PS$
MW	1056,92	256,48	MW	1088,98
Limiting?	***Yes***	No	Equivalents	
Equivalents	***1,00***	***0,13***	%Completion	
Sample Mass	***300,00mg***	9,10mg	Expected Mass	309,10mg
%Weight			Expected Moles	283,84µmol
Molarity			Measured Mass	***223,00mg***
Density			Purity	
Volume			Product Mass	223,00mg
Reactant Moles	283,84µmol	35,48µmol	Product Moles	204,78µmol
Reactant Mass	300,00mg	9,10mg	%Yield	72,14%

$PPh_4[Cx^{Et}Ge_2Cl]$ and sulfur (S_8) were dissolved in dichloromethane (3 mL) and the reaction mixture was stirred for 1 h at room temperature. The solvent of the solution was evaporated and the resulting the pink residue was washed with toluene (13 mL) and dried *in vacuo* overnight to give the title compound as a pink powder.

Final purification was performed by recrystallization by vapour diffusion of pentane into a concentrated tetrahydrofuran solution at –35 °C. The obtained crystals were isolated, washed with pentane and dried *in vacuo* for 4 h.

SCXRD: Single crystals suitable for SCXRD analysis were obtained by pentane vapour diffusion into a concentrated tetrahydrofuran solution at −35 °C.

Elemental Analysis for **$PPh_4[Cx^{Et}Ge_2ClS]$**: Calculated for **$PPh_4[Cx^{Et}Ge_2ClS]$** x ¼ toluene [%]: C: 66.70; H: 6.35; N: 5.04. Found: C: 66.84; H: 6.54; N: 4.81.

ESI(–)-MS: Calculated for **$[Cx^{Et}Ge_2ClS]^-$**: 749.1726. Found: 749.1769. (dichloromethane).

^{1}H NMR (600 MHz, 298 K, dichloromethane-*d2*): δ = 7.85 - 7.82 (m, 4H, *p*-PPh_4), 7.70-7.67 (m, 8H, *m*-PPh_4), 7.57 - 7.53 (m, 8H, *o*-PPh_4), 5.93 (d, 2H, ^3J = 6 Hz, β-C*H*), 5.88 (d, 2H, ^3J = 6 Hz, β-C*H*), 5.82 (d, 2H, ^3J = 6 Hz, β-C*H*), 5.75 (d, 2H, 3J = 6 Hz, pyrrole-CH), 2.73 (bs, 2 H, CH_2-ethyl), 2.48 – 2.36 (m, 8 H, CH_2-ethyl), 2.25 (bs, 2H, CH_2-ethyl), 2.02 – 1.98 (m, 4H, CH_2-ethyl), 1.93 (q, ^3J = 6 Hz, CH_2-ethyl), 1.03 (t, ^3J = 6 Hz, 6H, CH_3-methyl), 0.85 (t, ^3J = 6 Hz, 6H, CH_3-methyl), 0.81 (t, ^3J = 6 Hz, 3H, CH_3-methyl), 0.74 (t, ^3J = 6 Hz, 3H, CH_3-methyl), 0.59 – 0.54 (m, 6H, CH_3-methyl) ppm.

^{13}C{^{1}H} NMR (151 MHz, 298 K, dichloromethane-*d2*): δ = 144.3 (C_q, α-*C*), 141.7 (C_q, α-*C*), 139.9 (C_q, α-*C*), 138.8 (C_q, α-*C*), 136.2 (d, $^3J(^{31}P,^{13}C)$ = 15.1 Hz, *p*-PPh_4), 134.8 (d, $^3J(^{31}P,^{13}C)$ = 15.1 Hz, *m*-PPh_4), 131.0 (d, $^3J(^{31}P,^{13}C)$ = 15.1 Hz, *o*-PPh_4), 117.8 (d, $^3J(^{31}P,^{13}C)$ = 45 Hz, C_q,PPh_4), 107.1 (*C*H, β-C), 107.1 (*C*H, β-C), 106.9 (*C*H, β-C), 105.8 (*C*H, β-C), 44.9 (C_q, *meso*-C), 44.7 (C_q, 2C, *meso*-C), 44.7 (C_q, *meso*-C), 39.1 (*C*H_2-ethyl), 34.8 (*C*H_2-ethyl)$^+$, 31.3 (*C*H_2-ethyl), 28.7 (*C*H_2-ethyl), 28.5 (*C*H_2-ethyl), 28.1 (*C*H_2-ethyl), 21.6 (*C*H_2-ethyl)$^+$, 10.0 (*C*H_3-methyl), 9.7 (*C*H_3-methyl), 9.5 (*C*H_3-methyl), 9.5 (*C*H_3-methyl)*, 9.2 (*C*H_3-methyl), 9.2 (*C*H_3-methyl) ppm.

**Shoulder of peak at δ = 9.4 ppm.*

$^+$*Determined by ^{1}H-^{13}C HSQC.*

^{31}P{^{1}H} NMR (162 MHz, 298 K, dichloromethane-*d2*): δ = 23.2 ppm.

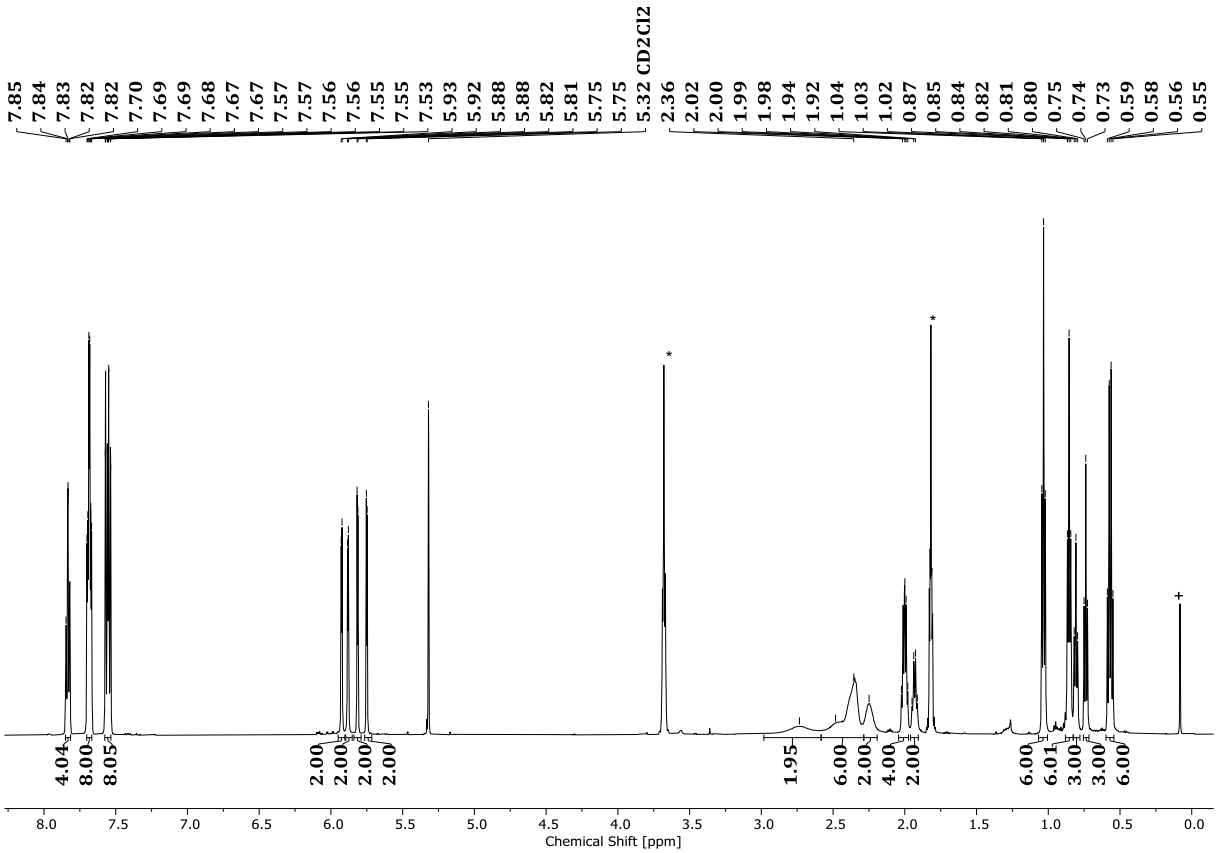


Figure S 1-37. ^{1}H NMR (600 MHz, 298 K, dichloromethane-*d2*) spectrum of **$PPh_4[Cx^{Et}Ge_2ClS]$.** * = Tetrahydrofuran from recrystallization, + = silicon grease.

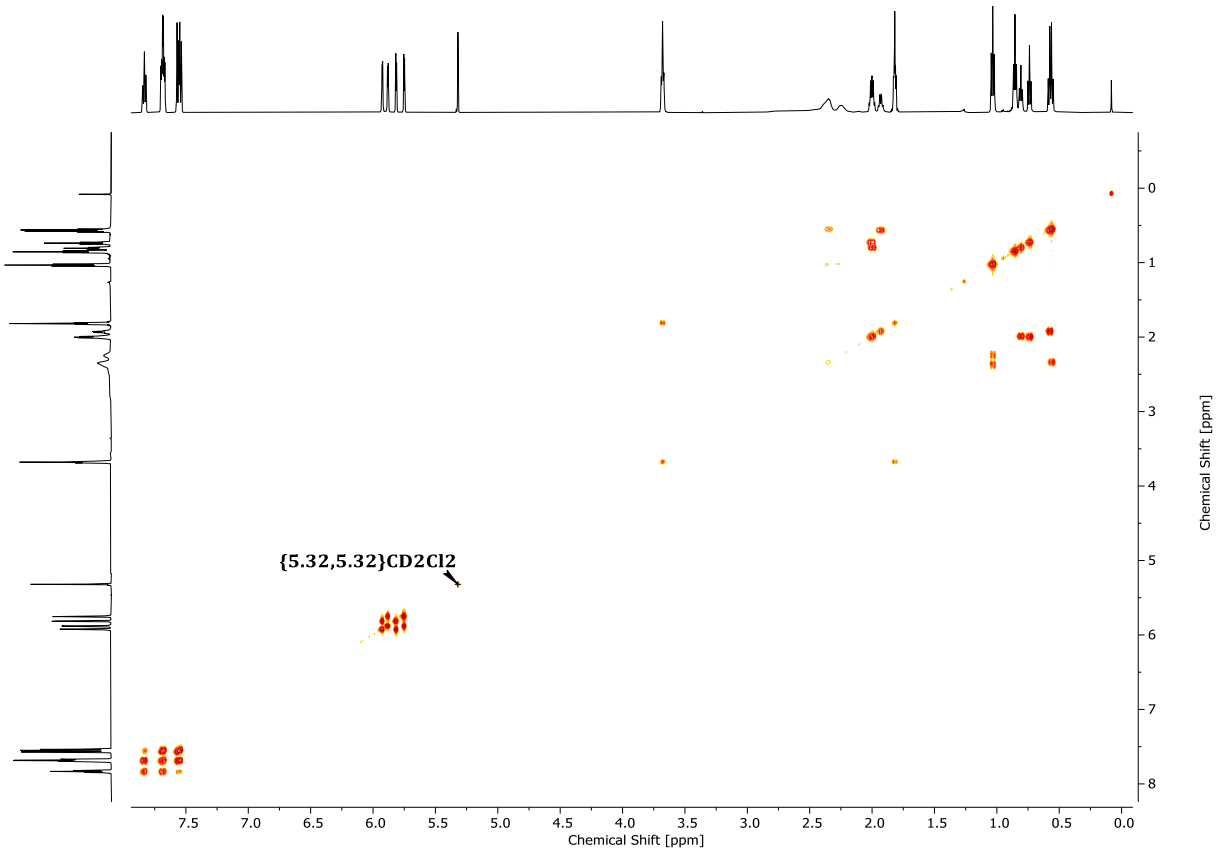


Figure S 1-38. ^{1}H-^{1}H COSY NMR (600 MHz, 298 K, dichloromethane-*d2*) spectrum of **$PPh_4[Cx^{E\text{-}t}Ge_2ClS]$.**

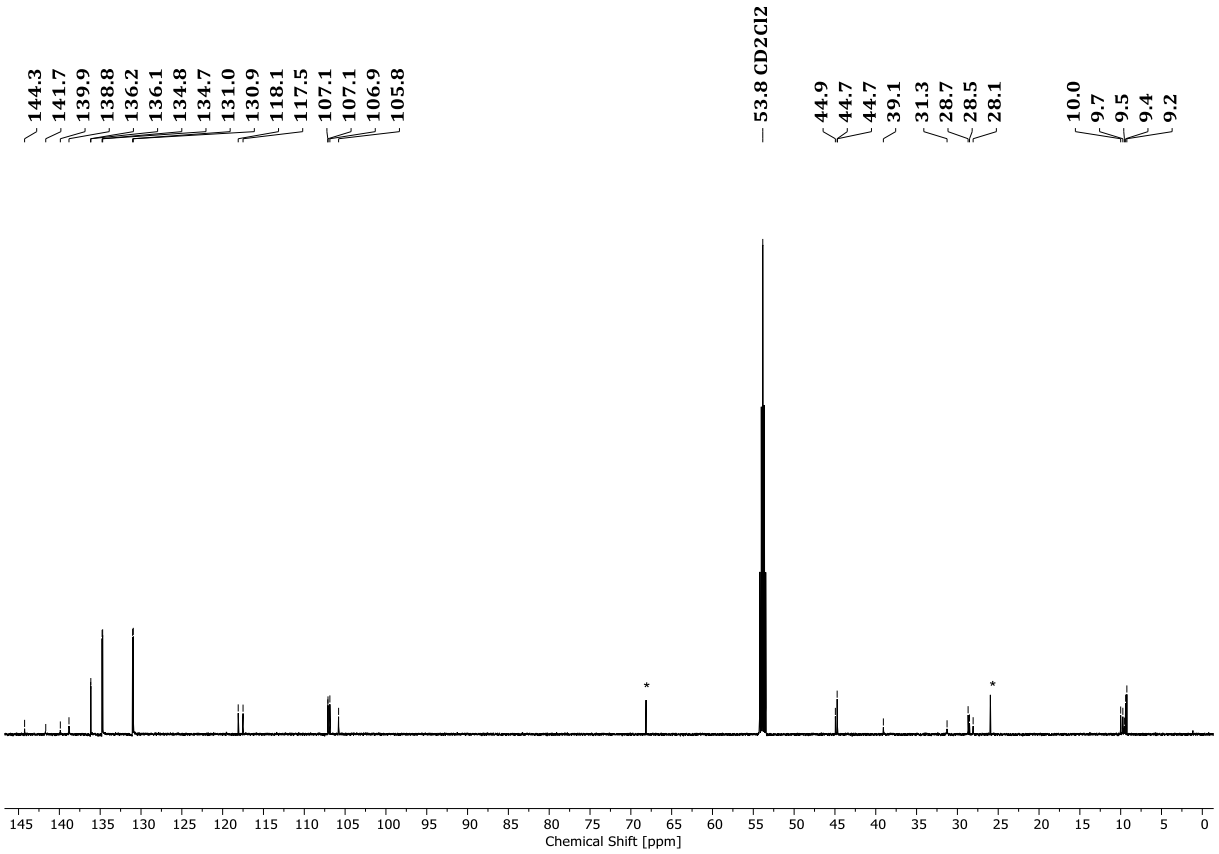


Figure S 1-39. $^{13}C\{^{1}H\}$ NMR (151 MHz, 298 K, dichloromethane-*d2*) spectrum of **$PPh_4[Cx^{Et}Ge_2ClS]$.** * = Tetrahydrofuran from recrystallization.

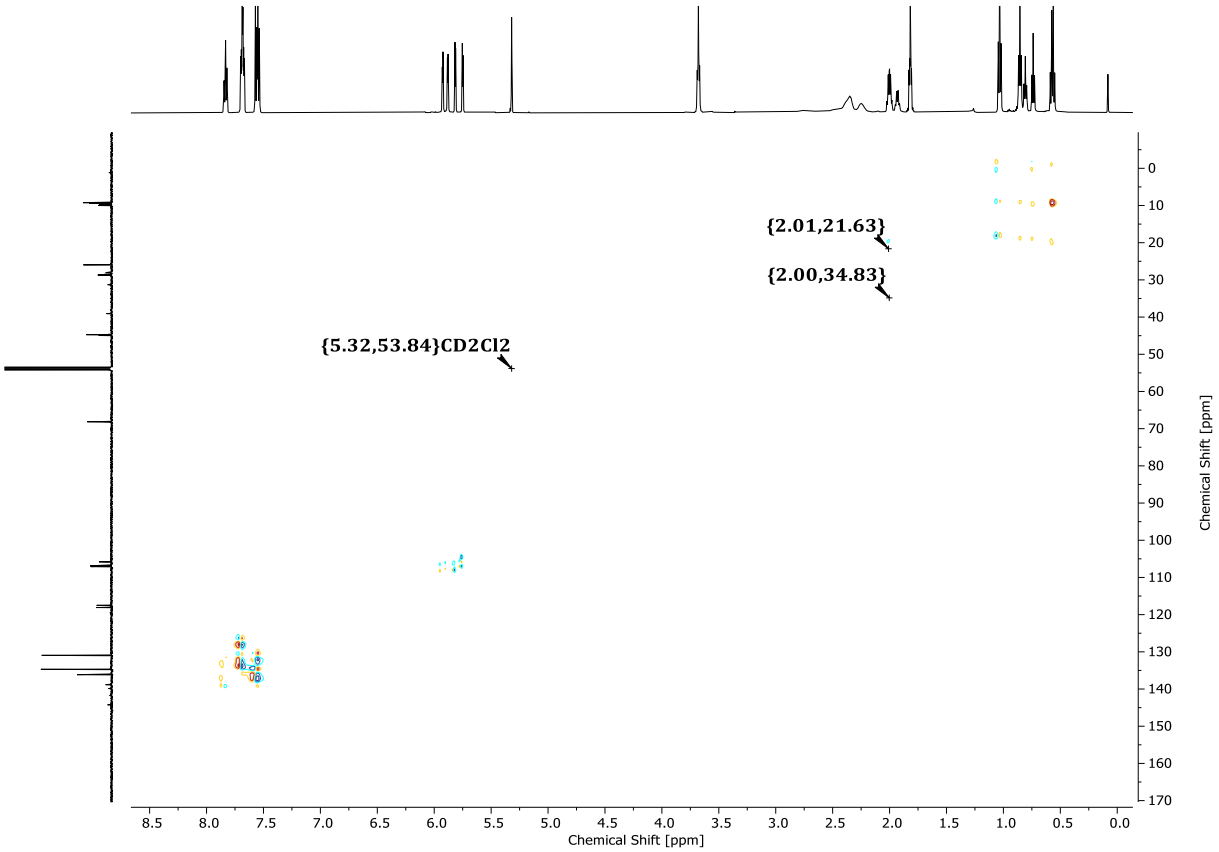


Figure S 1-40. ^{1}H-^{13}C HSQC NMR (600 MHz, 298 K, dichloromethane-*d2*) spectrum of **$PPh_4[Cx^{E\text{-}t}Ge_2ClS]$.**

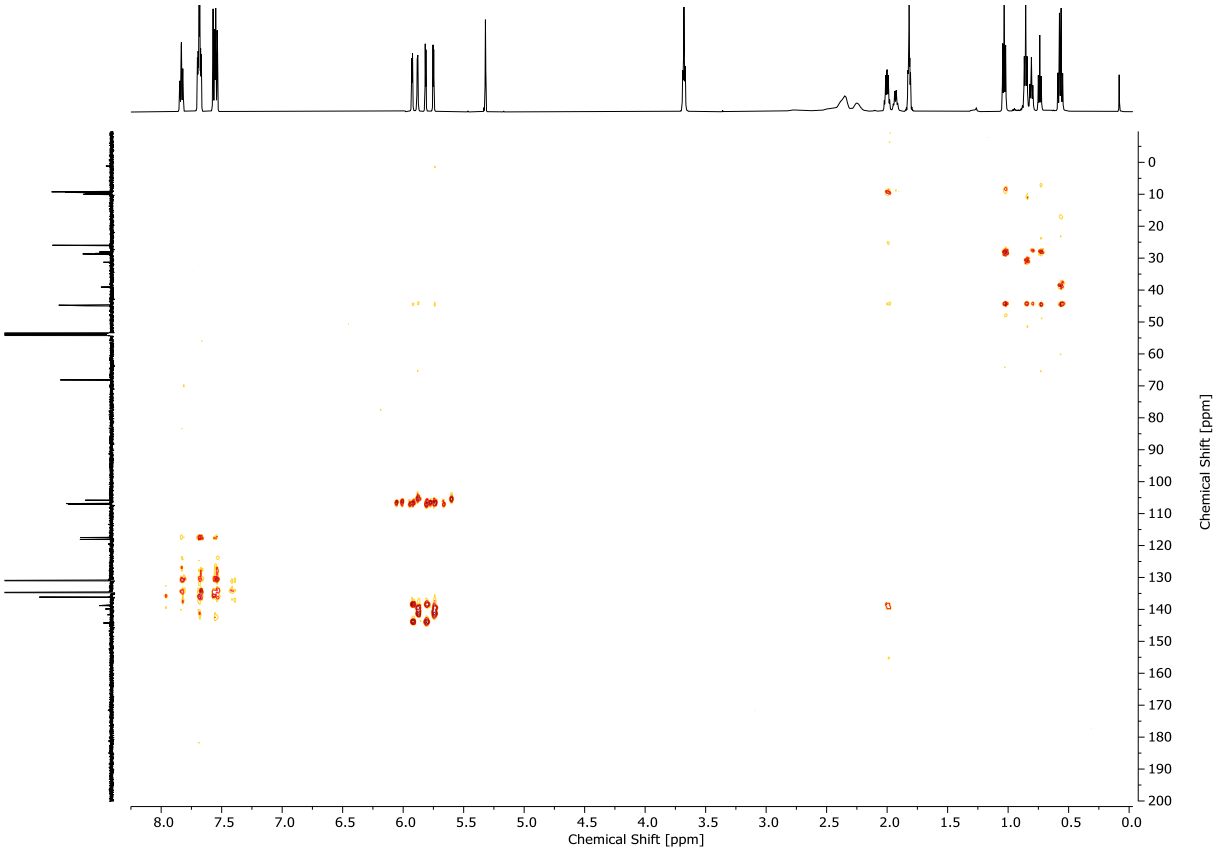


Figure S 1-41. ^{1}H-^{13}C HMBC NMR (600 MHz, 298 K, dichloromethane-*d2*) spectrum of **PPh$_4$[Cx^{E}-^{t}Ge$_2$ClS]**.

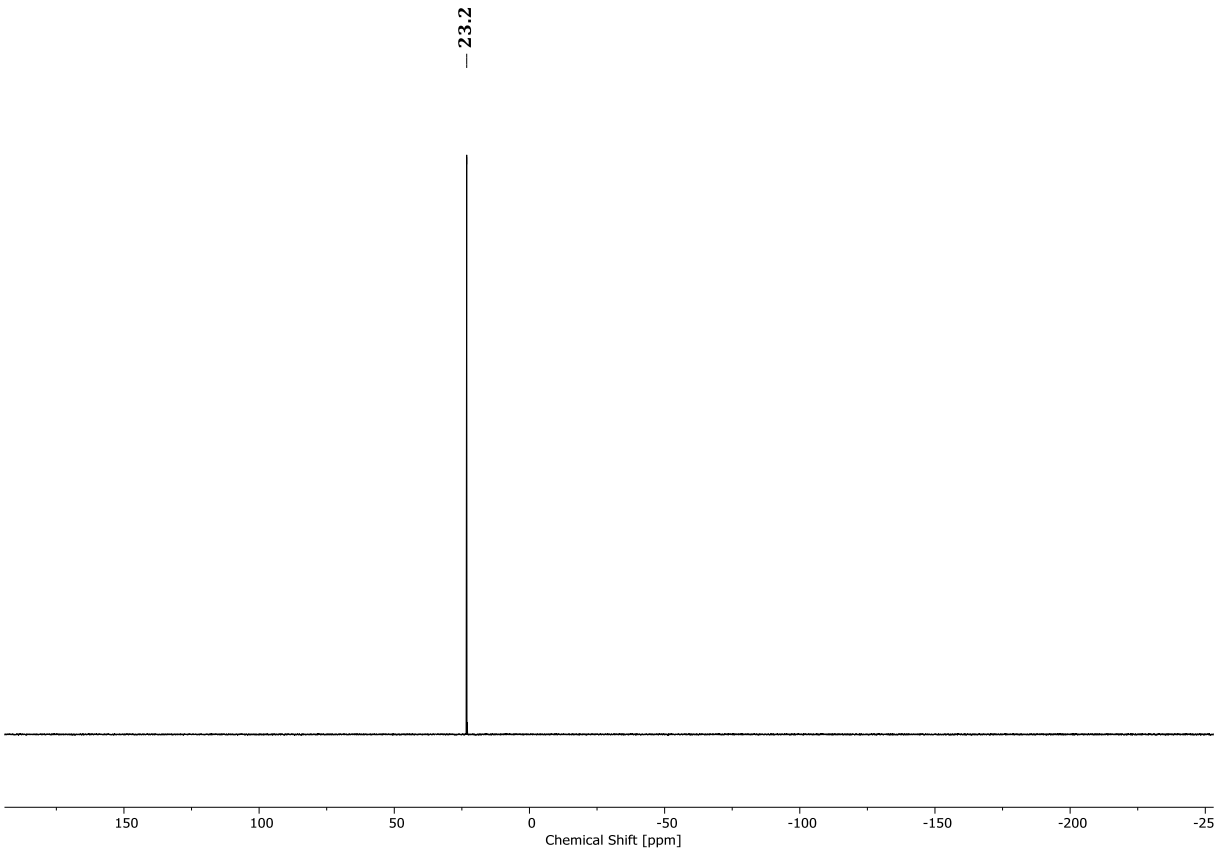
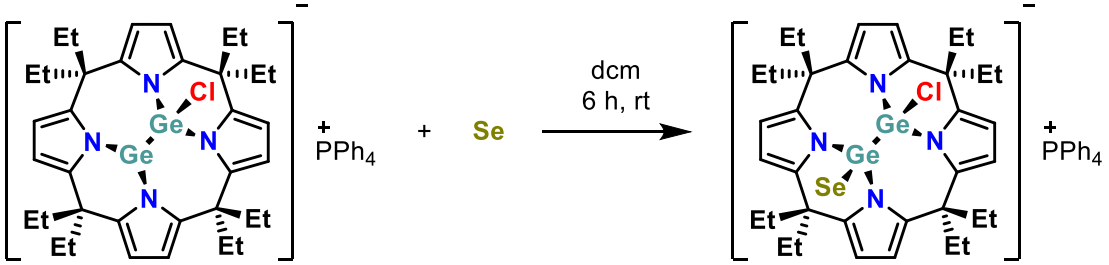


Figure S 1-42. ^{31}P{^{1}H} NMR (121 MHz, 298 K, dichloromethane-*d2*) spectrum of **PPh$_4$[CxGe$_2$ClS]**.

1.2.11 Synthesis of Tetraphenylphosphonium *meso*-Octaethylcalix[4]pyrrolato-2-chlorodigermane-1-selenolate $PPh_4[Cx^{Et}Ge_2ClSe]$



Reactants			*Products*	
Formula	$C_{60}H_{68}ClGe_2N_4P$	**Se**	Formula	$C_{60}H_{68}ClGe_2N_4PSe$
MW	1056,92	78,97	MW	1135,89
Limiting?	***Yes***	No	Equivalents	
Equivalents	***1,00***	***1,00***	%Completion	
Sample Mass	***150,00mg***	11,21mg	Expected Mass	161,21mg
%Weight			Expected Moles	141,92µmol
Molarity			Measured Mass	***145,00mg***
Density			Purity	
Volume			Product Mass	145,00mg
Reactant Moles	141,92µmol	141,92µmol	Product Moles	127,65µmol
Reactant Mass	150,00mg	11,21mg	%Yield	89,95%

$PPh_4[Cx^{Et}Ge_2Cl]$ and selenium powder were dissolved in dichloromethane (2.50 mL). The suspension mixture was stirred at room temperature for 6 h until all of the selenium was consumed. The solvent of the solution was removed under reduced pressure and the red residue was dried *in vacuo* overnight to give the title compound as an off-white solid.

SCXRD: Single crystals suitable for SCXRD analysis were obtained by pentane vapour diffusion into a concentrated tetrahydrofuran solution at −35 °C.

Elemental Analysis for **$PPh_4[Cx^{Et}Ge_2ClSe]$**: Calculated for $C_{60}H_{68}Ge_2N_4ClSeP$ x ½ dichloromethane (fits NMR): C: 61.67, N: 4.75; H: 5.90. Found: C: 61.49; N: 4.81, H: 5.76.

ESI(–)-MS: Calculated for **$[Cx^{Et}GeClGeSe]^-$**: 797.1170. Found: 797.0954 (dichloromethane).

^{1}H NMR (600 MHz, 298 K, dichloromethane-*d2*): δ = 7.84 - 7.82 (m, 4H, *p*-PPh_4), 7.70-7.67 (m, 8H, *m*-PPh_4), 7.57 - 7.54 (m, 8H, *o*-PPh_4), 5.92 (d, 2H, ^3J = 6 Hz, β-C*H*), 5.89 (d, 2H, ^3J = 6 Hz, β-C*H*), 5.80 (d, 2H, ^3J = 6 Hz, β-C*H*), 5.75 (d, 2H, 3J = 6 Hz, pyrrole-CH), 2.75 (bs, 2 H, CH_2-ethyl), 2.38 (m, 6 H, CH_2-ethyl), 2.24 (bs, 2H, CH_2-ethyl), 2.02 – 1.99 (m, 4H, CH_2-ethyl), 1.94 (q, ^3J = 6 Hz, CH_2-ethyl), 1.03 (t, ^3J = 6 Hz, 6H, CH_3-methyl), 0.85 (t, ^3J = 6 Hz, 6H, CH_3-methyl), 0.77 (t, ^3J = 6 Hz,3H, CH_3-methyl), 0.71 (t, ^3J = 6 Hz, 3H, CH_3-methyl), 0.59 – 0.54 (m, 6H, CH_3-methyl) ppm.

^{13}C{^{1}H} NMR (151 MHz, 298 K, dichloromethane-*d2*): δ = 144.3 (C_q, α-*C*), 141.7 (C_q, α-*C*), 139.7 (C_q, α-*C*), 138.8 (C_q, α-*C*), 136.2 (d, $^3J(^{31}P,^{13}C)$ = 15.1 Hz, *p*-PPh_4), 134.8 (d, $^3J(^{31}P,^{13}C)$ = 15.1 Hz, *m*-PPh_4), 131.0 (d, $^3J(^{31}P,^{13}C)$ = 15.1 Hz, *o*-PPh_4), 117.8 (d, $^3J(^{31}P,^{13}C)$ = 90.6 Hz, C_q,PPh_4), 107.1

(*C*H, β-C), 107.1 (*C*H, β-C), 107.0 (*C*H, β-C), 106.0 (*C*H, β-C), 44.9 (C_q, *meso*-C), 44.8 (C_q, 2C, *meso*-C), 44.8 (C_q, *meso*-C)*, 39.0 (*C*H_2-ethyl), 38.0 (*C*H_2-ethyl), 31.4 (*C*H_2-ethyl), 28.6 (*C*H_2-ethyl), 28.6 (*C*H_2-ethyl), 28.3 (*C*H_2-ethyl), 10.0 (*C*H_3-methyl), 9.7 (*C*H_3-methyl), 9.7 (*C*H_3-methyl), 9.4 (*C*H_3-methyl), 9.4 (*C*H_3-methyl), 9.2 (*C*H_3-methyl) ppm.

*Shoulder of peak at δ = 44.8 ppm.

$^{31}P\{^1H\}$ NMR (162 MHz, 298 K, dichloromethane-*d2*): δ = 23.2 ppm.

*Note: No signal was observed for **$PPh_4[Cx^{Et}Ge_2ClSe]$** in ^{77}Se NMR or ^1H-^{77}Se HMBC NMR experiments.*

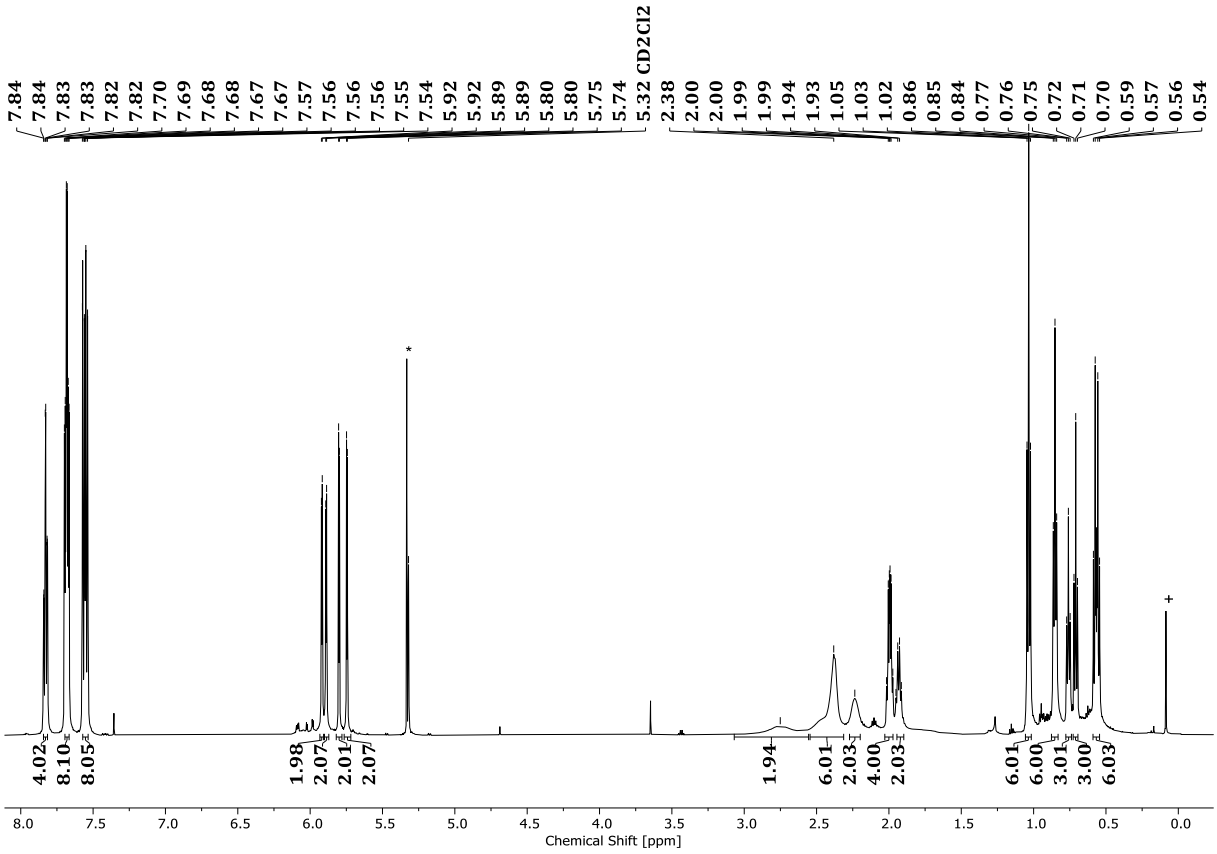


Figure S 1-43. ^1H NMR (600 MHz, 298 K, dichloromethane-*d2*) spectrum of **$PPh_4[Cx^{Et}Ge_2ClSe]$.** * = Dichloromethane, + = silicon grease.

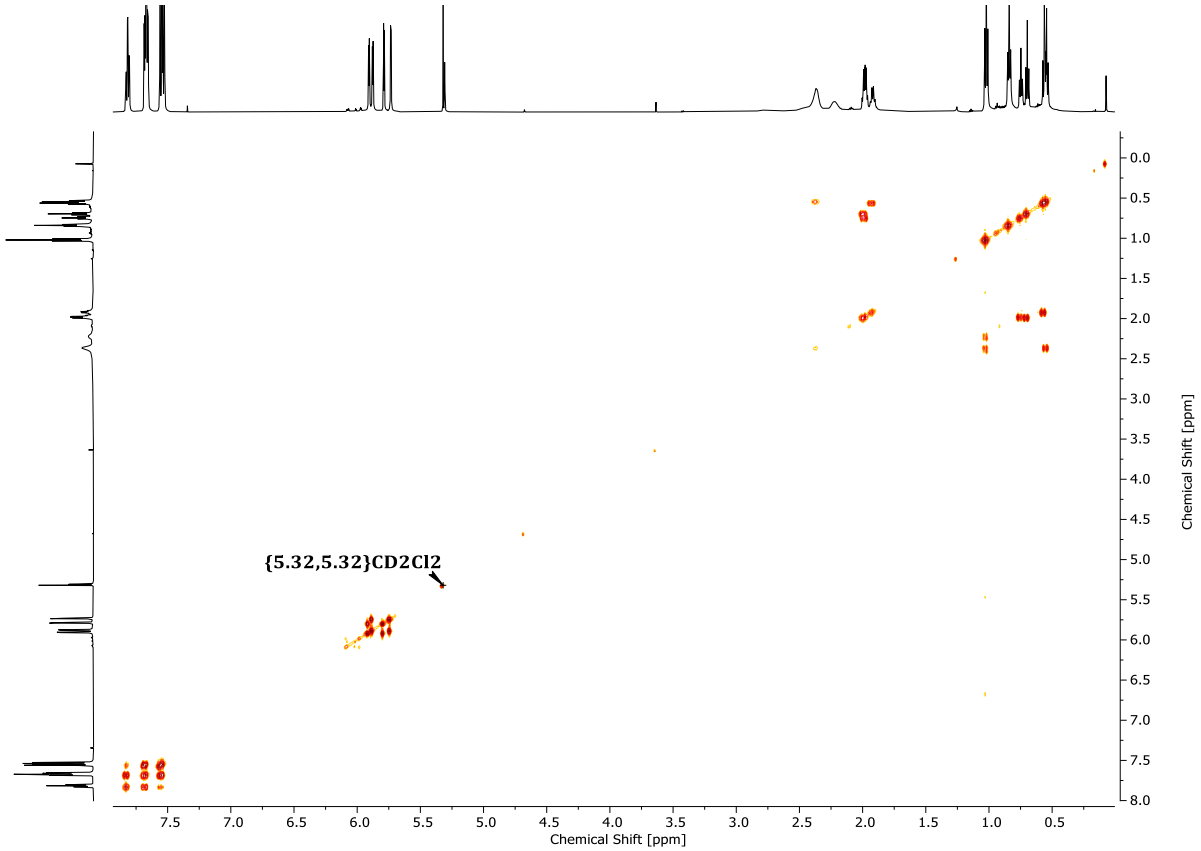


Figure S 1-44. ^{1}H-^{1}H COSY NMR (600 MHz, 298 K, dichloromethane-*d2*) spectrum of **PPh$_4$[Cx^{E}-^{t}Ge$_2$ClSe]**.

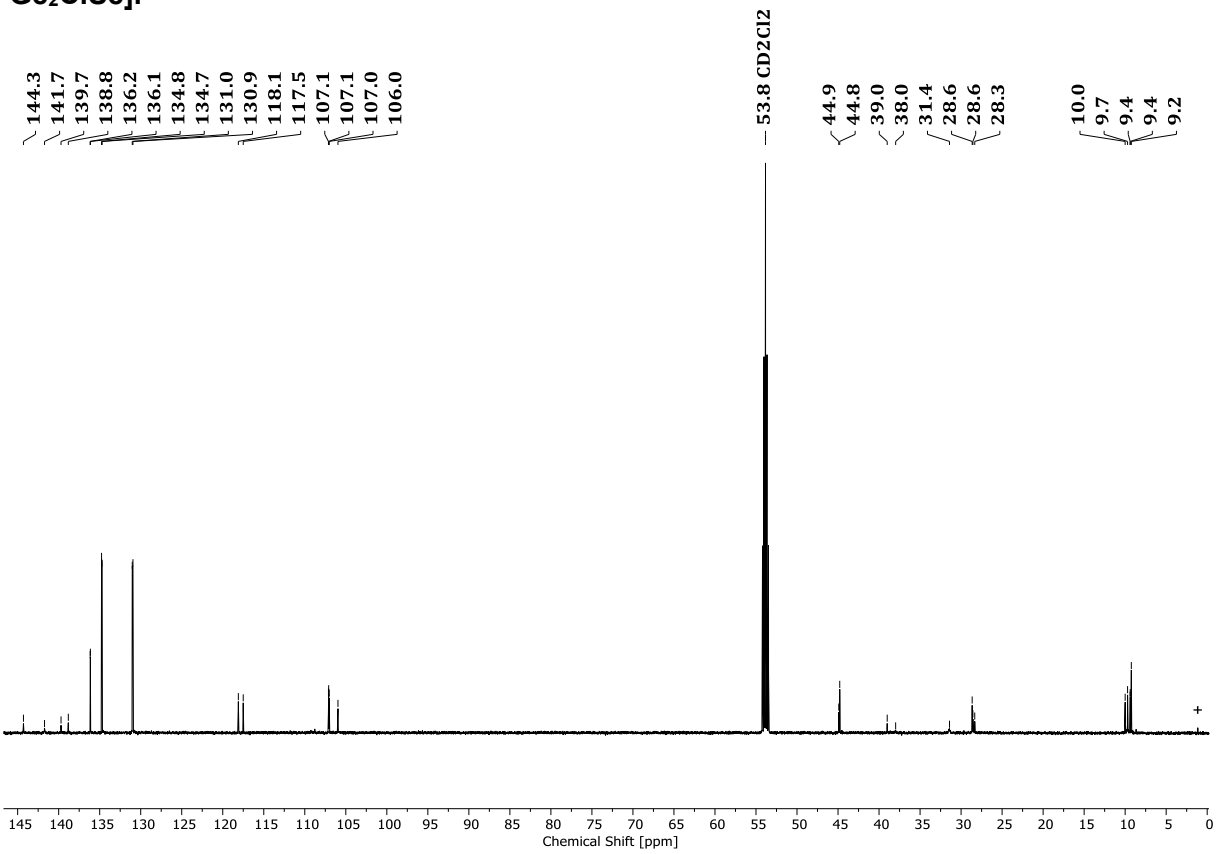


Figure S 1-45. ^{13}C{^{1}H} NMR (151 MHz, 298 K, dichloromethane-*d2*) spectrum of **PPh$_4$[Cx^{E}-^{t}Ge$_2$ClSe]**. + = silicon grease.

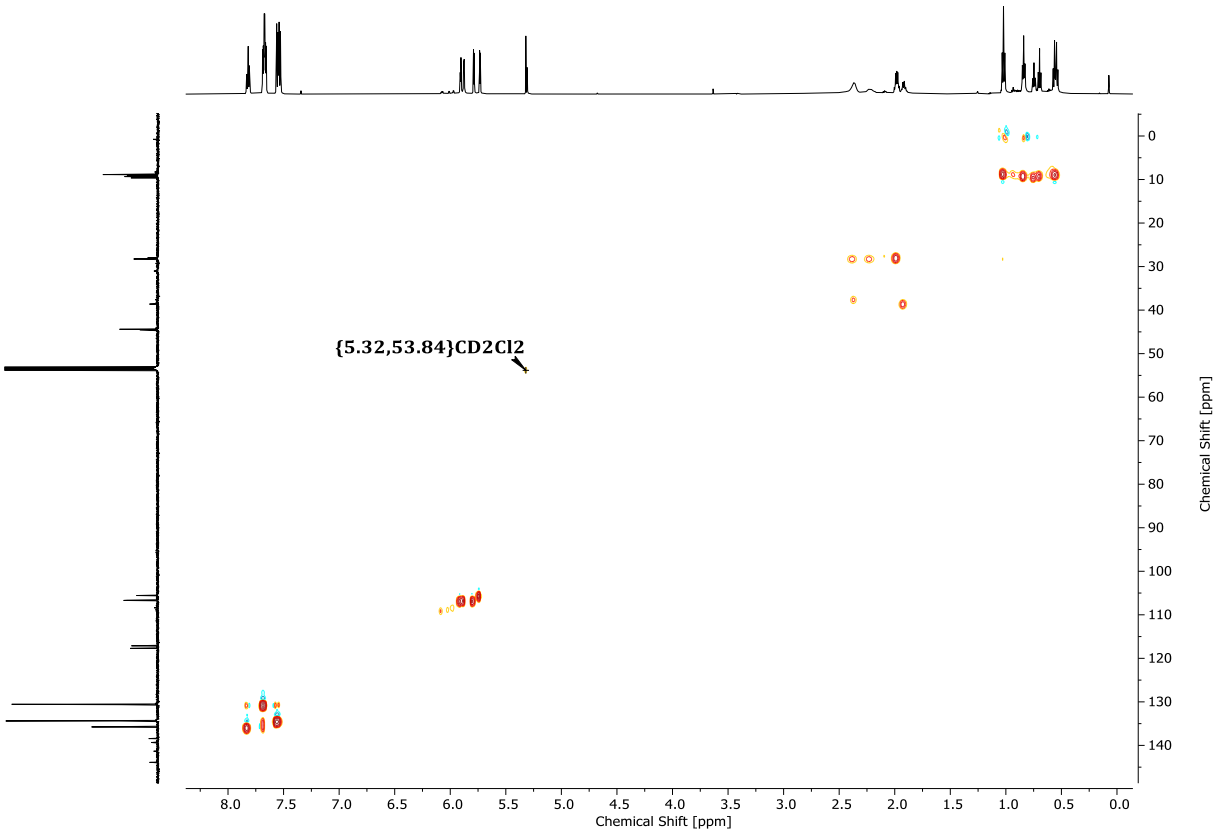


Figure S 1-46. ^{1}H-^{13}C HSQC NMR (600 MHz, 298 K, dichloromethane-*d2*) spectrum of **PPh_4[Cx^{E}-^{t}Ge_2ClSe]**.

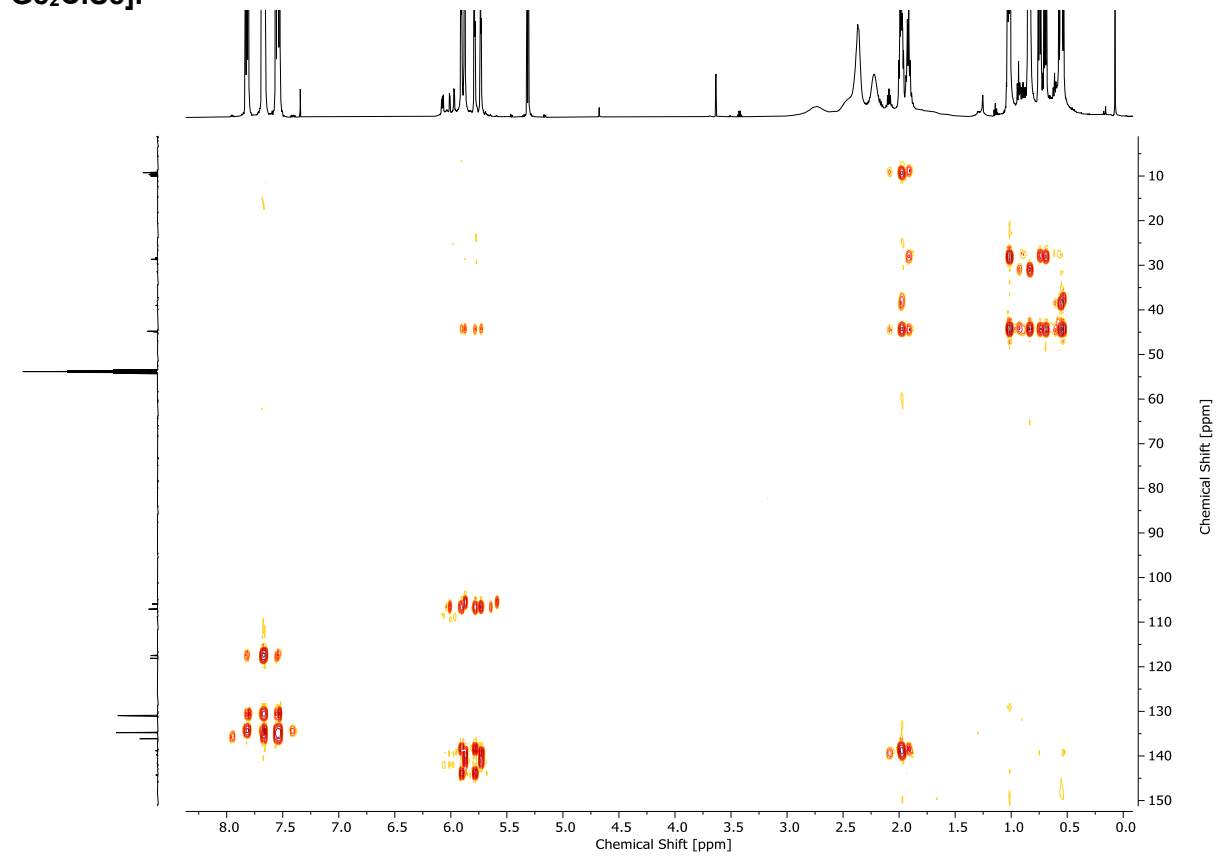


Figure S 1-47. ^{1}H-^{13}C HMBC NMR (600 MHz, 298 K, dichloromethane-*d2*) spectrum of **PPh_4[Cx^{E}-^{t}Ge_2ClSe]**.

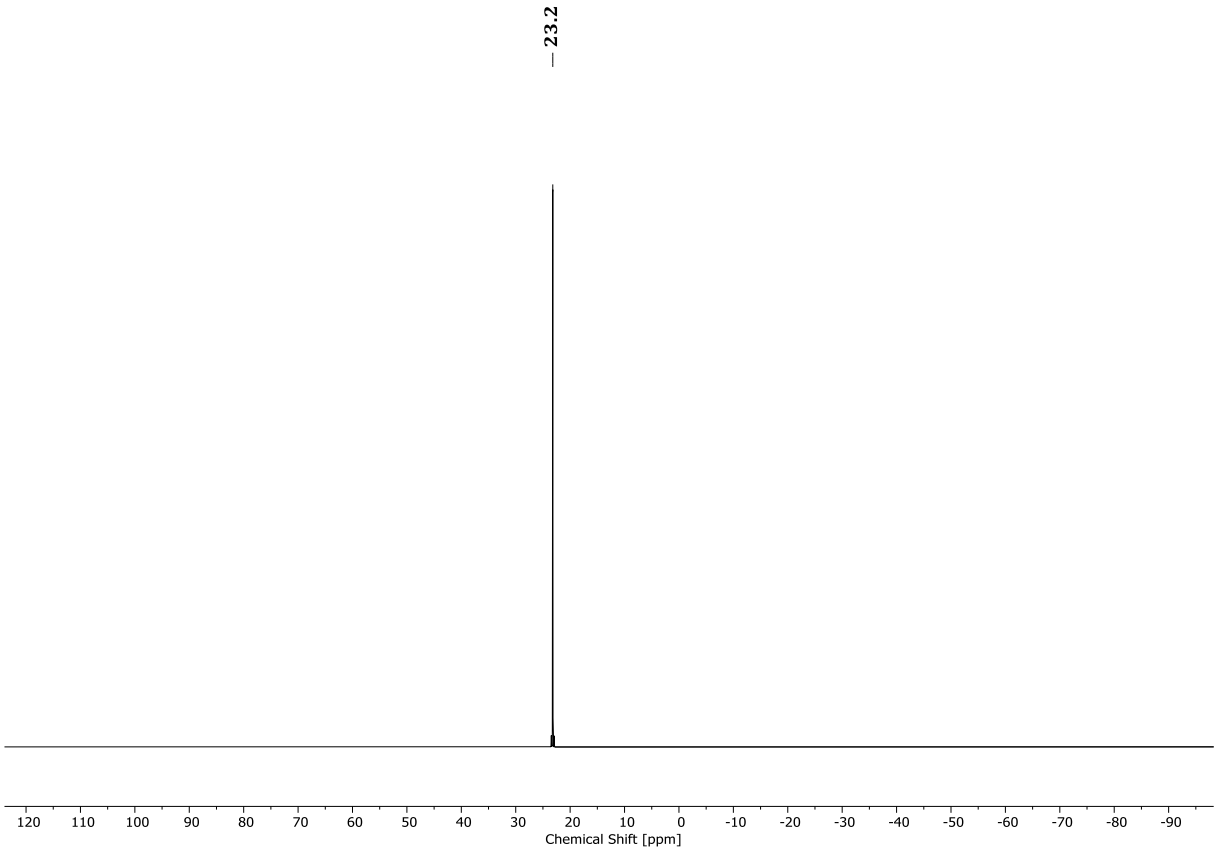
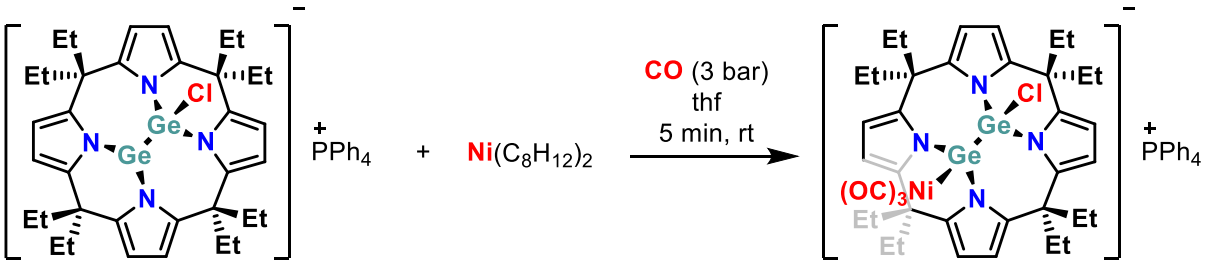


Figure S 1-48. $^{31}P\{^{1}H\}$ NMR (121 MHz, 298 K, dichloromethane-*d2*) spectrum of **$PPh_4[Cx^{E\text{-}t}Ge_2ClSe]$.**

Synthesis of Tetraphenylphosphonium *meso*-Octaethylcalix[4]pyrrolato-2-chlorodigermante-nickel-tricarbonyle $PPh_4[Cx^{Et}Ge_2Cl(Ni(CO)_3)]$



Reactants			*Products*	
Formula	$C_{60}H_{68}ClGe_2N_4P$	$C_{16}H_{24}Ni$	Formula	$C_{63}H_{68}ClGe_2N_4NiO_3P$
MW	1056,92	275,06	MW	1199,64
Limiting?	***Yes***	No	Equivalents	
Equivalents	***1,00***	***1,05***	%Completion	
Sample Mass	***98,60mg***	26,94mg	Expected Mass	111,91 mg
%Weight			Expected Moles	93,29µmol
Molarity			Measured Mass	***39,00mg***
Density			Purity	
Volume			Product Mass	39,00mg
Reactant Moles	93,29µmol	97,95µmol	Product Moles	32,51µmol
Reactant Mass	98,60mg	26,94mg	%Yield	34,85%

Nickel(bis-cyclooctadiene) was dissolved in tetrahydrofuran (0.70 mL) in a NMR pressure tube. The pressure tube was pressurized with carbon monoxide (3 bar) leading to the discoloration of the light-yellow solution. The pressure was released and **$PPh_4[Cx^{Et}Ge_2Cl]$** was added to the solution and the reaction mixture was stirred for 5 minutes. Pentane (16.0 mL) was added to the solution and it was stirred for 20 minutes while an off-white precipitate formed. The precipitate was isolated and dried *in vacuo* to give the title compound as a light pink solid.

Note: The poor yield is explained by incomplete precipitation of the product. To avoid this, alternatively the solvent of the tetrahydrofuran solution can be evaporated and the product can be isolated as the solid residue.

SCXRD: Crystals suitable for SCXRD were grown from a concentrated tetrahydrofuran solution at –35 °C.

Elemental Analysis for **$PPh_4[Cx^{Et}Ge_2Cl(Ni(CO)_3)]$**: Calculated for **$PPh_4[Cx^{Et}Ge_2Cl(Ni(CO)_3)]$:** C: 63.08, H: 5.71, N: 4.67. Found: C: 62.52, H: 5.37, N: 4.77.

^{1}H NMR (600 MHz, 298 K, tetrahydrofuran-d_8): δ = 7.50 – 7.43 (m, 20H, PPh_4), 5.78 (d, *J* = 3.31 Hz, 2H, β-C*H*), 5.73 (d, *J* = 3.40 Hz, 2H, β-C*H*), 5.54 (d, *J* = 3.34 Hz, 2H, β-C*H*), 5.51 (d, *J* = 3.38 Hz, 2H, β-C*H*), 2.81 (brs, 2H, ethyl-CH_2), 2.43 (brs, 2H, ethyl-CH_2), 2.28 (brs, 2H, ethyl-CH_2), 2.20 (brs, 2H, ethyl-CH_2), 2.13 (m, 2H, , ethyl-CH_2), 1.91 (q, *J* = 7.46 Hz, 2H, ethyl-CH_2), 1.85 (q, *J* = 7.03 Hz, 2H, , ethyl-CH_2), 1.79 (q, *J* = 7.14 Hz, 2H, ethyl-CH_2), 1.03 (t, *J* = 7.19 Hz, 6H, methyl-CH_3), 0.90 (t, *J* = 6.80 Hz, 6H, methyl-CH_3), 0.58 (t, *J* = 7.29 Hz, 3H, methyl-CH_3), 0.51 (t, *J* = 7.38 Hz, 3H, methyl-CH_3), 0.34 (s, 3H, methyl-CH_3), 0.06 (s, 3H, methyl-CH_3) ppm.

^{13}C{^{1}H} NMR (151 MHz, 298 K, tetrahydrofuran-d_8): δ = 198.7 (C_q, *C*O), 145.2 (C_q, α-C), 142.9 (C_q, α-C), 139.5 (C_q, α-C), 138.8 (C_q, α-C), 136.6 (d, $^4J(^{31}P\text{-}^{13}C)$ = 3.2 Hz, *p*-C(PPh_4), 135.4 (d, $^3J(^{31}P\text{-}^{13}C)$ = 10.6 Hz, *m*-C(PPh_4)), 131.4 (d, $^2J(^{31}P\text{-}^{13}C)$ = 12.1 Hz, *o*-C(PPh_4)), 118.8 (117.4 (d, $^2J(^{31}P\text{-}^{13}C)$ =60.4 Hz, C_q(PPh_4)), 107.0 (*C*H, β-*C*), 106.8 (*C*H, β-*C*), 106.7 (*C*H, β-*C*), 106.1 (*C*H, β-*C*), 45.7 (C_q, 2C, *meso*-C), 45.6 (C_q, *meso*-C), 45.0 (C_q, *meso*-C), 39.9 (*C*H_2-ethyl), 39.4 (*C*H_2-ethyl)*, 37.5 (*C*H_2-ethyl)*, 31.3 (*C*H_2-ethyl), 30.7 (*C*H_2-ethyl), 29.5 (*C*H_2-ethyl), 28.9 (*C*H_2-ethyl), 28.6 (*C*H_2-ethyl), 28.5(*C*H_2-ethyl)*, 10.6 (*C*H_3-methyl), 10.1 (*C*H_3-methyl), 9.9 (*C*H_3-methyl), 9.8 (*C*H_3-methyl), 9.7 (*C*H_3-methyl), 9.4 (*C*H_3-methyl) ppm.

^{31}P{^{1}H} NMR (121 MHz, 298 K, tetrahydrofuran-*d8*): δ = 20.9 ppm.

ESI(–)-MS: [m/z]: Calculated: 859.1206. Measured: 859.1216 (tetrahydrofuran).

IR-ATR: v = 2051 (s, A_1-CO vibration mode) cm^{-1}.

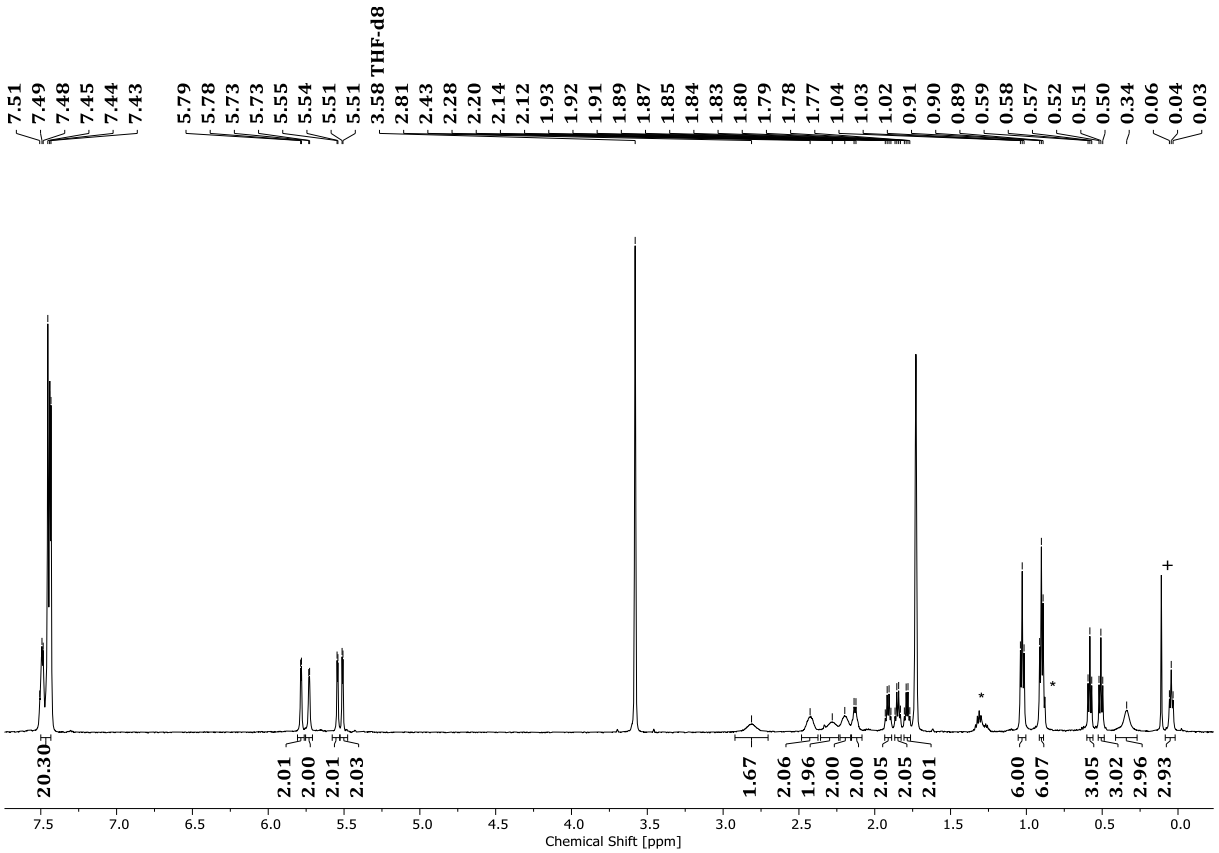


Figure S 1-49. ^{1}H NMR (600 MHz, 298 K, tetrahydrofuran-*d8*) spectrum of **PPh$_4$[Cx^{E}-^{t}Ge$_2$Cl(Ni(CO)$_3$)]**. * = Pentane, + = silicon grease.

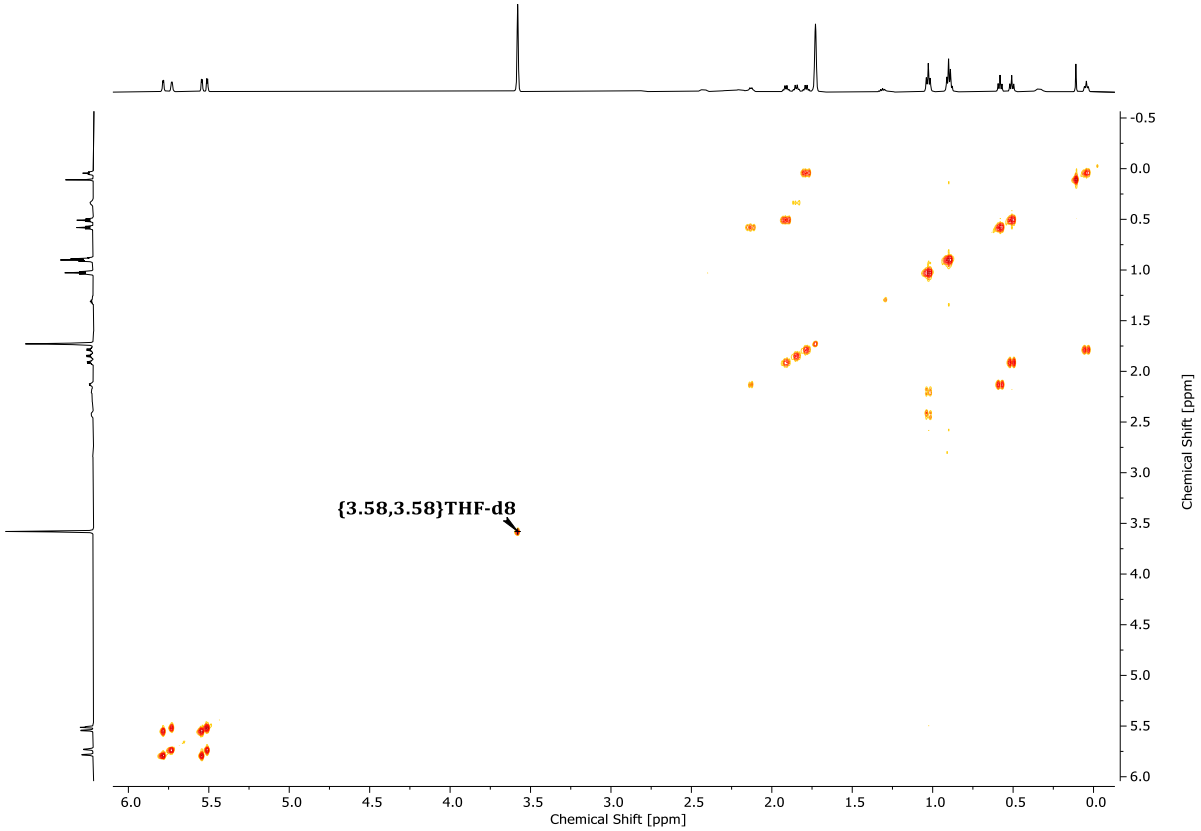


Figure S 1-50. ^{1}H-^{1}H COSY NMR (600 MHz, 298 K, tetrahydrofuran-*d8*) spectrum of **PPh$_4$[Cx^{E}-^{t}Ge$_2$Cl(Ni(CO)$_3$)]**.

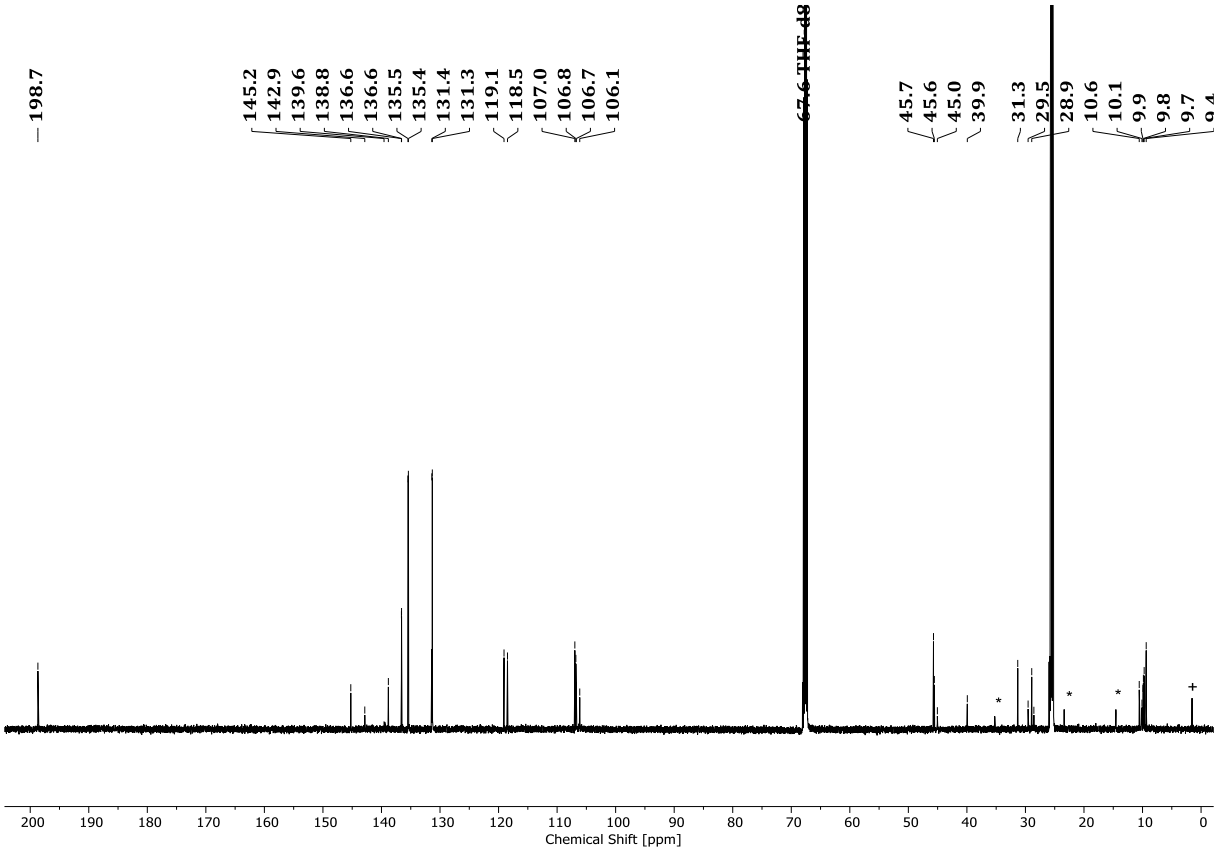


Figure S 1-51. $^{13}C\{^{1}H\}$ NMR (151 MHz, 298 K, tetrahydrofuran-*d8*) spectrum of **$PPh_4[Cx^{E}$-$^{t}Ge_2Cl(Ni(CO)_3)]$.** * = Pentane, + = silicon grease.

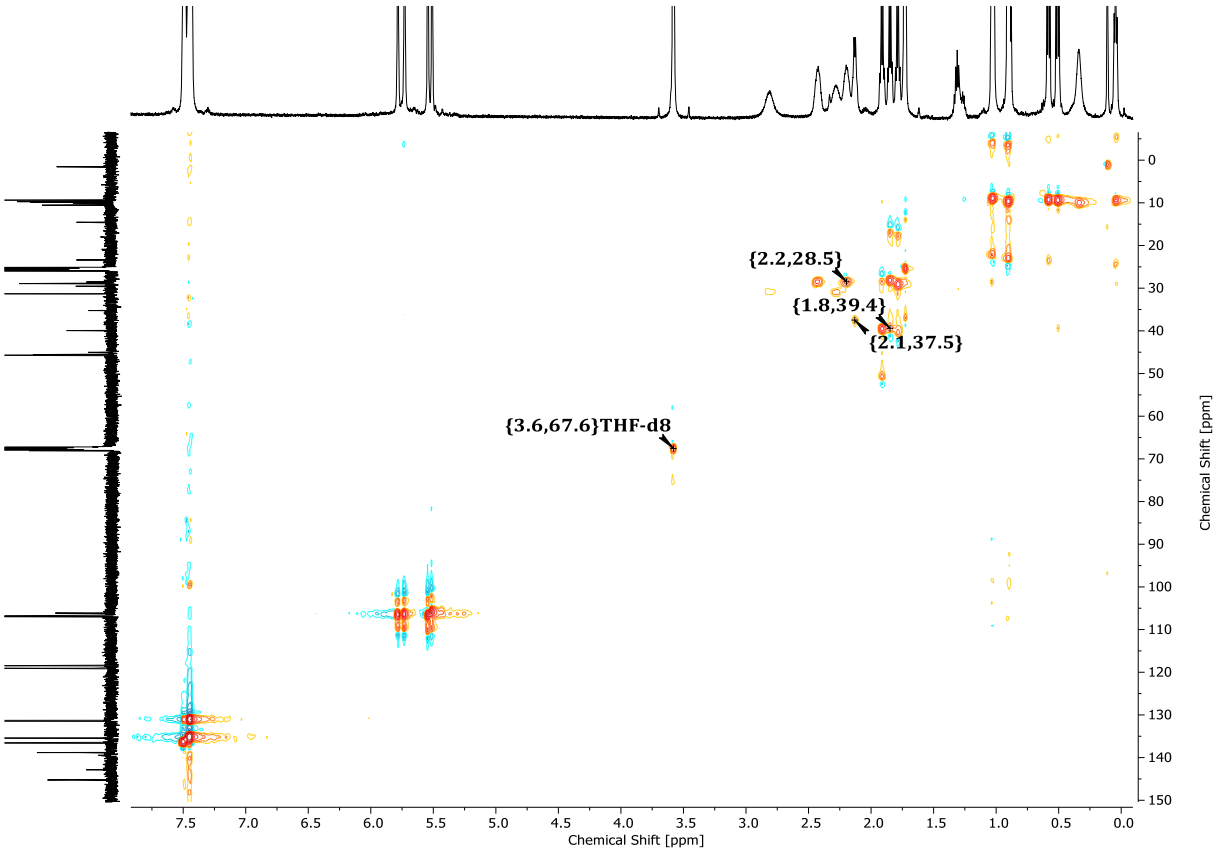


Figure S 1-52. ^{1}H-^{13}C HSQC NMR (600 MHz, 298 K, tetrahydrofuran-*d8*) spectrum of **$PPh_4[Cx^{E}$-$^{t}Ge_2Cl(Ni(CO)_3)]$.**

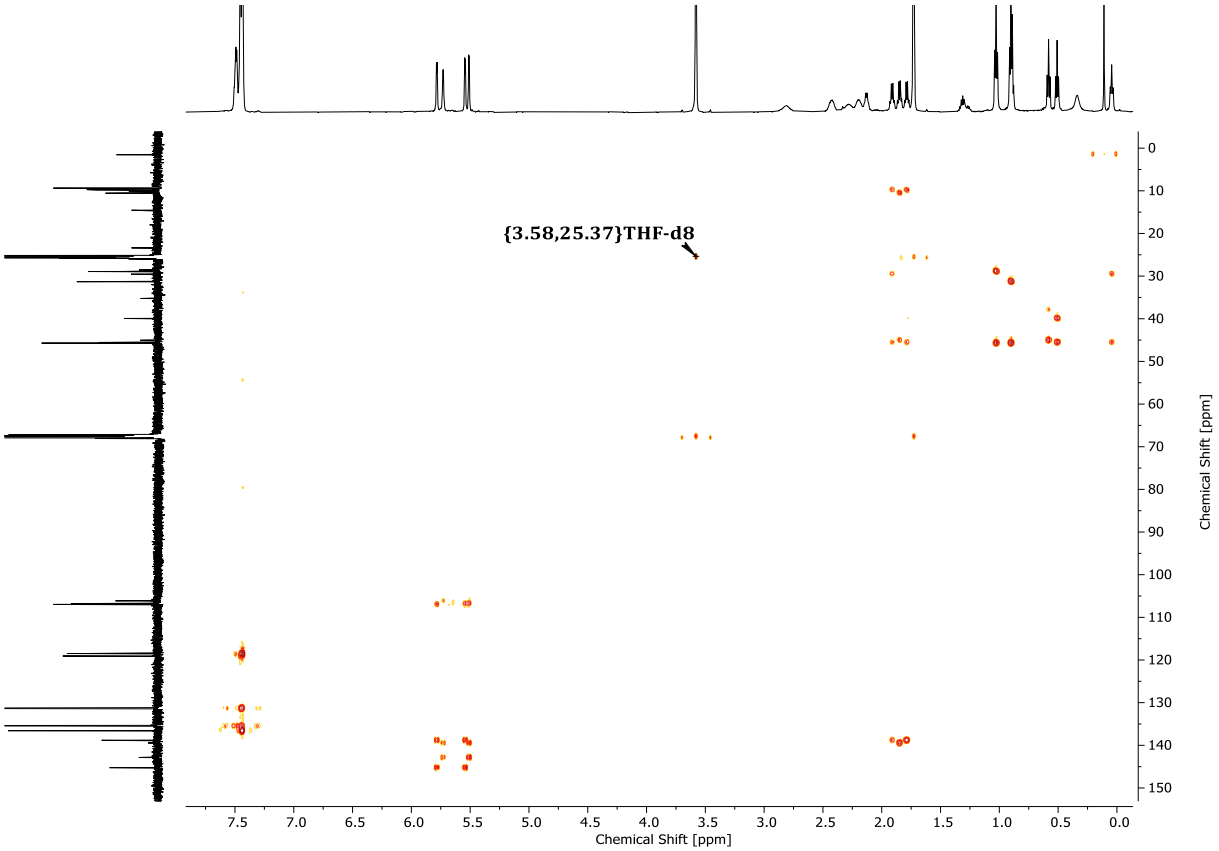


Figure S 1-53. ^{1}H-^{13}C HMBC NMR (600 MHz, 298 K, tetrahydrofuran-*d8*) spectrum of **PPh$_4$[Cx^{E}-^{t}Ge$_2$Cl(Ni(CO)$_3$)]**.

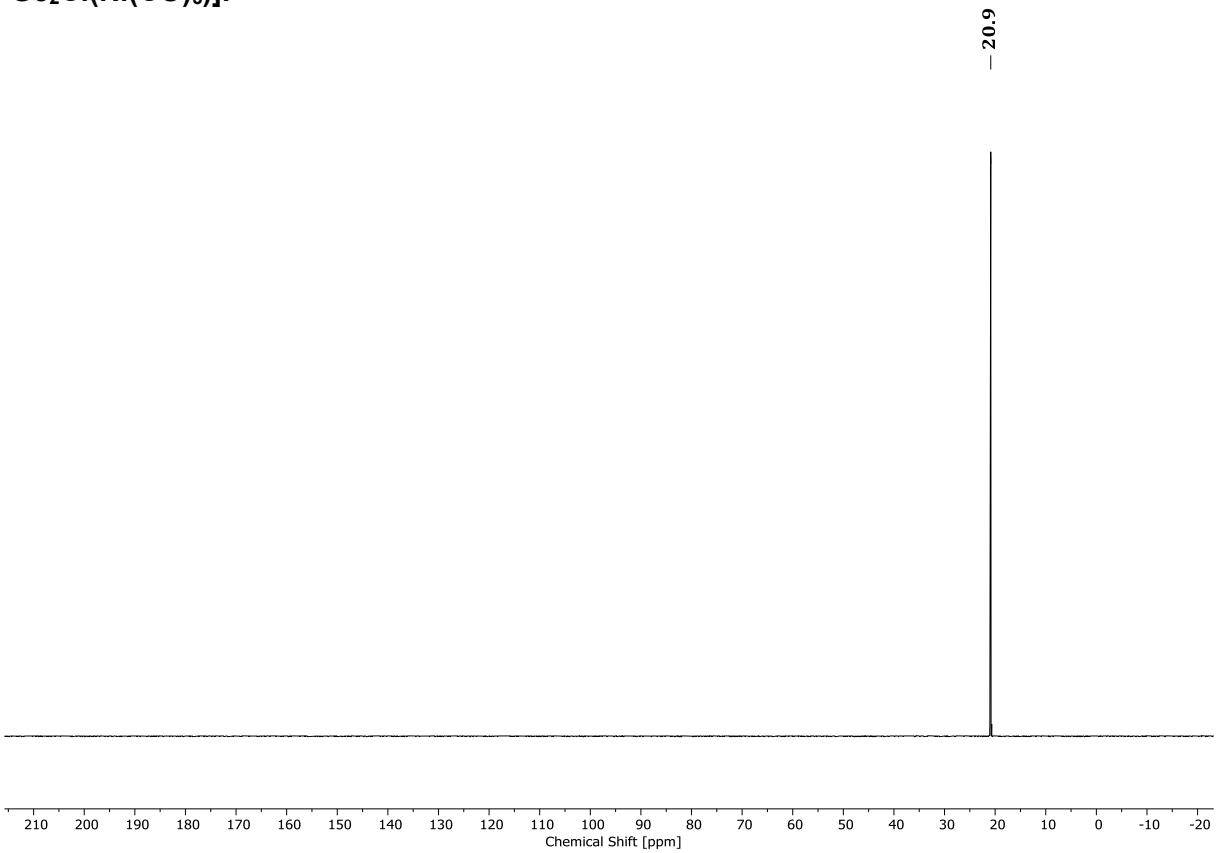


Figure S 1-54. ^{31}P{^{1}H} NMR (121 MHz, 298 K, tetrahydrofuran-*d8*) spectrum of **PPh$_4$[Cx^{E}-^{t}Ge$_2$Cl(Ni(CO)$_3$)]**.

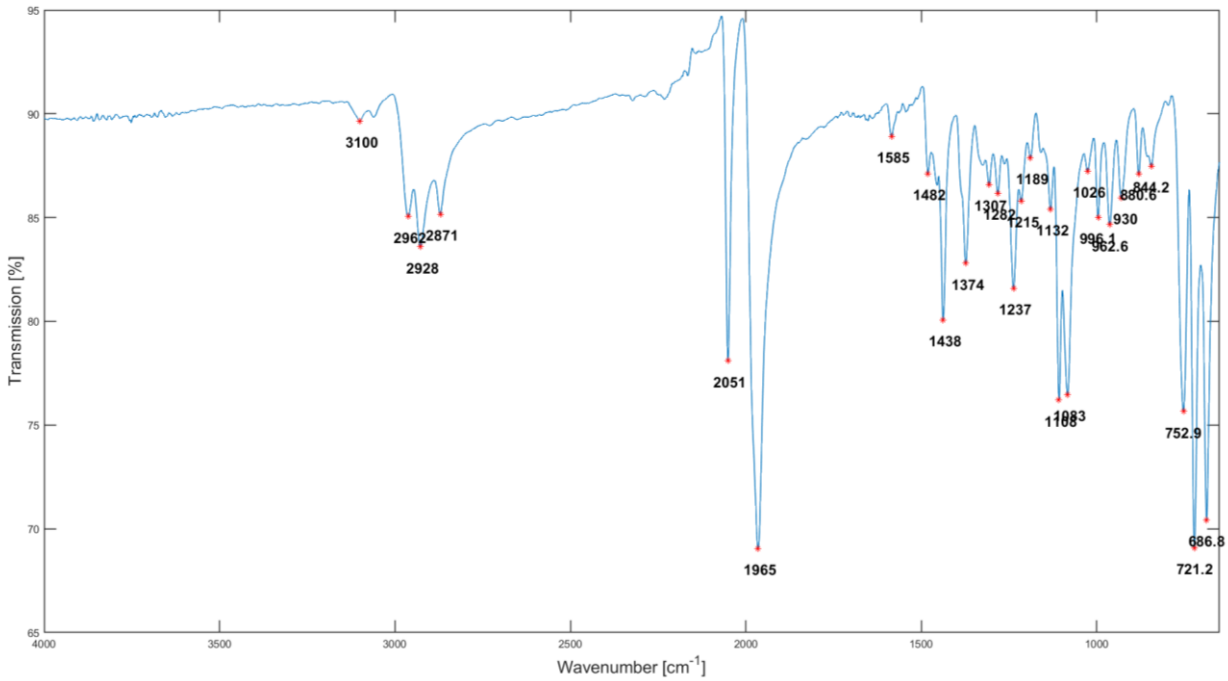
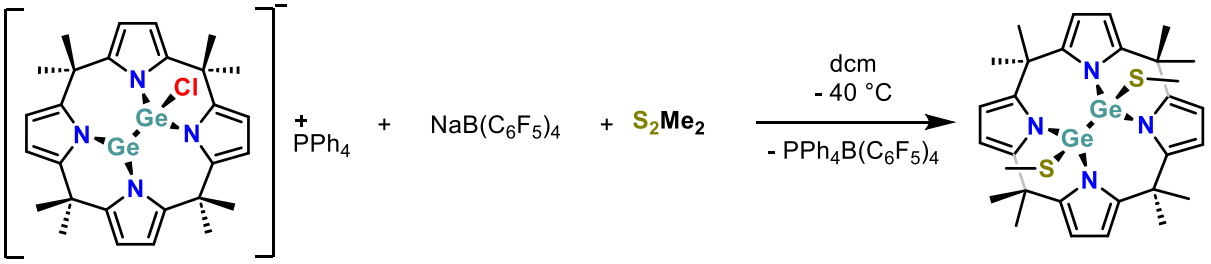


Figure S 1-55. IR-ATR spectra of **$PPh_4[Cx^{Et}Ge_2Cl(Ni(CO)_3)]$.**

1.2.12 Synthesis of *meso*-Octamethylcalix[4]pyrrole-1,2-bis(methylthiolato)-digermane $[Cx^{Me}Ge_2(SMe)_2]$



Reactants				*Products*	
Formula	$C_{52}H_{52}ClGe_2N_4P$	$C_{24}BF_{20}Na$	$C_2H_6S_2$	Formula	$C_{30}H_{38}Ge_2N_4S_2$
MW	944.70	702.03	94.19	MW	664.04
Limiting?	***Yes***	No	No	Equivalents	
Equivalents	***1.00***	***1.00***	***2.00***	%Completion	
Sample Mass	***20.00mg***	14.86mg	3.99mg	Expected Mass	14.06mg
%Weight				Expected Moles	21.17µmol
Molarity				Measured Mass	***13.00mg***
Density			***1.06g/mL***	Purity	
Volume			3.76mmL	Product Mass	13.00mg
Reactant Moles	21.17µmol	21.17µmol	42.34µmol	Product Moles	19.58µmol
Reactant Mass	20.00mg	14.86mg	3.99mg	%Yield	92.47%

$PPh_4[Cx^{Me}Ge_2Cl]$, $NaB(C_6F_5)_4$ and dimethyl disulfide were dissolved in dichloromethane-*d2* (0.45 mL). The mixture turned turbid due to the precipitation of NaCl. The mixture was stirred for 5 minutes. Hexane (1.20 mL) was added to precipitate $PPh_4B(C_6F_5)_4$ out of the reaction mixture. The suspension was filtrated using a syringe filter and the solvent of the filtrate was evaporated under reduced pressure. The solid residue was dissolved in dichloromethane (0.20 mL) and the solution was stored

at −35 °C for 2 days to yield colourless crystals. The crystals were crushed and dried *in vacuo* for 3 h to give the title compound as a colourless powder.

SCXRD: Single crystals suitable for SCXRD analysis were obtained by storing a concentrated dichloromethane solution at −35 °C.

^{1}H-NMR (600 MHz, 298 K, benzene-d_6) δ = 6.21 (d, *J* = 3.5 Hz, 2H, β-C*H*), 5.98 (d, *J* = 3.5 Hz, 2H, β-C*H*), 1.93 (s, 6H, methyl-CH_3), 1.83 (s, 6H, methyl-CH_3), 1.72 (s, 6H, methyl-CH_3), 1.71 (s, 6H, methylthiolate-SCH_3), 1.51 (s, 6H, methyl-CH_3), 0.30 (s, 6H, methyl-CH_3) ppm.

^{13}C{^{1}H} NMR (151 MHz, 298 K, tetrahydrofuran-d_8) δ = 143.9 (C_q, α-*C*), 142.6 (C_q, α-*C*), 108.1 (β-*C*H), 106.5 (β-*C*H), 36.7 (C_q, *meso*-C), 36.4 (C_q, *meso*-C), 35.2 (*C*H_3-methyl), 31.4 (*C*H_3-methyl), 30.5 (*C*H_3-methyl), 27.8 (*C*H_3-methyl), 11.3 (methylthiolate-S*C*H_3-methyl) ppm.

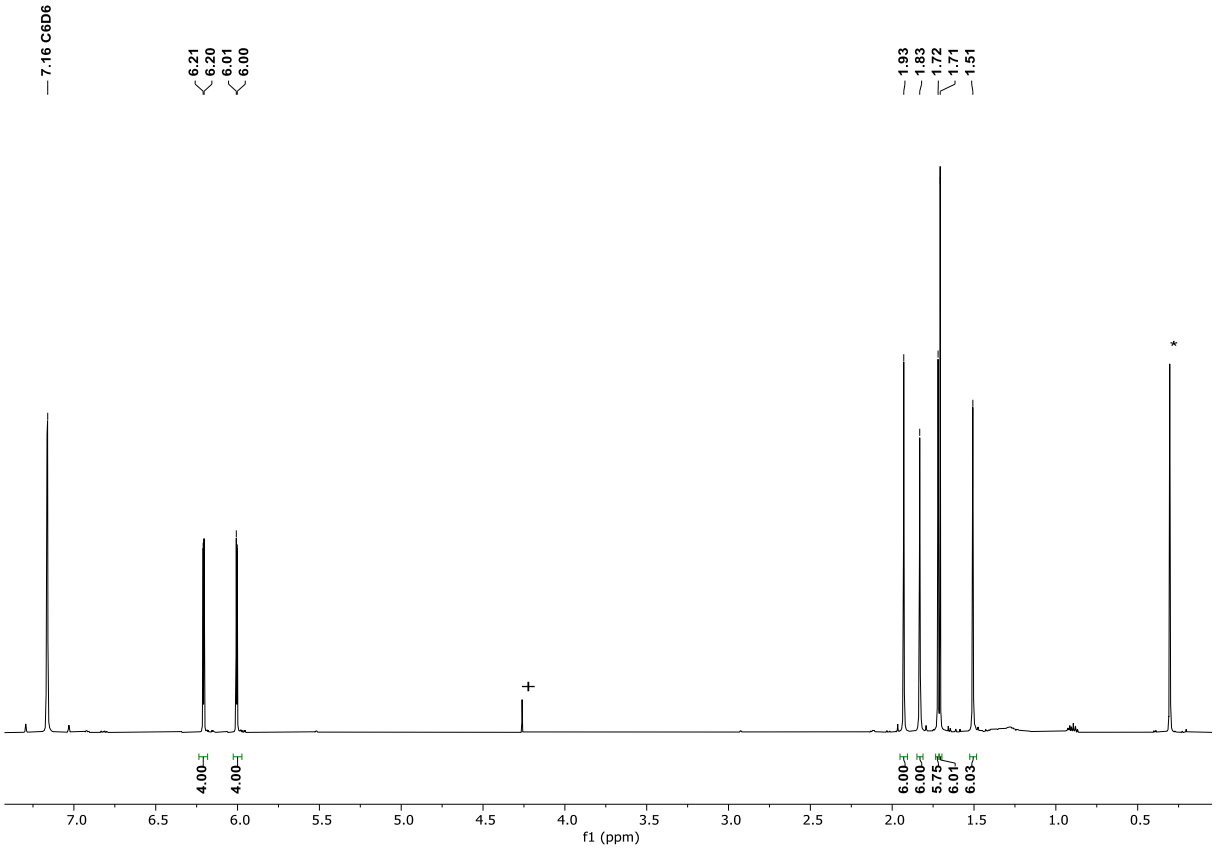


Figure S 1-56. ^{1}H NMR (600 MHz, 298 K, benzene-*d6*) spectrum of **$Cx^{Me}Ge_2(SMe)_2$.** * = Silicon grease, + = dichloromethane.

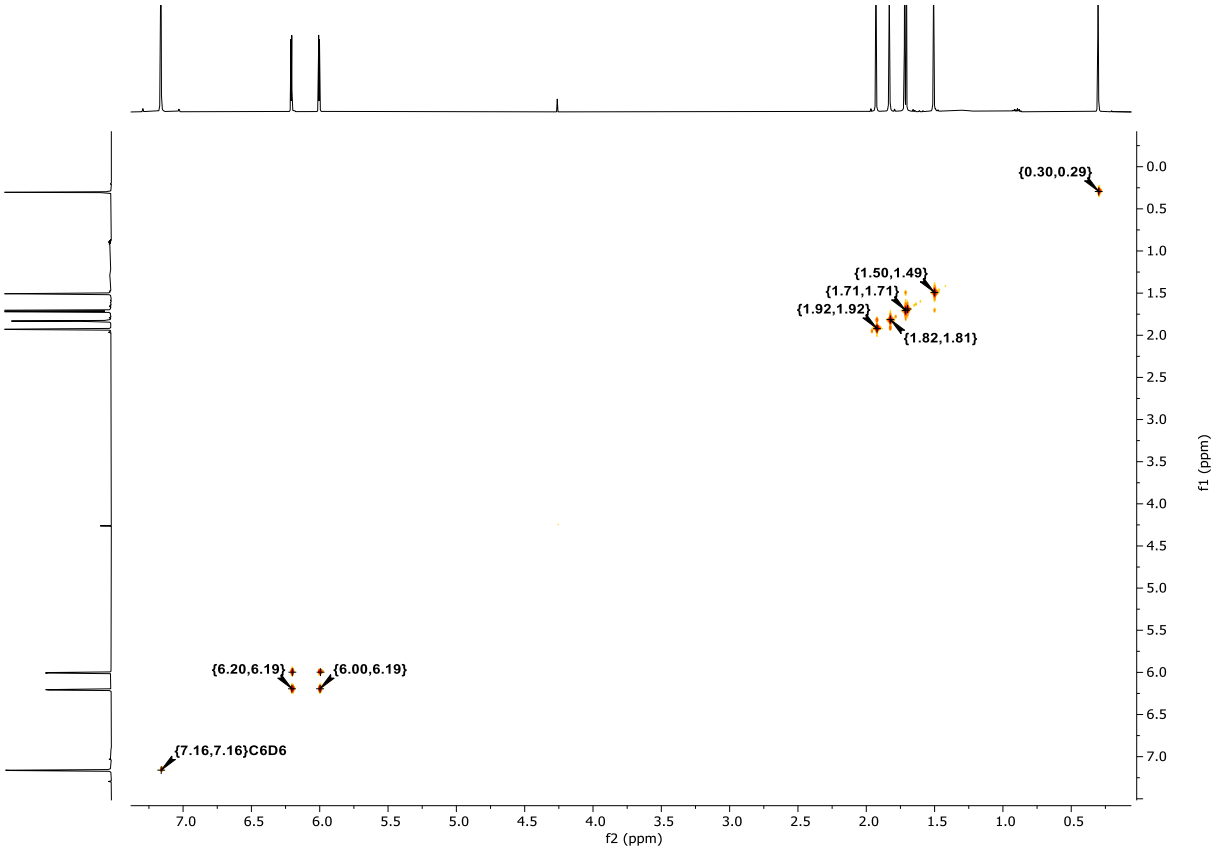


Figure S 1-57. ^{1}H-^{1}H COSY NMR (600 MHz, 298 K, benzene-*d6*) spectrum of **Cx^{Me}Ge$_2$(SMe)$_2$.**

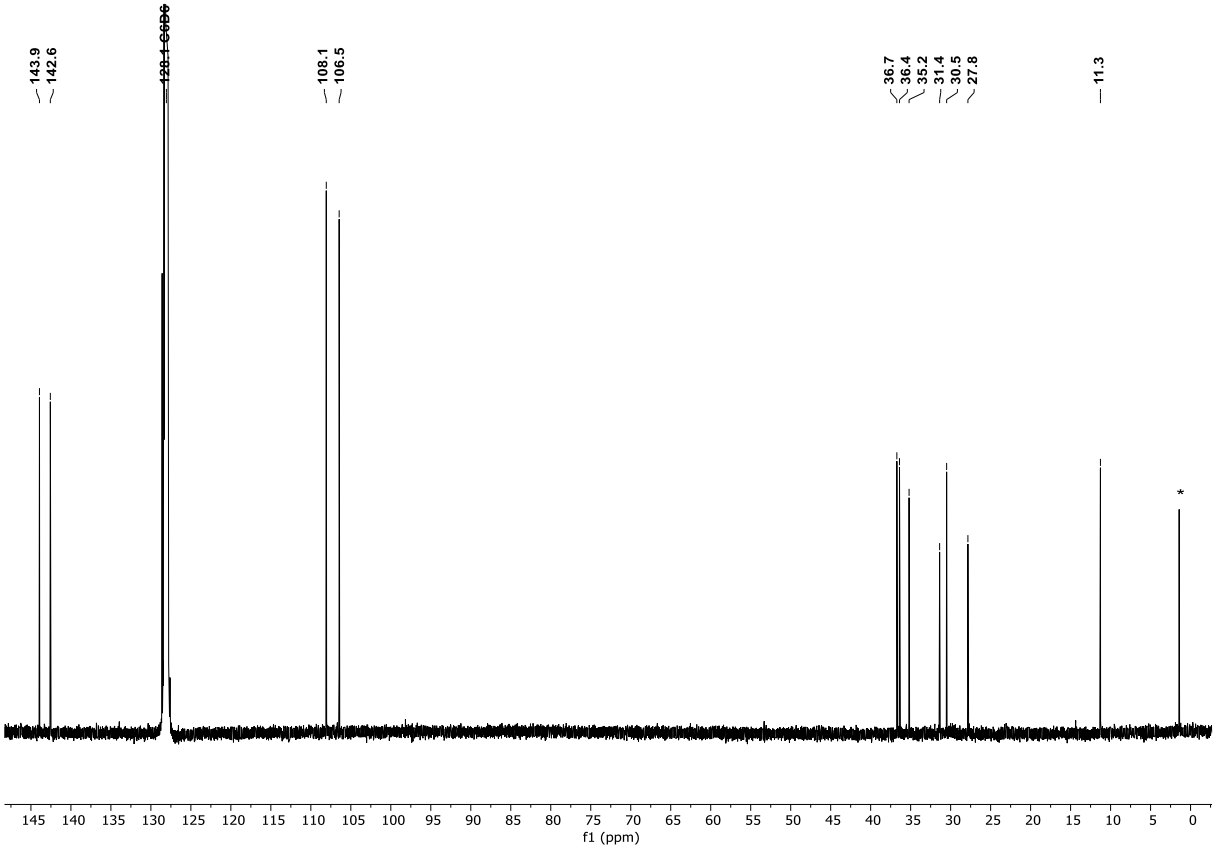


Figure S 1-58. ^{13}C{^{1}H} NMR (151 MHz, 298 K, benzene-*d6*) spectrum of **Cx^{Me}Ge$_2$(SMe)$_2$. *** = Silicon grease.

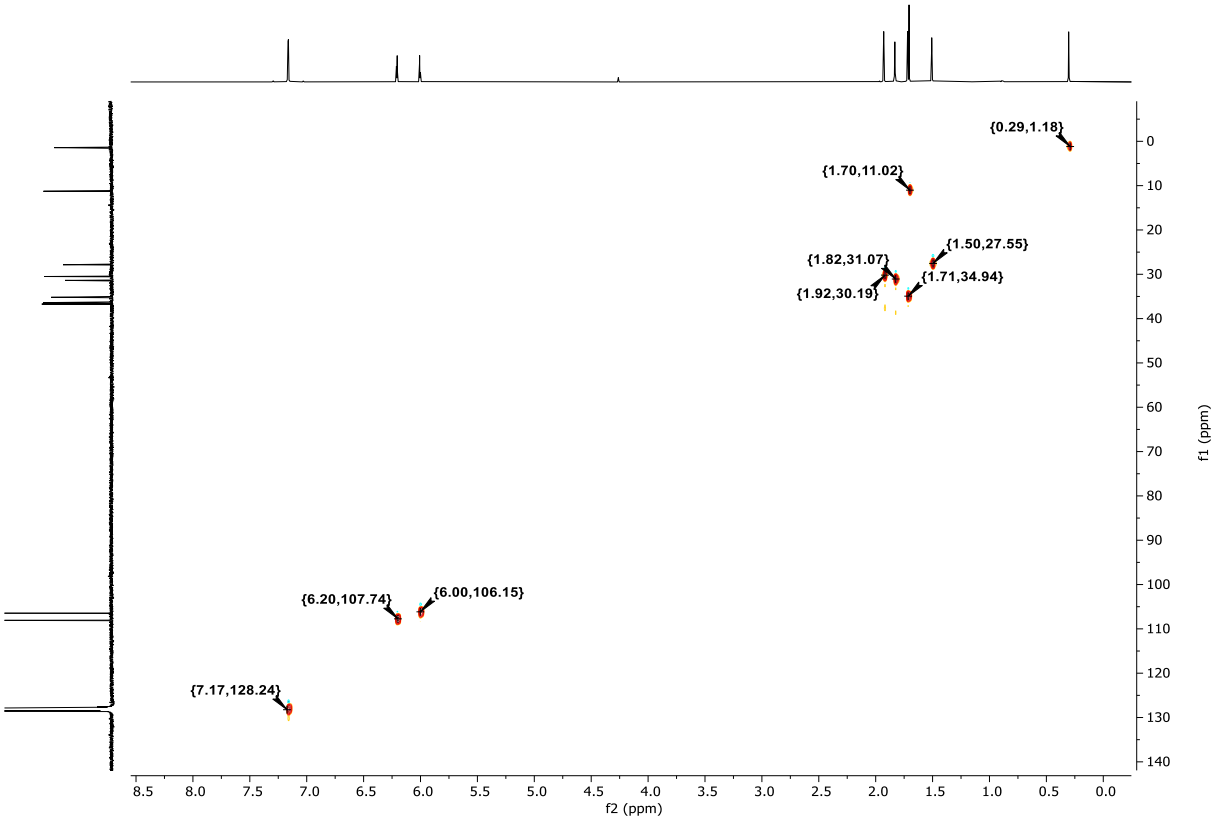


Figure S 1-59. ^{1}H-^{13}C HSQC NMR (600 MHz, 298 K, benzene-*d6*) spectrum of **Cx^{Me}Ge$_2$(SMe)$_2$.**

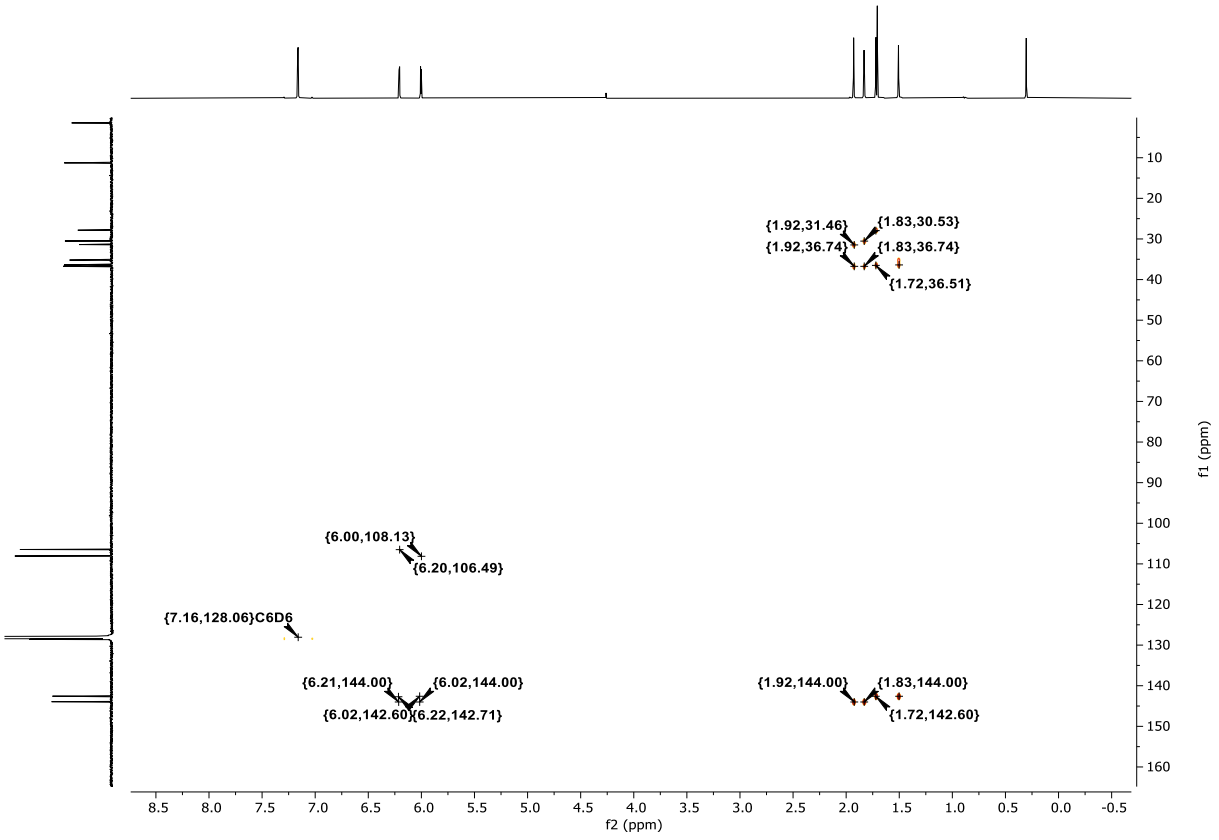
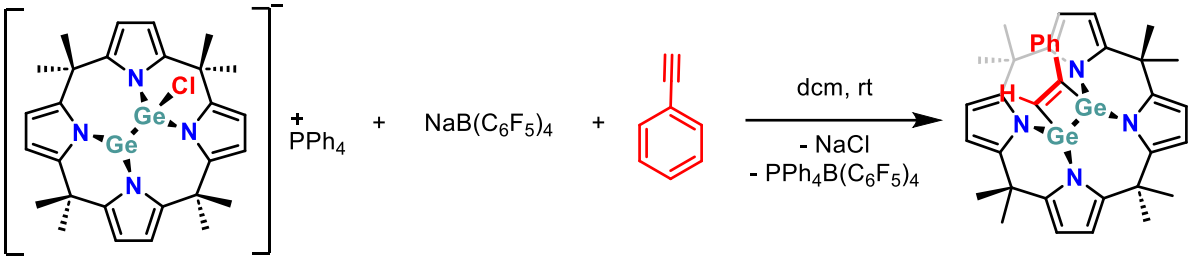


Figure S 1-60. ^{1}H-^{13}C HMBC NMR (600 MHz, 298 K, benzene-*d6*) spectrum of **Cx^{Me}Ge$_2$(SMe)$_2$.**

1.2.13 Synthesis of *meso*-Octamethylcalix[4]pyrrolato-1,2-digerma-3-phenyl-cyclobuta-3-ene $Cx^{Me}Ge_2$(PhCCH)



Reactants				*Products*	
Formula	$C_{52}H_{52}ClGe_2N_4P$	$C_{24}BF_{20}Na$	C_8H_6	Formula	$C_{36}H_{38}Ge_2N_4$
MW	944.70	702.03	102.14	MW	671.99
Limiting?	***Yes***	No	No	Equivalents	
Equivalents	***1.00***	***1.00***	***1.00***	%Completion	
Sample Mass	***40.00mg***	29.73mg	4.32mg	Expected Mass	28.45mg
%Weight				Expected Moles	42.34µmol
Molarity				Measured Mass	***13.40mg***
Density			***920.00mg/mL***	Purity	
Volume			4.70mmL	Product Mass	13.40mg
Reactant Moles	42.34µmol	42.34µmol	42.34µmol	Product Moles	19.94µmol
Reactant Mass	40.00mg	29.73mg	4.32mg	%Yield	47.10%

$PPh_4[Cx^{Me}Ge_2Cl]$, $NaB(C_6F_5)_4$ and phenylacetylene were suspended in dichloromethane-*d*2 (0.80 mL). The mixture turned turbid due to the precipitation of NaCl. The mixture was stirred for 4 hours. The solvent of the suspension was evaporated under reduced pressure and benzene (0.30 mL) was added. The suspension was stirred for 1 minute, the solvent of the suspension was evaporated under reduced pressure and the solid residue was dried *in vacuo* for 30 minutes. The solid residue was suspended in a mixture of benzene (1.00 mL) and hexane (0.80 mL), syringe filtered and the solvent of the filtrate was evaporated and the solid residue subsequently dried *in vacuo* for 4 hours to yield the title compound as a yellow powder.

SCXRD: Single crystals suitable for SCXRD analysis were obtained by slow evaporation of the solvent of a concentrated benzene solution at room temperature.

Elemental Analysis of **$Cx^{Me}Ge_2$(PhCCH)**: Calculated for **$Cx^{Me}Ge_2$(PhCCH)** x 0.30 eq. silicon grease ($HSi(CH_3)_2OH$) [%]: C: 63.10; H: 5.89; N: 8.02. Found: C: 63.31; H: 5.64; N: 7.79.

^{1}H NMR (600 MHz, 298 K, benzene-*d6*): δ = 7.95 (s, 1H, C=C*H*), 7.36 – 7.35 (m, 2H, Ph-C*H*), 7.13 – 7.06 (m, 3H, Ph-C*H*), 6.13 (d, ^3J = 3.4 Hz, 4H, β-C*H*), 6.03 (d, ^3J = 3.4 Hz, 2H, β-C*H*), 6.01 (d, ^3J = 3.4 Hz, 2H, β-C*H*), 1.85 (s, 6H, CH_3-methyl), 1.82 (s, 6H, CH_3-methyl), 1.81 (s, 3H, CH_3-methyl), 1.72 (s, 3H, CH_3-methyl), 1.67 (s, 3H, CH_3-methyl), 1.64 (s, 3H, CH_3-methyl) ppm.

^{13}C{^{1}H} NMR (151 MHz, 298 K, benzene-d_6) δ = 183.7 (C_q, *C*CH), 159.2 (CH, C*C*H), 147.0 (C_q, α-*C*), 147.0 (C_q, α-*C*), 144.6 (C_q, α-*C*), 144.5 (C_q, α-*C*), 139.9 (C_q, Ph), 129.4 (CH, Ph), 129.2 (CH, Ph), 127.2 (CH, Ph), 110.6 (*C*H, 2C, β-C), 105.2 (*C*H, β-C), 105.1 (*C*H, β-C), 38.1 (C_q, 2C, *meso*-C), 36.1

(C_q, *meso*-C), 35.9 (C_q, *meso*-C), 34.8 (2C, CH_3-methyl), 33.7 (CH_3-methyl), 33.1 (CH_3-methyl), 31.1 (2C, CH_3-methyl), 25.0 (CH_3-methyl), 24.7 (CH_3-methyl) ppm.

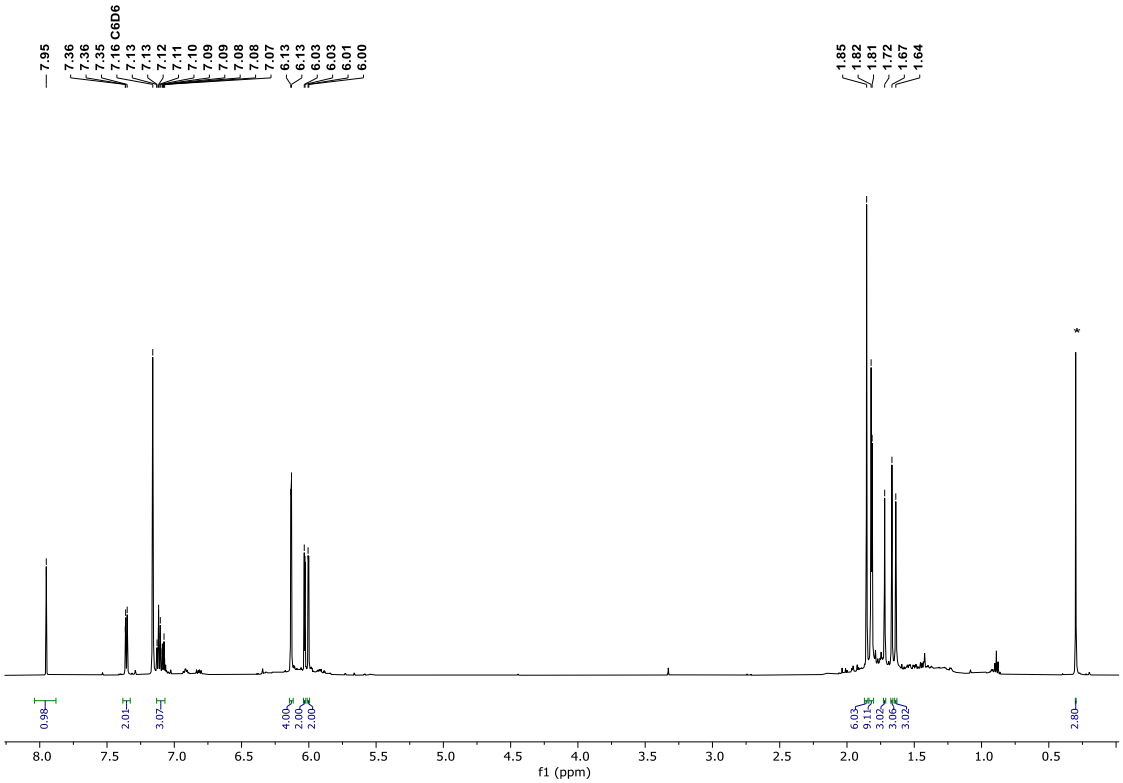


Figure S 1-61. ^{1}H NMR (600 MHz, 298 K, benzene-*d2*) spectrum of **Cx^{Me}Ge$_2$(PhCCH).** * = Silicon grease.

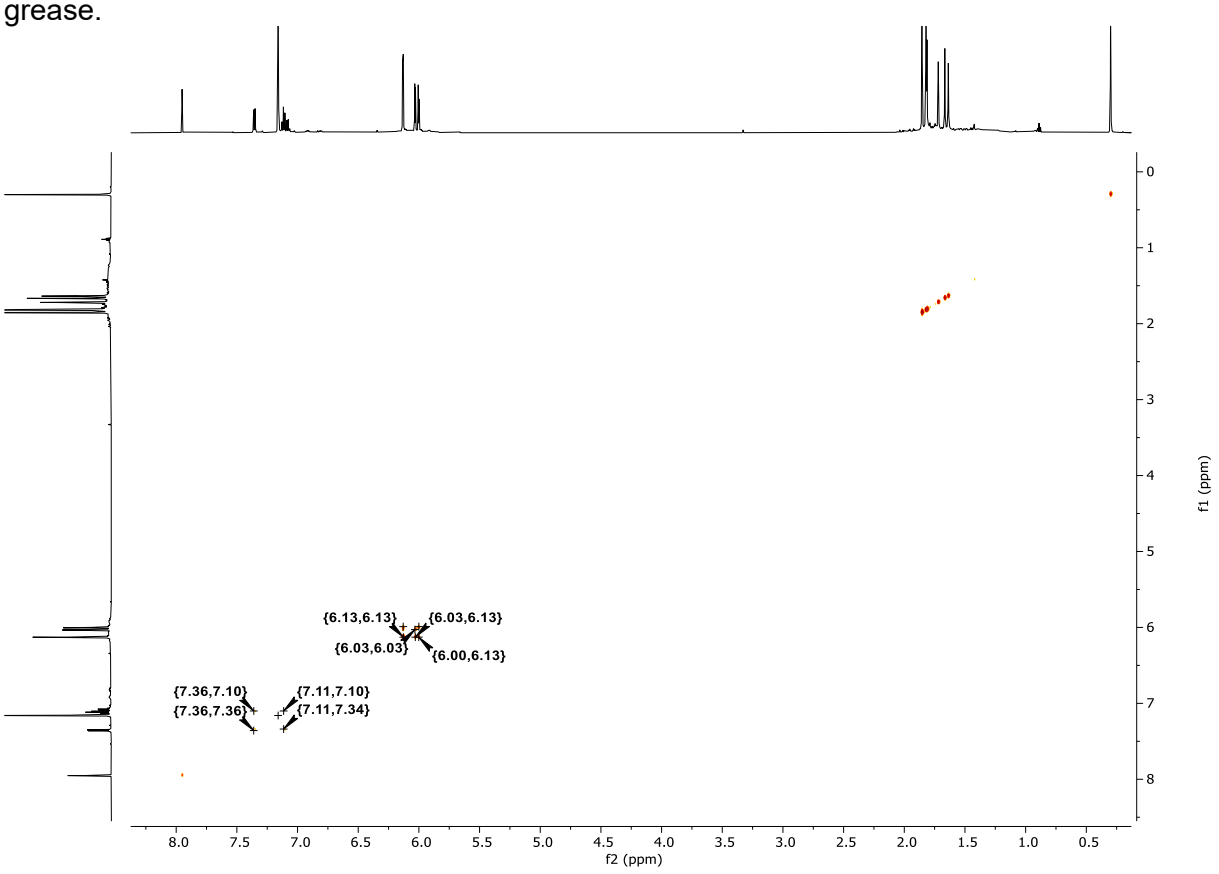


Figure S 1-62. ^{1}H-^{1}H COSY NMR (600 MHz, 298 K, benzene-*d6*) spectrum of **Cx^{Me}Ge$_2$(PhCCH).**

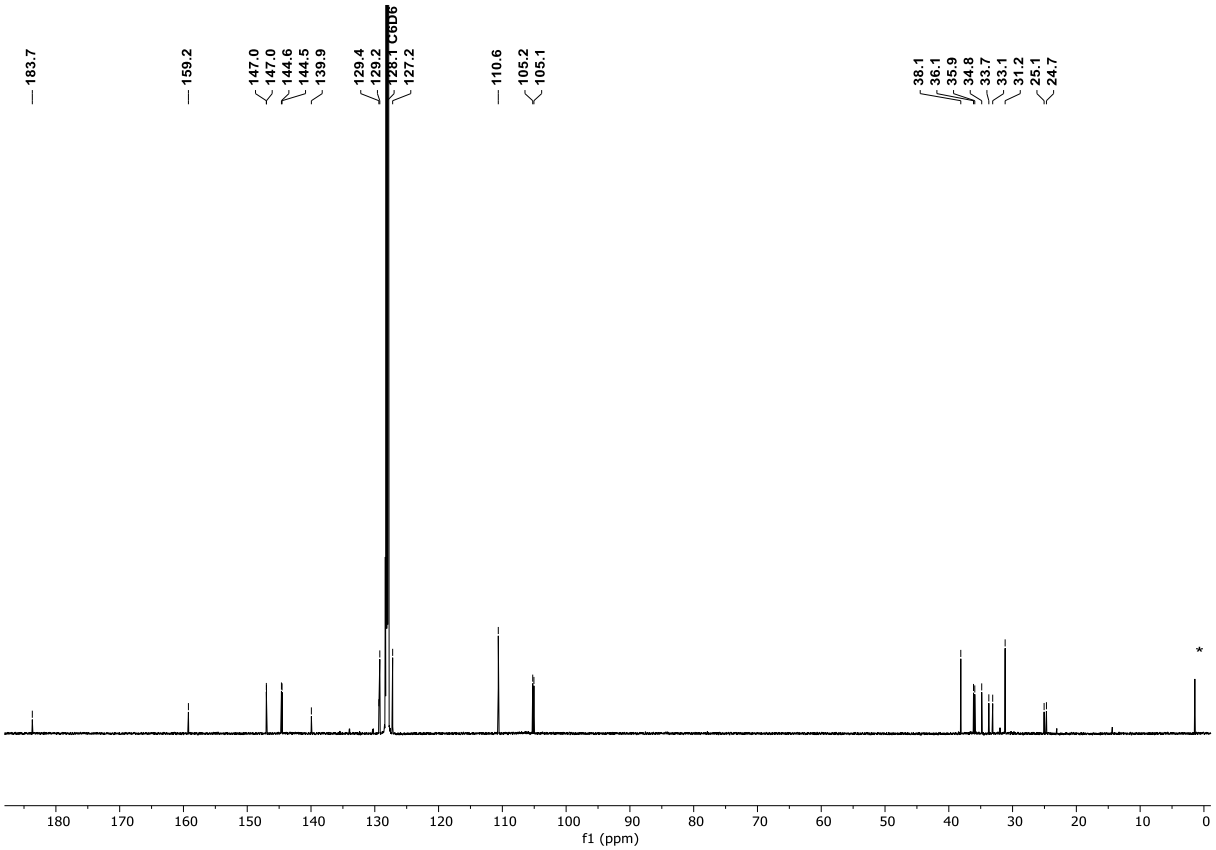


Figure S 1-63. $^{13}C\{^{1}H\}$ NMR (151 MHz, 298 K, benzene-*d6*) spectrum of **Cx^{Me}Ge$_2$(PhCCH).** * = Silicon grease.

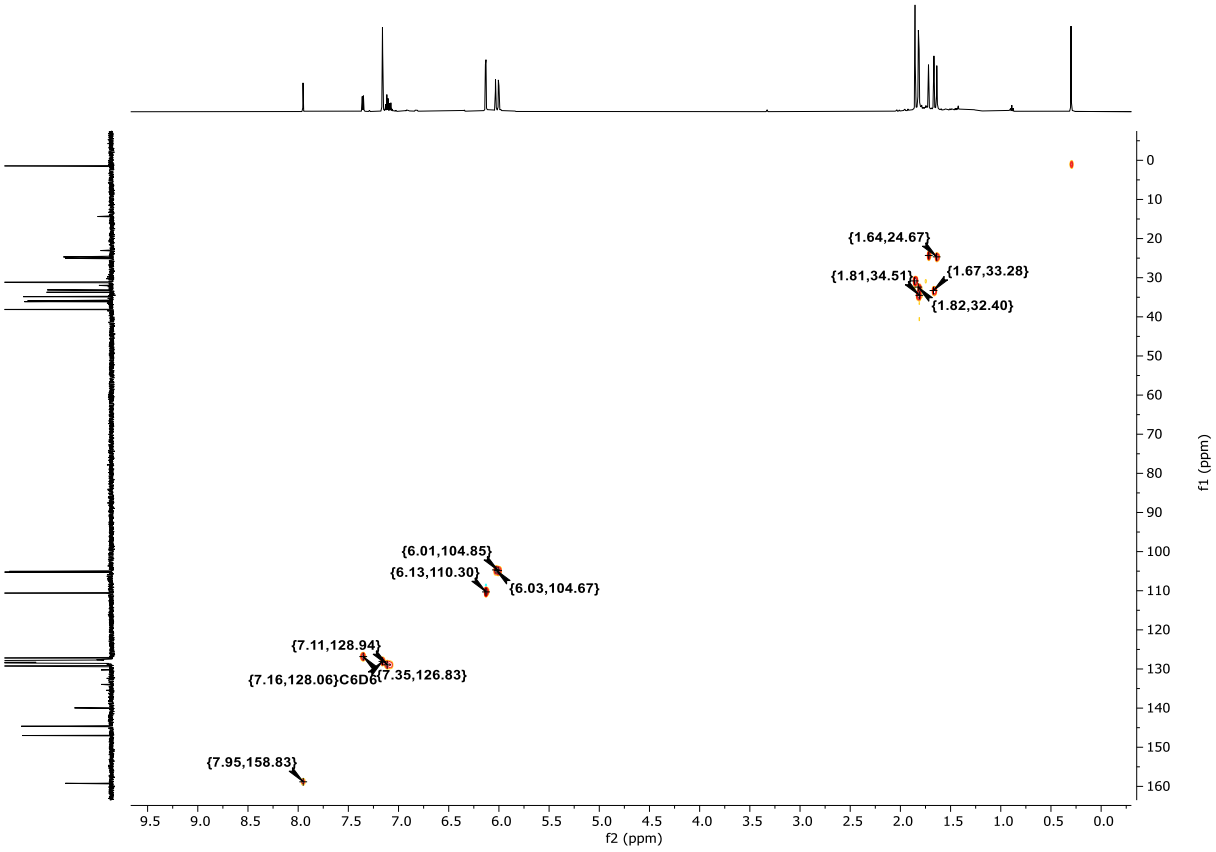


Figure S 1-64. ^{1}H-^{13}C HSQC NMR (600 MHz, 298 K, benzene-*d6*) spectrum of **Cx^{Me}Ge$_2$(PhCCH).**

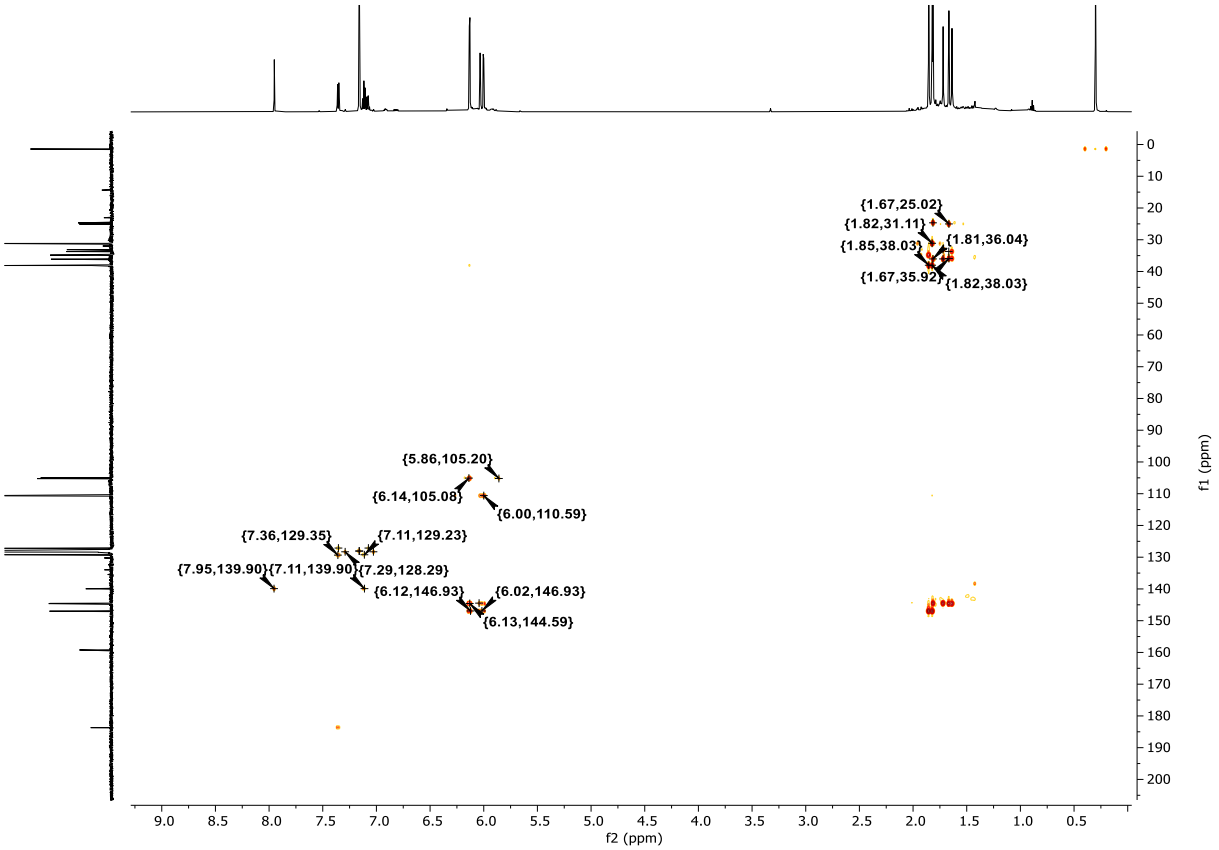
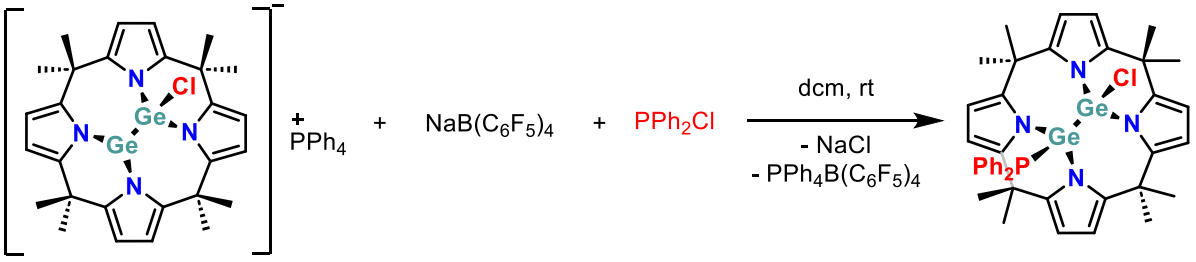


Figure S 1-65. ^{1}H-^{13}C HMBC NMR (600 MHz, 298 K, benzene-*d6*) spectrum of **Cx^{Me}Ge$_2$(PhCCH).**

1.2.14 Synthesis of *meso*-Octamethylcalix[4]pyrrole-chloro-diphenylphosphino-digermane Cx^{Me}Ge(Cl)Ge(PPh$_2$)



Reactants				*Products*	
Formula	**$C_{52}H_{52}ClGe_2N_4P$**	**$C_{24}BF_{20}Na$**	**$C_{12}H_{10}ClP$**	Formula	**$C_{40}H_{42}ClGe_2N_4P$**
MW	944.70	702.03	220.64	MW	790.49
Limiting?	***Yes***	No	No	Equivalents	
Equivalents	***1.00***	***1.00***	***1.00***	%Completion	
Sample Mass	***40.00mg***	29.73mg	9.34mg	Expected Mass	33.47mg
%Weight				Expected Moles	42.34µmol
Molarity				Measured Mass	***11.90mg***
Density			***1.20g/mL***	Purity	
Volume			7.79mmL	Product Mass	11.90mg
Reactant Moles	42.34µmol	42.34µmol	42.34µmol	Product Moles	15.05µmol
Reactant Mass	40.00mg	29.73mg	9.34mg	%Yield	35.55%

PPh$_4$[Cx^{Me}Ge$_2$Cl], NaB(C$_6$F$_5$)$_4$ and diphenylchlorophosphine were suspended in dichloromethane (0.70 mL). The mixture turned turbid due to the precipitation of NaCl. The mixture was stirred for 15 minutes. The solvent of the suspension was evaporated under reduced pressure and the solid

residue dried for 1 hour. The solid was extracted with a mixture of benzene (0.90 mL) of hexane (0.40 mL) and filtrated *via* a syringe filter. The solvent of the filtrate was evaporated under reduced pressure and the solid residue was dried *in vacuo* for 30 minutes. The solid residue was recrystallized from benzene at room temperature to yield colourless crystals, which were washed with benzene (0.70 mL), crushed and dried *in vacuo* for 16 hours to yield the title compound as a colourless powder.

*Note: **$Cx^{Me}Ge(Cl)Ge(PPh_2)$** decomposes readily in solution (dichloromethane or benzene) over the period of 48 hours at room temperature forming $Cx^{Me}H_4$.*

SCXRD: Single crystals suitable for SCXRD analysis were obtained by slow evaporation of the solvent of a concentrated benzene solution at room temperature.

Elemental Analysis of **$Cx^{Me}Ge(Cl)Ge(PPh_2)$**: Calculated for **$Cx^{Me}Ge(Cl)Ge(PPh_2)$** x 0.7 CH_2Cl_2 x 1.05 C_6H_6 [%]: Calculated: C: 60.58; H: 5.38; N: 6.01. Found: C: 60.64; H: 5.29; N: 5.99.

^{1}H NMR (600 MHz, 298 K, dichloromethane-*d2*): δ = 7.42 – 7.40 (m, 2H, *p*-*H*-PPh_2), 7.33 (td, *J* = 7.8, 2.0 Hz, 4H, *m*-*H*-PPh_2), 7.23 (td, *J* = 8.2, 1.3 Hz, 4H, *o*-*H*-PPh_2), 6.18 (d, ^3J = 3.4 Hz, 2H, β-C*H*), 6.10 (d, ^3J = 3.5 Hz, 2H, β-C*H*), 5.97 (d, ^3J = 3.4 Hz, 2H, β-C*H*), 5.95 (d, ^3J = 3.4 Hz, 2H, β-C*H*), 1.77 (s, 6H, *C*H_3-methyl), 1.65 (s, 3H, *C*H_3-methyl), 1.63 (s, 3H, *C*H_3-methyl), 1.56 (s, 3H, *C*H_3-methyl), 1.46 (s, 6H, *C*H_3-methyl), 1.37 (s, 3H, *C*H_3-methyl) ppm.

^{13}C{^{1}H} NMR (151 MHz, 298 K, dichloromethane-*d2*) δ = 144.5 (C_q, α-*C*), 143.5 (C_q, α-*C*), 143.2 (C_q, α-*C*), 142.9 (C_q, α-*C*), 135.5 (d, ^1J = 20.4 Hz, C_q, PPh_2), 130.5 (*C*H, *p*-*C*H-PPh_2) , 129.9 (d, ^3J = 22.8 Hz, *C*H, *m*-*C*H-PPh_2), 129.6 (d, ^2J = 7.2 Hz, *C*H, *o*-*C*H-PPh_2), 108.8 (*C*H, β-C), 107.0 (*C*H, β-C), 106.9 (*C*H, β-C), 105.9 (*C*H, β-C), 37.8 (d, ^5J = 10.7 Hz, *C*H_3-methyl), 36.6 (C_q, *meso*-C), 36.5 (C_q, *meso*-C), 36.4 (C_q, *meso*-C), 35.8 (C_q, *meso*-C), 32.4 (*C*H_3-methyl), 32.4 (*C*H_3-methyl), 30.9 (*C*H_3-methyl), 30.4 (*C*H_3-methyl), 27.6 (*C*H_3-methyl) ppm.

^{31}P{^{1}H} NMR (162 MHz, 298 K, dichloromethane-*d2*): δ = −9.5 ppm.

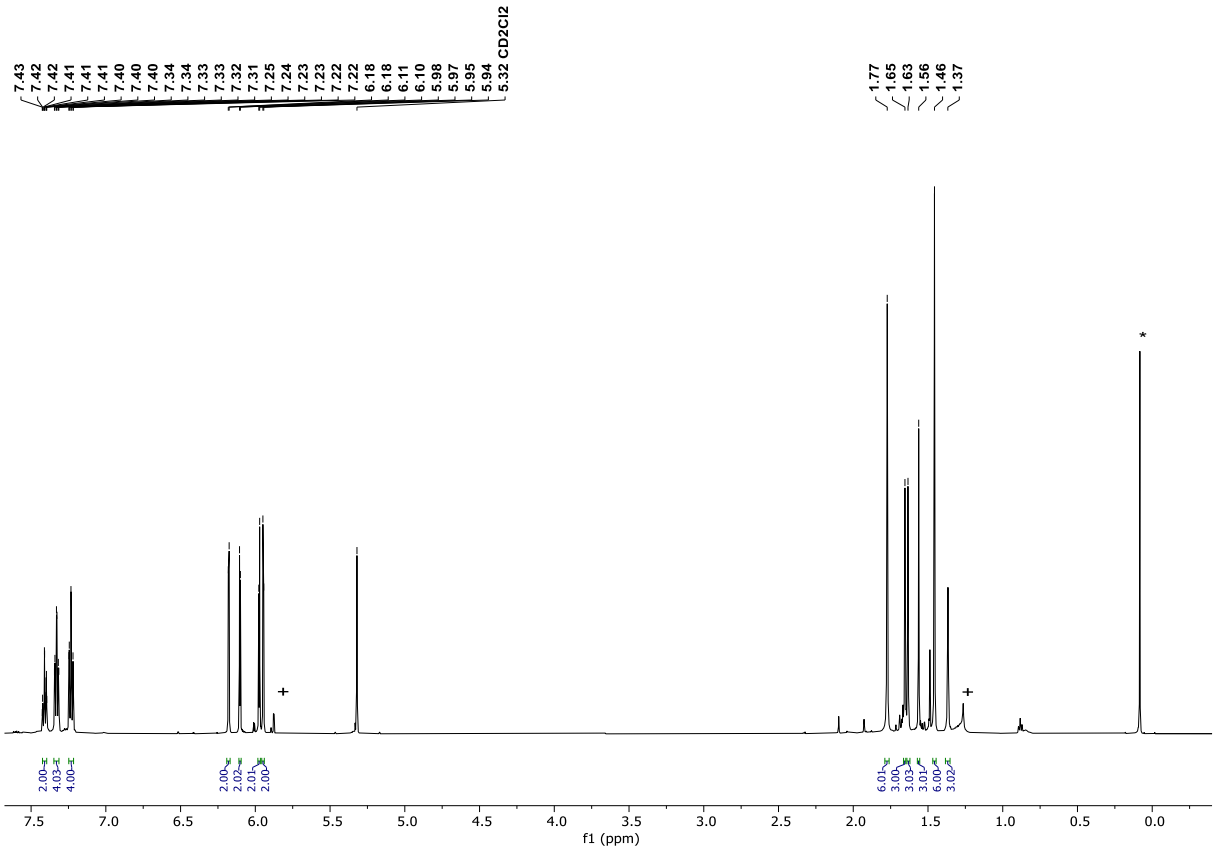


Figure S 1-66. ^{1}H NMR (600 MHz, 298 K, dichloromethane-*d2*) spectrum of **Cx^{Me}Ge(Cl)Ge(PPh$_2$)**. * = Silicon grease, + = Cx^{Me}H$_4$.

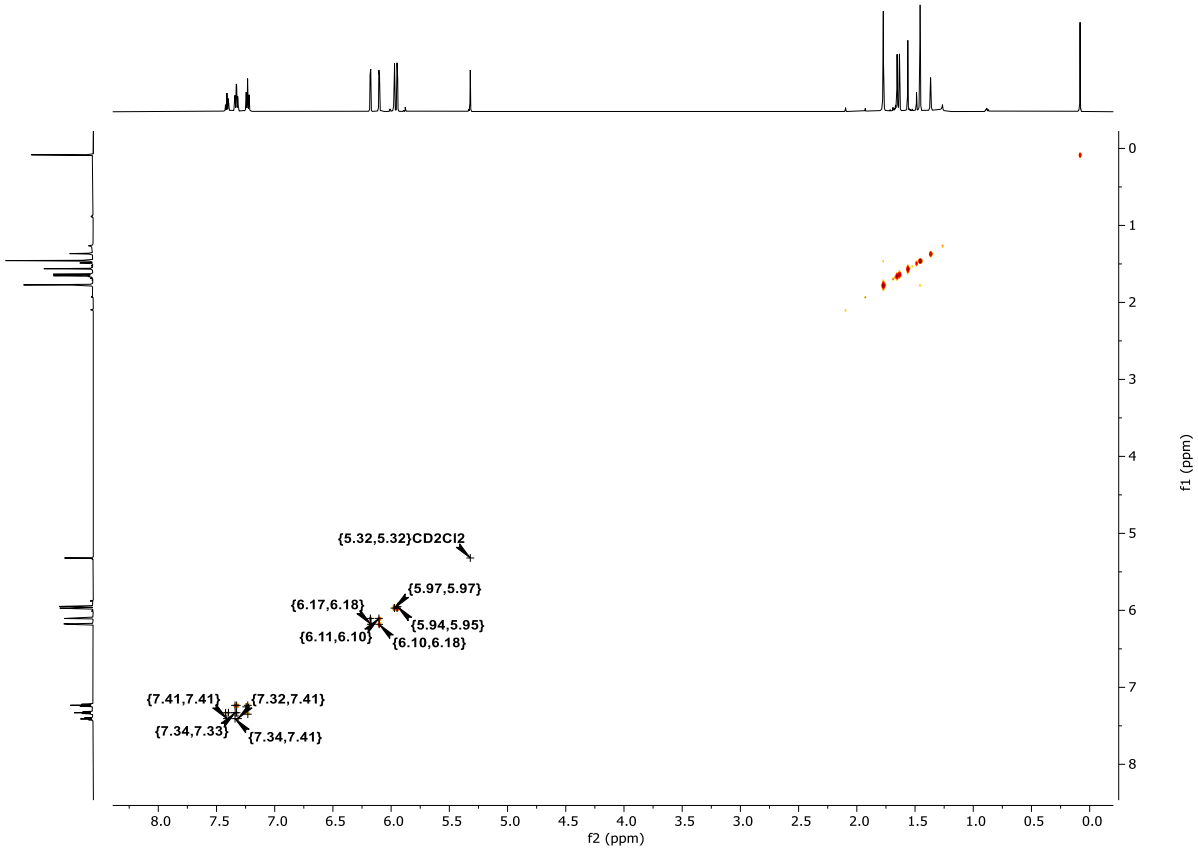


Figure S 1-67. ^{1}H-^{1}H COSY NMR (600 MHz, 298 K, dichloromethane-*d2*) spectrum of **Cx^{Me}Ge(Cl)Ge(PPh$_2$).**

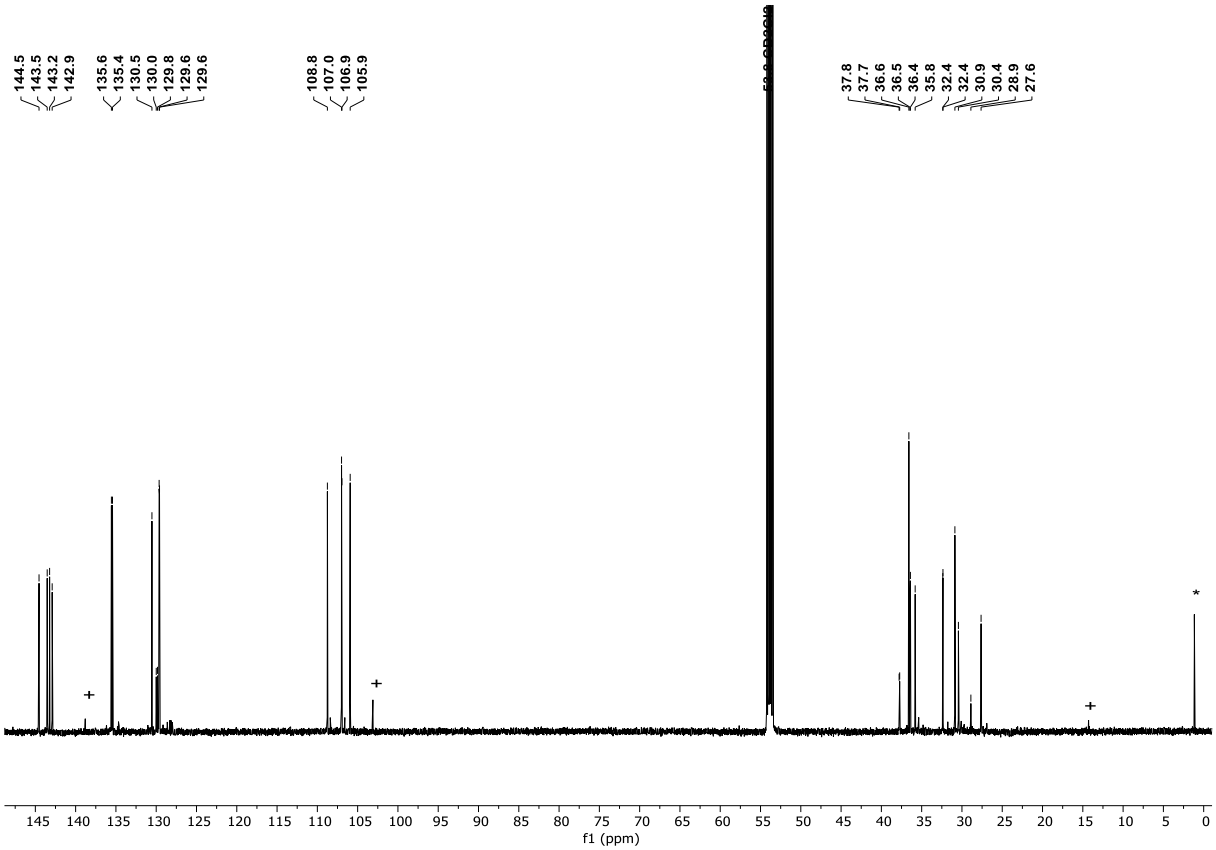


Figure S 1-68. $^{13}C\{^{1}H\}$ NMR (151 MHz, 298 K, dichloromethane-*d2*) spectrum of **$Cx^{Me}Ge(Cl)Ge(PPh_2)$.** * = Silicon grease, + = $Cx^{Me}H_4$.

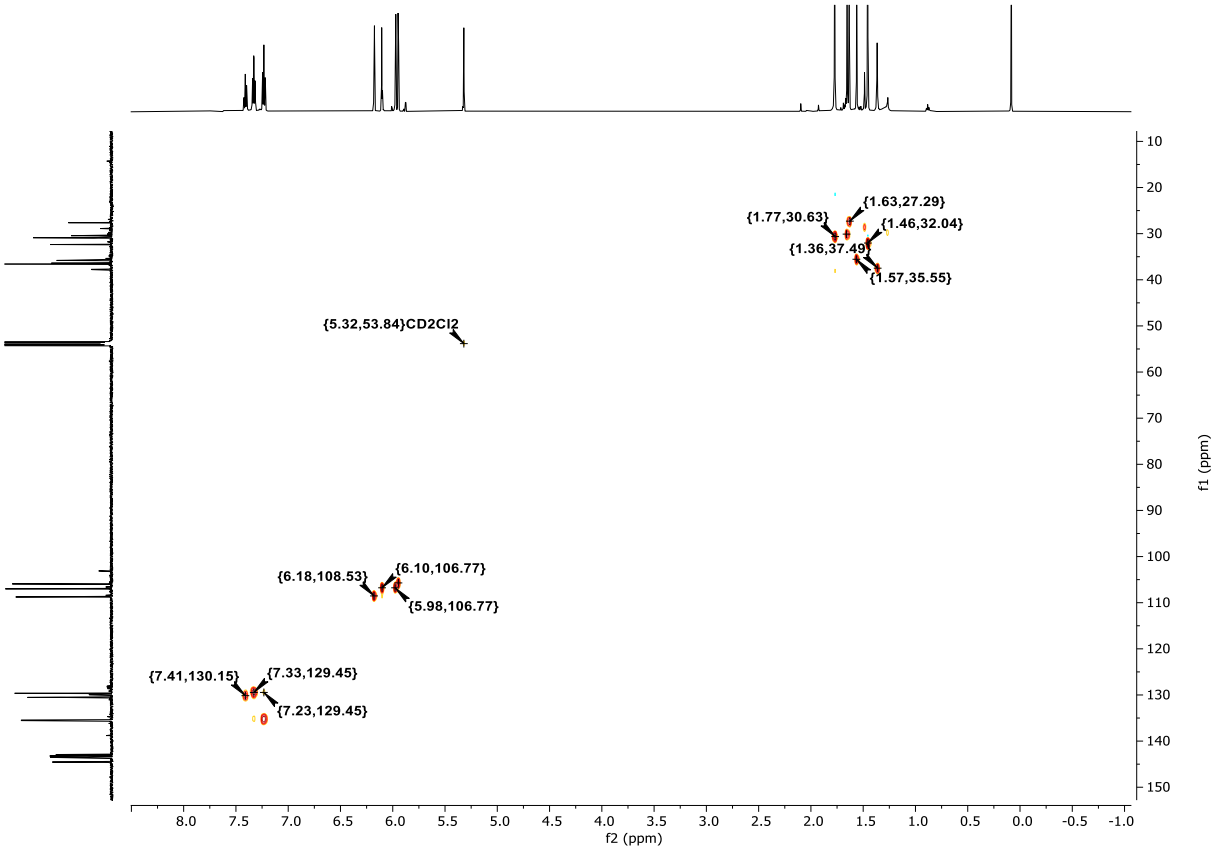


Figure S 1-69. ^{1}H-^{13}C HSQC NMR (600 MHz, 298 K, dichloromethane-*d2*) spectrum of **$Cx^{Me}Ge(Cl)Ge(PPh_2)$.**

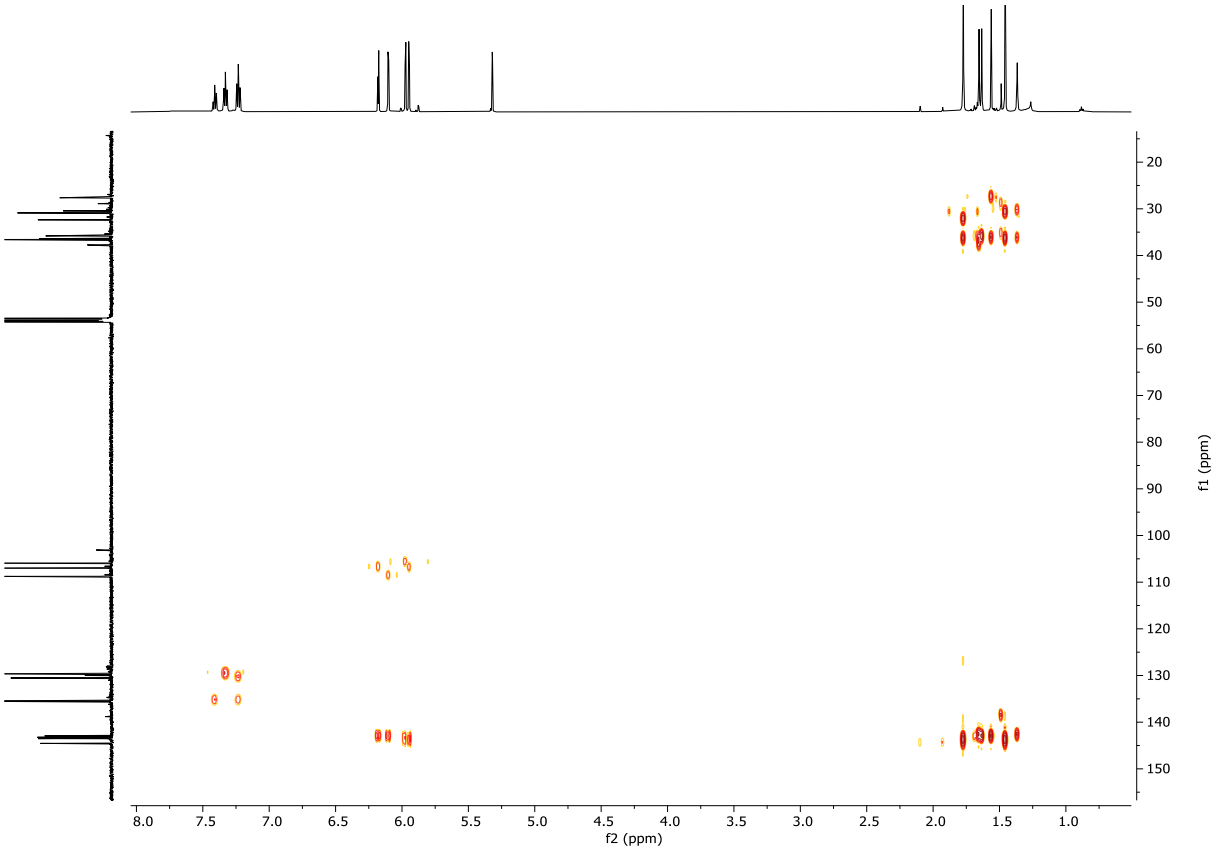


Figure S 1-70. ^{1}H-^{13}C HMBC NMR (600 MHz, 298 K, dichloromethane-*d2*) spectrum of **$Cx^{Me}Ge(Cl)Ge(PPh_2)$.**

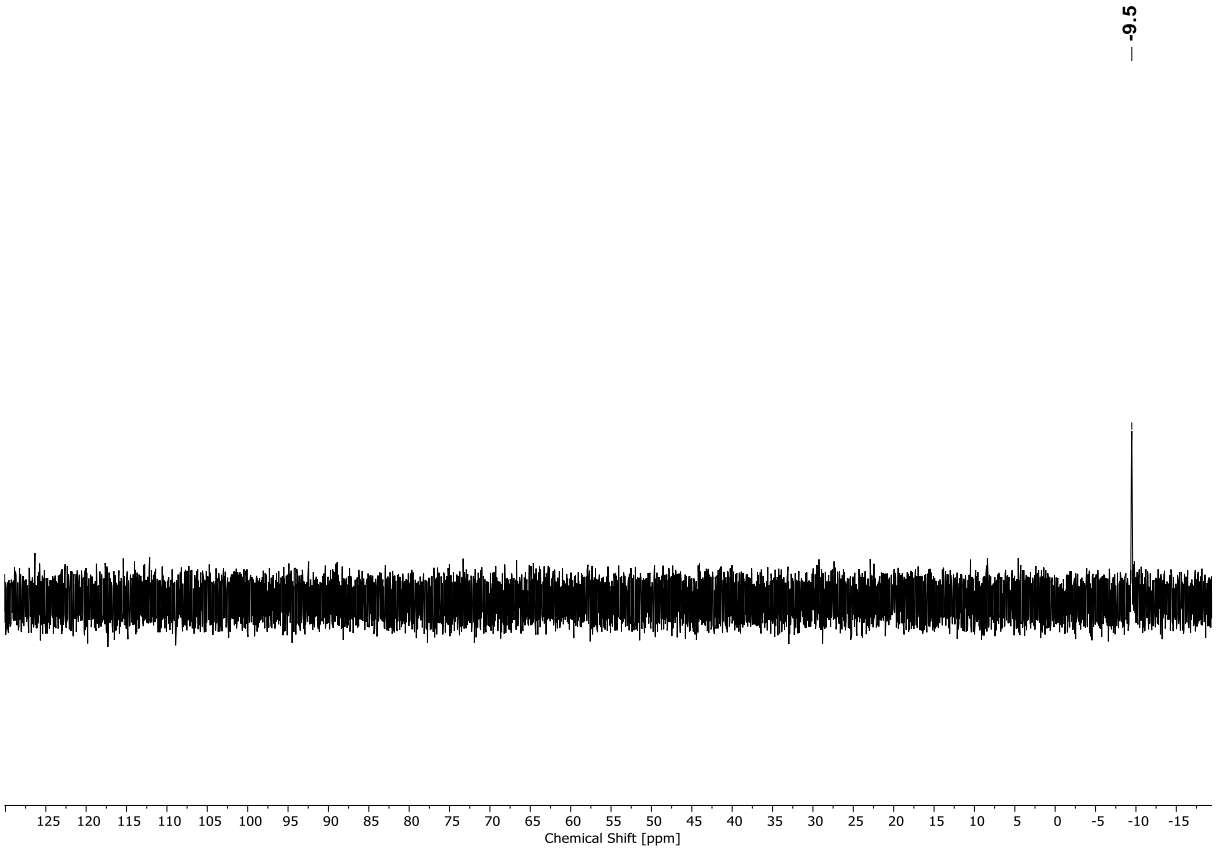
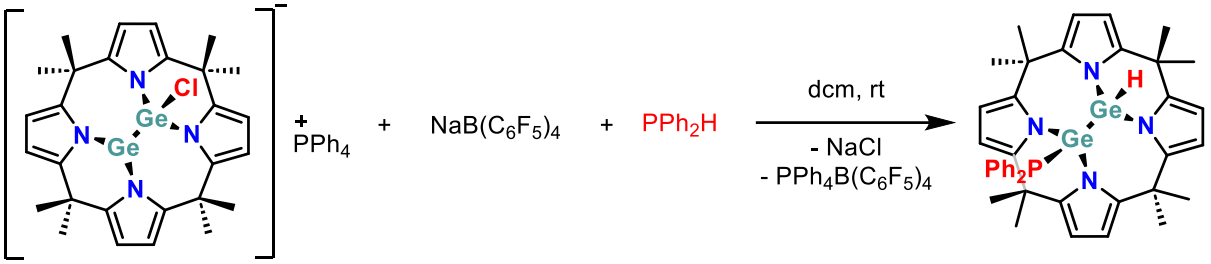


Figure S 1-71. $^{31}P\{^{1}H\}$ NMR (121 MHz, 298 K, dichloromethane-*d2*) spectrum of **$Cx^{Me}Ge(Cl)Ge(PPh_2)$.**

1.2.15 Synthesis of *meso*-Octamethylcalix[4]pyrrole-diphenylphosphino-digermane $Cx^{Me}Ge(H)Ge(PPh_2)$



Reactants				*Products*	
Formula	$C_{52}H_{52}ClGe_2N_4P$	$C_{24}BF_{20}Na$	$C_{12}H_{11}P$	Formula	$C_{40}H_{43}Ge_2N_4P$
MW	944.70	702.03	186.19	MW	756.05
Limiting?	***Yes***	No	No	Equivalents	
Equivalents	***1.00***	***1.00***	***1.00***	%Completion	
Sample Mass	***10.00mg***	7.43mg	1.97mg	Expected Mass	8.00mg
%Weight				Expected Moles	10.59µmol
Molarity				Measured Mass	***8.00mg***
Density			***1.07g/mL***	Purity	***76.00%***
Volume			1.84mmL	Product Mass	6.08mg
Reactant Moles	10.59µmol	10.59µmol	10.59µmol	Product Moles	8.04µmol
Reactant Mass	10.00mg	7.43mg	1.97mg	%Yield [1]	75.97%

$PPh_4[Cx^{Me}Ge_2Cl]$, $NaB(C_6F_5)_4$ and diphenylchlorophosphine were suspended in dichloromethane-*d2* (0.45 mL). The mixture turned turbid due to the precipitation of NaCl. The mixture was stirred for 15 minutes. Further work-up was not performed.

Note: [1]Yield determined by ^1H NMR. ***$Cx^{Me}Ge(H)Ge(PPh_2)$*** *decomposes readily in solution (dichloromethane or benzene) over the period of 16 hours at room temperature forming $Cx^{Me}H_4$. Attempts to isolate the title compound led to isolating $Cx^{Me}H4$ as the main product.*

^1H NMR (600 MHz, 298 K, dichloromethane-*d2*): δ = 7.33 – 7.27 (m, 8H, *m/o-H*-PPh_2), 7.23 – 7.21 (m, 2H, *p-H*-PPh_2), 6.15 (d, ^3J = 3.4 Hz, 2H, β-C*H*), 6.13 (d, ^3J = 3.5 Hz, 2H, β-C*H*), 5.91 (d, ^3J = 3.4 Hz, 2H, β-C*H*), 5.87 (d, ^3J = 3.4 Hz, 2H, β-C*H*), 1.83 (d, *J* = 2.4 Hz, 3H, *C*H_3-methyl), 1.74 (s, 3H, *C*H_3-methyl), 1.71 (s, 6H, *C*H_3-methyl), 1.62 (s, 3H, *C*H_3-methyl), 1.38 (s, 3H, *C*H_3-methyl), 1.19 (s, 6H, *C*H_3-methyl) ppm.

$^{31}P\{^1H\}$ NMR (162 MHz, 298 K, dichloromethane-*d2*): δ = −14.2 ppm.

Note: Alongside the title compound a species showing (among others) 2 doublets at δ = 6.03 and δ = 5.95 ppm with a corresponding signal in ^{31}P NMR at δ = −16.1 ppm could belong to a symmetrical substituted digermane species ***$Cx^{Me}Ge(PPh_2)Ge(PPh_2)$***.

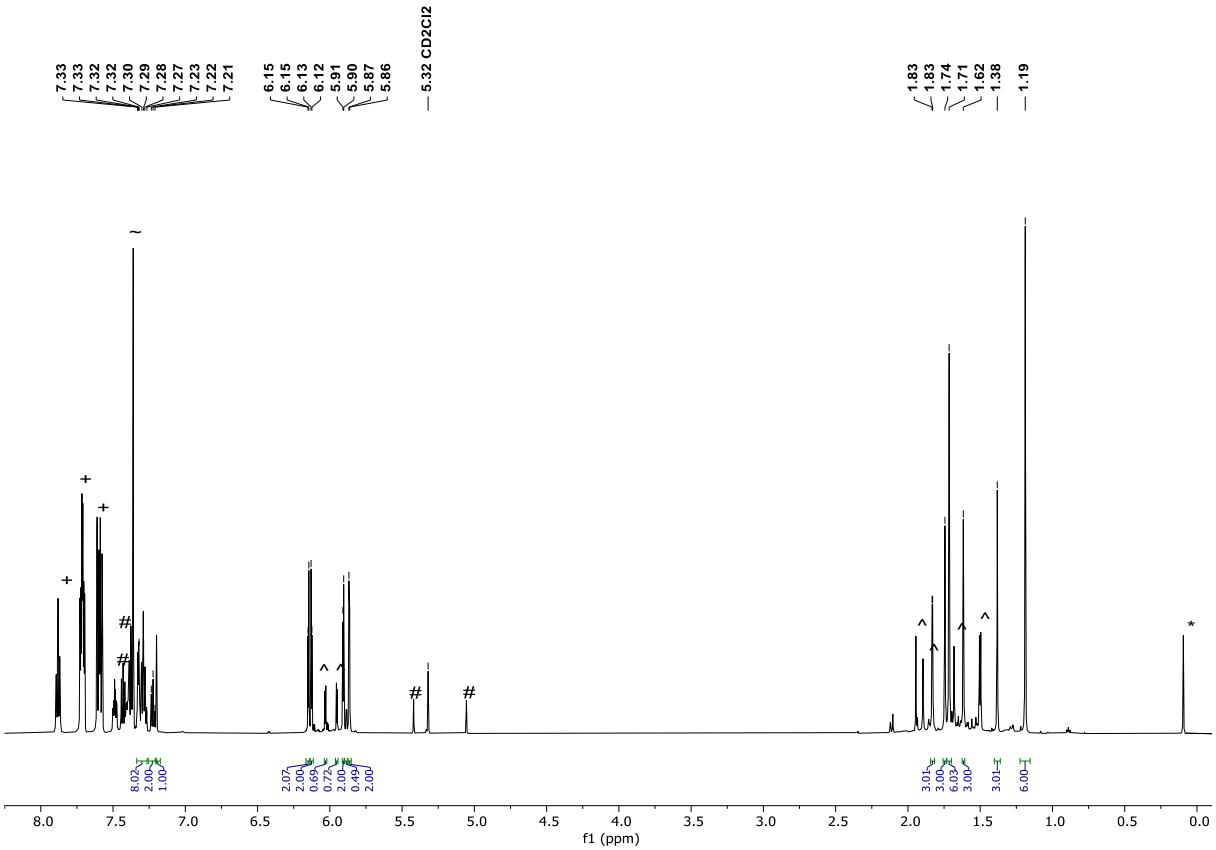


Figure S 1-72. ^{1}H NMR (600 MHz, 298 K, dichloromethane-*d2*) spectrum of **Cx^{Me}Ge(H)Ge(PPh$_2$).** * = Silicon grease, + = PPh4B(C_6F_5)$_4$, # = PPh2H, ^ = unknown impurity (see note above).

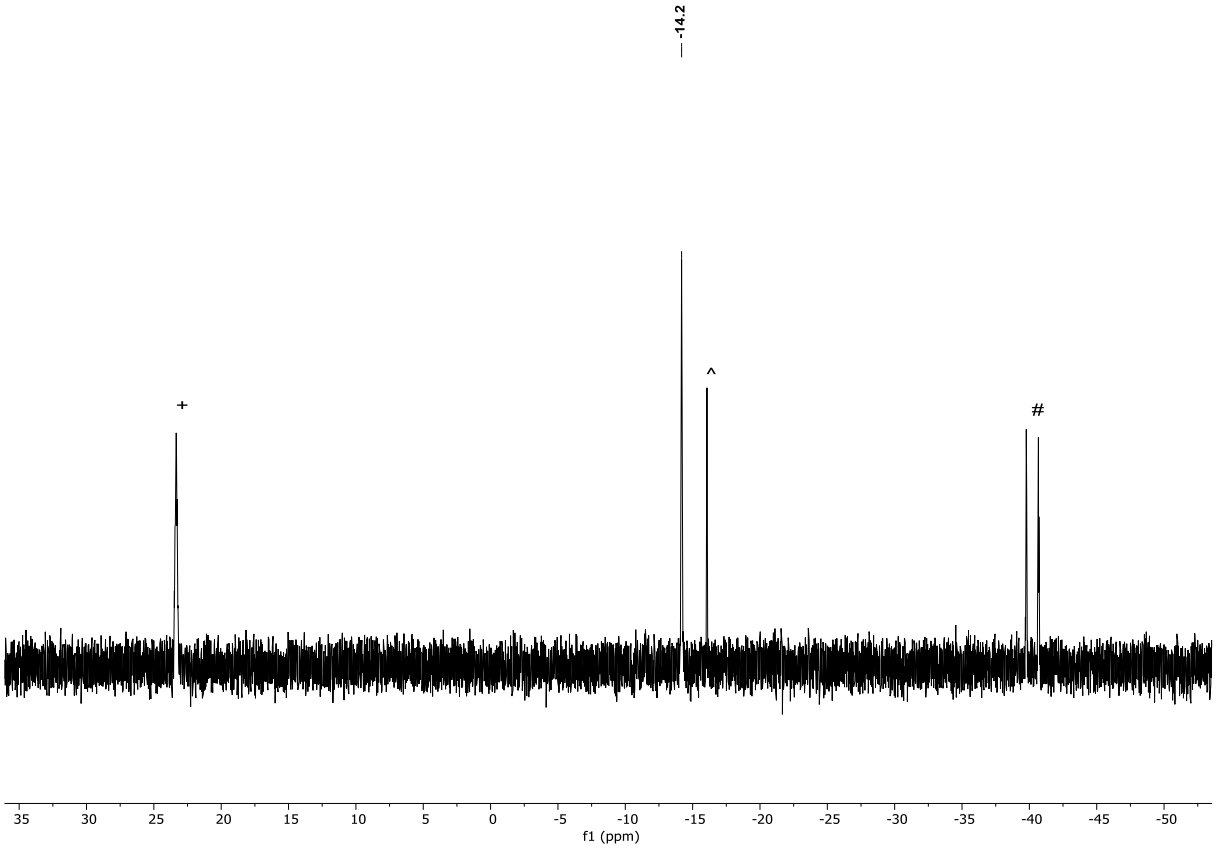
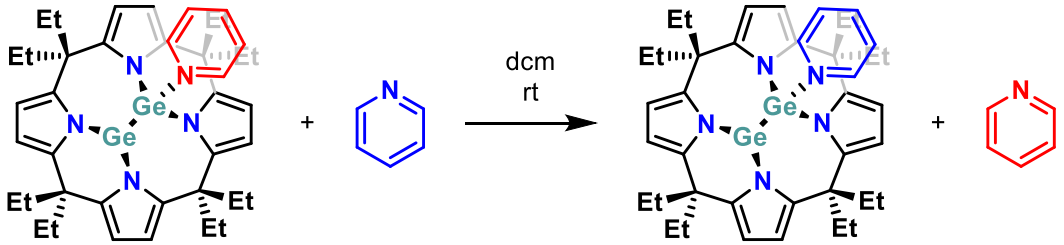


Figure S 1-73. ^{31}P{^{1}H} NMR (162 MHz, 298 K, dichloromethane-*d2*) spectrum of **Cx^{Me}Ge(H)Ge(PPh$_2$).** + = $PPh_4B(C_6F_5)_4$, # = PPh_2H, ^ = unknown impurity (see note above).

1.3 Pyridine Exchange Dynamics of $Cx^{Et}Ge_2$(pyridine)



Reactants			*Products*		
Formula	$C_{41}H_{53}Ge_2N_5$	C_5H_5N	Formula	$C_{41}H_{53}Ge_2N_5$	C_5H_5N
MW	761,17	79,10	MW	761,17	79,10
Limiting?	***Yes***	No	Equivalents		
Equivalents	***1,00***	***2,20***	%Completion		
Sample Mass	***7,20mg***	1,65mg	Expected Mass	7,20mg	748,24µg
%Weight			Expected Moles	9,46µmol	9,46µmol
Molarity			Measured Mass		
Density		***980,00mg/mL***	Purity		
Volume		1,68mmL	Product Mass		
Reactant Moles	9,46µmol	20,81µmol	Product Moles		
Reactant Mass	7,20mg	1,65mg	%Yield		

In a J. Young NMR tube **$Cx^{Et}Ge_2$(pyridine)** was dissolved in dichloromethane-*d2* (0.50 mL) and pyridine was added. The samples were then subjected to ^{1}H NMR spectroscopy at room temperature. Two sets of signals were observed for free and bound pyridine. The exchange dynamic was quantified using ^{1}H,^{1}H EXSY NMR spectroscopy. The *meta* protons of the pyridines are used for integration (normalized). Now, having two sites with unequal populations (mol fractions X_A = 0.313 and X_B = 0.687), the relative intensity ratio of cross peaks to diagonal peaks was calculated using

$$r = 4X_AX_B\frac{I_{AA}+I_{BB}}{I_{AB}+I_{BA}} - (X_A - X_B)^2.$$[6]

Two different mixing times τ_m were used. EXSY plots of the relative signal intensities of the cross peaks to diagonal peaks are shown in the figures below. For the simplest two site case, the rate constant can be calculated using

$$k = \frac{1}{\tau_m} ln\frac{r+1}{r-1}$$

with r = (I_{AA} + I_{BB})/(I_{AB}+I_{BA}) where I_{AA} and I_{BB} are the intensities of the diagonal peaks and I_{AB} and I_{BA} the intensities of the exchange peaks.[6] Using the rate constants, the Gibbs free energy of activation is calculated using the Eyring equation:

$$k = \chi\frac{k_bT}{h}e^{\frac{-\Delta G^{\ddagger}}{RT}}$$

And with χ = 1:

$$\Delta G^{\ddagger} = RT(23.76 - ln\frac{k}{T}).$$

The measured and calculated values are listed in the table below.

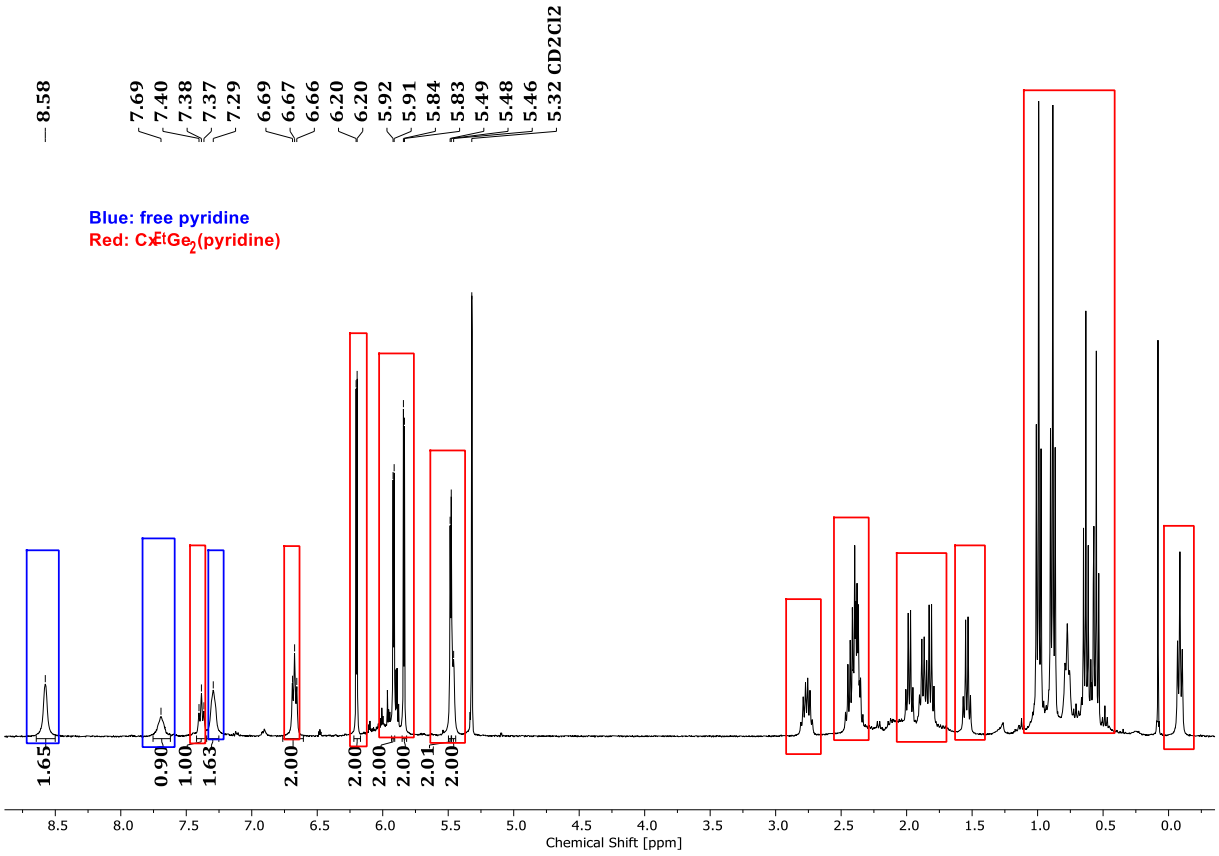


Figure S 1-74. ^{1}H NMR spectrum (dichloromethane-*d2*, 600 MHz, 298 K) of **Cx^{Et}Ge$_2$(pyridine)** in the presence of additional pyridine.

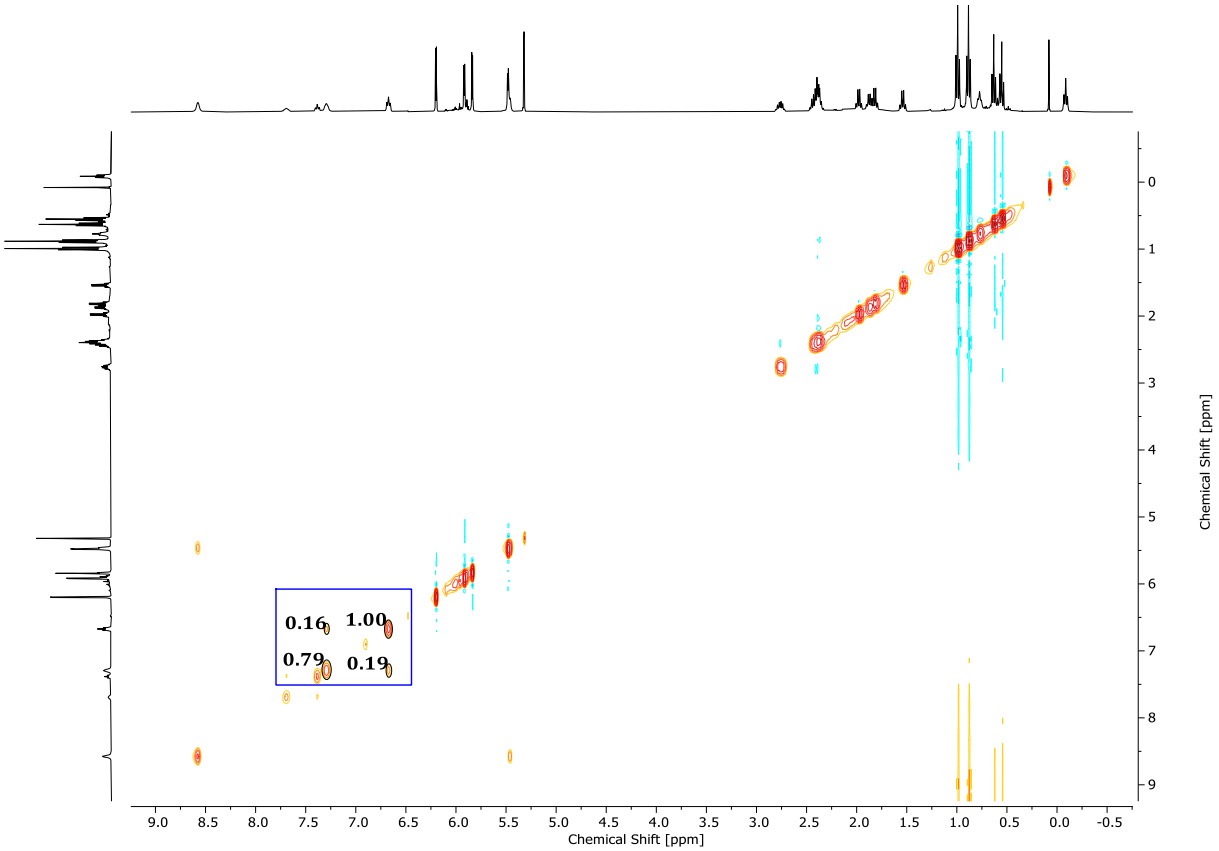


Figure S 1-75. Exemplary $^{1}H,^{1}H$ EXSY NMR spectrum (dichloromethane-d2, 600 MHz, 298 K, τm = 0.04 s) of **$Cx^{Et}Ge_2$(pyridine)** in the presence of additional pyridine.

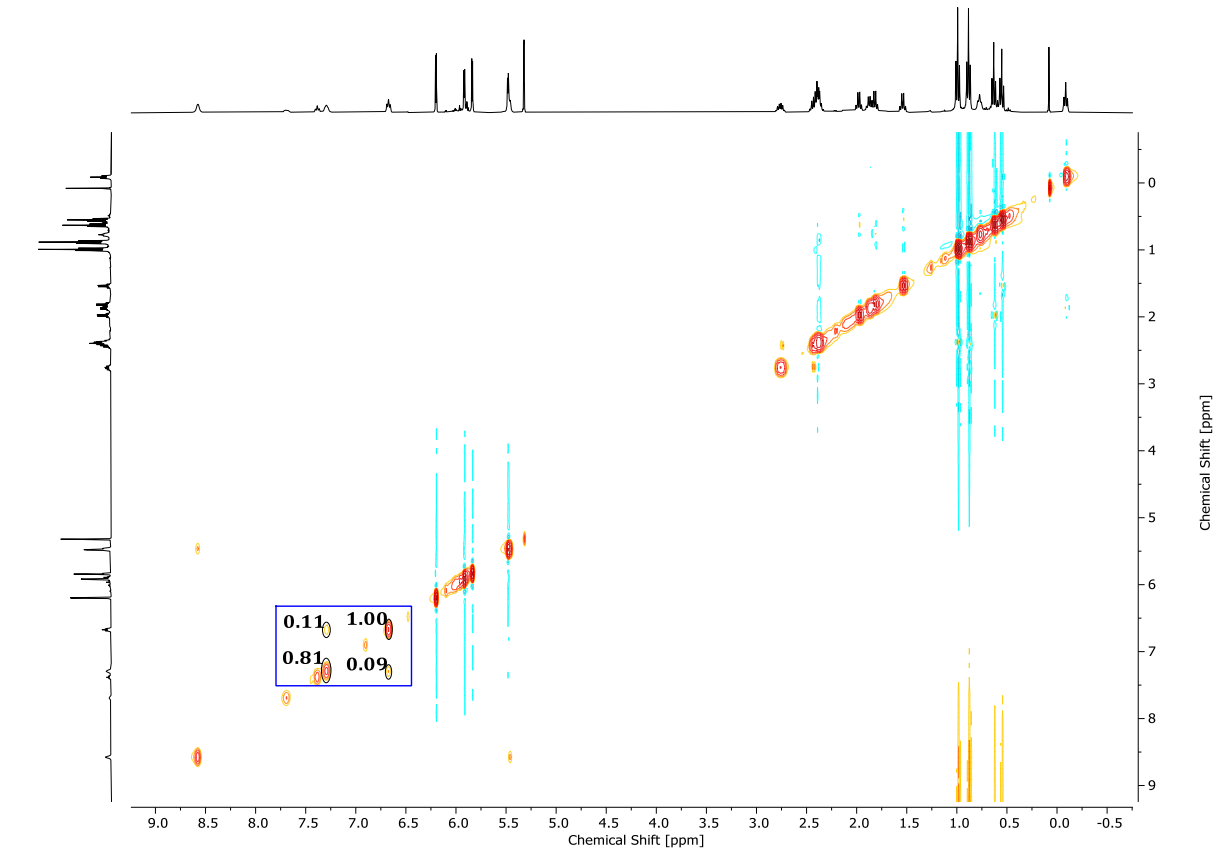


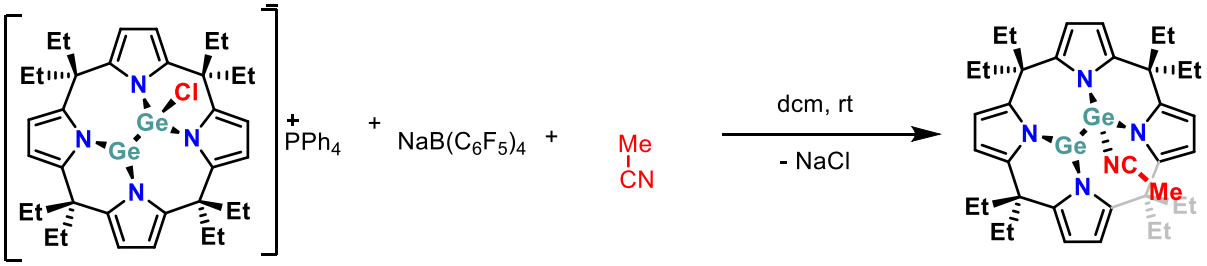
Figure S 1-76. Exemplary $^{1}H,^{1}H$ EXSY NMR spectrum (dichloromethane-d2, 600 MHz, 298 K, τm = 0.02 s) of $Cx^{Et}Ge_2$(pyridine) in the presence of additional pyridine.

Table S 1-1: Obtained EXSY data for the pyridine exchange of free and bound pyridine at **Cx^{E}-^{t}Ge$_2$(pyridine).**

	τ_m	I_{AA}	I_{AB}	I_{BB}	I_{BA}	$I_{AA} + I_{BB}$	$I_{AB} + I_{BA}$	r	k [1/s]	$\Delta G^{\ddagger}$ [kJ/mol]
Py-meta	0.04	1.00	0.79	0.16	0.19	1.79	0.35	4.26	11.95	66.34
Py-meta	0.02	1.00	0.81	0.11	0.09	1.81	0.20	7.64	13.15	65.90

Average $\Delta G^{\ddagger}$ = 66.12 kJ/mol

1.4 Non-Appearance of [2+2] Cycloaddition of in-situ Generated Cx^{Et}Ge$_2$ and MeCN



Reactants				*Products*	
Formula	**$C_{60}H_{68}ClGe_2N_4P$**	**$C_{24}BF_{20}Na$**	**C_2H_3N**	Formula	**$C_{38}H_{51}Ge_2N_5$**
MW	1056,92	702,03	41,05	MW	723,12
Limiting?	***Yes***	No	No	Equivalents	
Equivalents	***1,00***	***1,00***	***100,00***	%Completion	
Sample Mass	***15,00mg***	9,96mg	58,26mg	Expected Mass	10,26mg
%Weight				Expected Moles	14,19µmol
Molarity				Measured Mass	
Density			***786,00mg/mL***	Purity	
Volume			74,13mmL	Product Mass	
Reactant Moles	14,19µmol	14,19µmol	1,42mmol	Product Moles	
Reactant Mass	15,00mg	9,96mg	58,26mg	%Yield	

In a J. Young NMR tube, **PPh$_4$[Cx^{Et}Ge$_2$Cl]**, NaB(C_6F_5)$_4$ and acetonitrile were mixed and dissolved in dichloromethane-*d2* (0.45 mL). The sample was then subjected to ^{1}H NMR spectroscopy at room temperature. Only one signal for the CH_3-group of acetonitrile belonging to the in-situ generated acetonitrile-digermene σ-adduct **Cx^{Et}Ge$_2$(CN-Me)** was observed. Therefore, it was concluded, that no cycloaddition occurred.

Furthermore, **Cx^{Et}Ge$_2$(CN-Me)** decomposes readily upon work-up of the crude product or in solution at room temperature, being in line with the weak donor ability of acetonitrile. The hypothetical [2+2] cycloaddition product would be expected to show a higher thermal stability.

^{1}H NMR (600 MHz, 298 K, dichloromethane-*d2*): δ = 5.47 (d, ^3J = 3.36 Hz, 2H, β-C*H*), 5.41 (d, ^3J = 3.27 Hz, 2H, β-C*H*), 5.36 (d, ^3J = 3.28 Hz, 2H, β-C*H*), 5.32 (d, ^3J = 3.27 Hz, 2H, β-C*H*), 2.18 – 2.05 (m, 2H, CH_2-ethyl), 2.03 – 1.96 (m, 2H, CH_2-ethyl), 1.94 – 1.77 (m, 4H, CH_2-ethyl), 1.51 (s, CH_3-

acetonitrile), 0.61 (t, ^3J = 7.25 Hz, 6H, *C*H_3-methyl), 0.52 – 0.40 (m, 9H, *C*H_3-methyl), 0.24 (t, ^3J = 7.21 Hz, 3H, *C*H_3-methyl), 0.19 – 0.12 (m, 6H, *C*H_3-methyl) ppm.

Note: The high excess of acetonitrile in the reaction mixture results in a very intense signal in the ^1H NMR spectra. Signals of the CH_2-ethyl groups (8 protons) of ***Cx^{Et}Ge$_2$(CN-Me)*** *are hidden below that signal and therefore, cannot be detected in the spectra.*

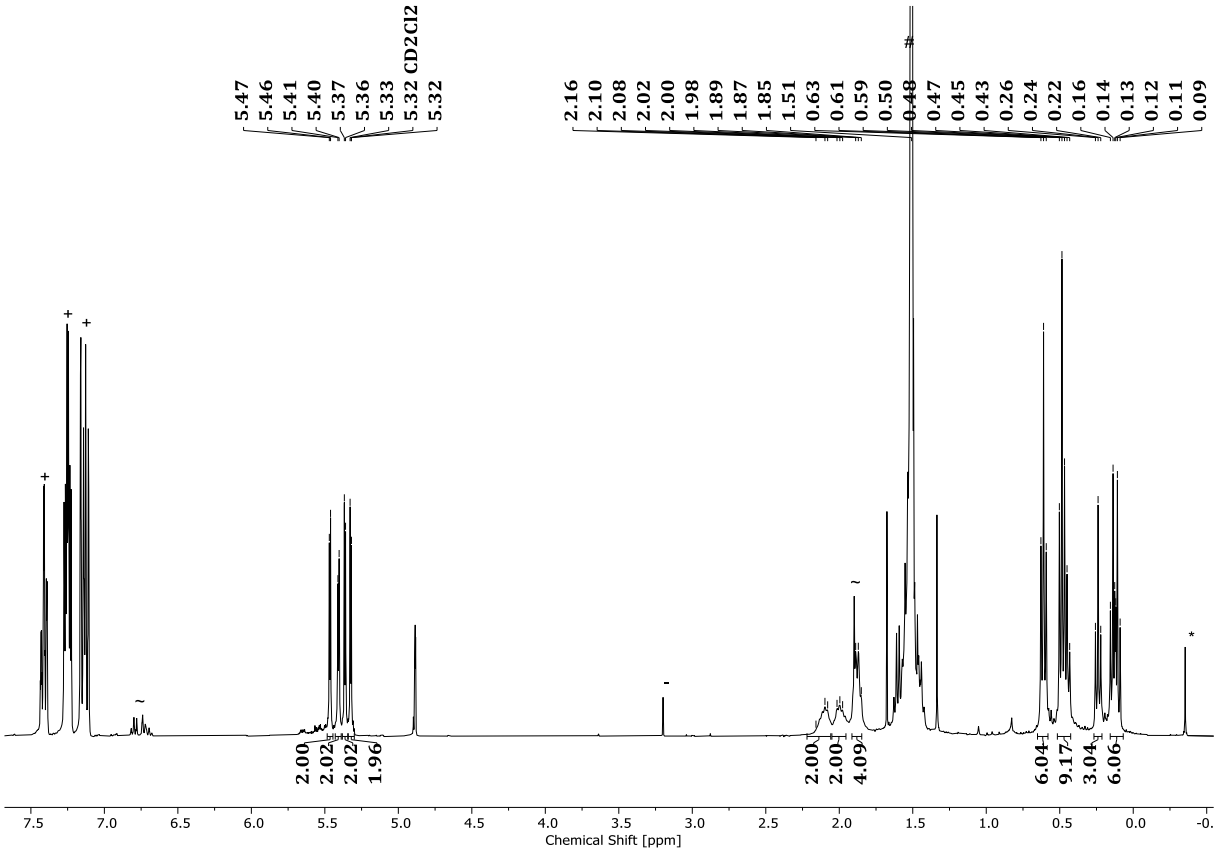
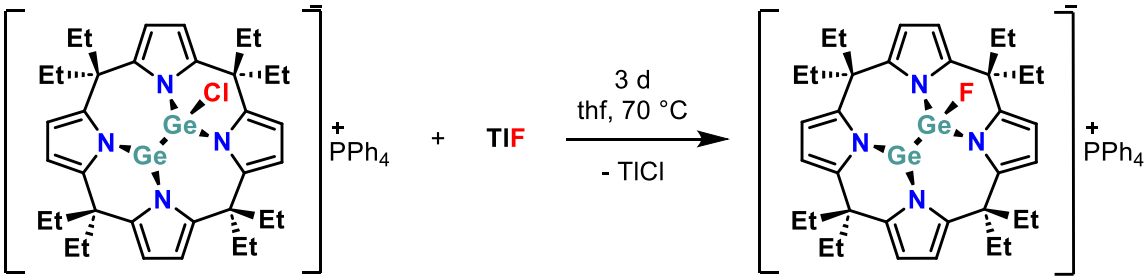


Figure S 1-77. ^{1}H NMR (600 MHz, 298 K, dichloromethane-*d2*) spectrum of Cx^{Et}Ge$_2$(CN-Me)**.** * = Silicon grease, + = $PPh_4B(C_6F_5)_4$, # excess acetonitrile, ~ toluene.

1.5 Experimental Determination of Lewis-Acidity

1.5.1 Synthesis of Tetraphenylphosphonium *meso*-Octaethylcalix[4]pyrrolato-2-fluorodigermanate $PPh_4[Cx^{Et}Ge_2F]$



Reactants			*Products*	
Formula	$C_{60}H_{68}ClGe_2N_4P$	FTl	Formula	$C_{60}H_{68}ClGe_2N_4P$
MW	1056.92	223.38	MW	1056.92
Limiting?	***Yes***	No	Equivalents	
Equivalents	***1.00***	***4.20***	%Completion	
Sample Mass	***26.40mg***	23.43mg	Expected Mass	26.40mg
%Weight			Expected Moles	24.98µmol
Molarity			Measured Mass	***19.80mg***
Density			Purity	***84.00%***
Volume			Product Mass	16.63mg
Reactant Moles	24.98µmol	104.91µmol	Product Moles	15.74µmol
Reactant Mass	26.40mg	23.43mg	%Yield	63.00%

$PPh_4[Cx^{Et}Ge_2Cl]$ and TlF were suspended in tetrahydrofuran (0.45 mL). The suspension was heated for 3 days at 70 °C and precipitation of a blue-greyish solid was observed which should correspond to TlCl. The suspension was filtrated using a syringe filter. The solvent of the filtrate was evaporated and the solid residue was dried in vacuo for 6 hours to yield the title compound as a colourless powder, which contains 0.75 eq. of TlF which could not be removed even after several extraction/filtration cycles.

Elemental Analysis of **$PPh_4[Cx^{Et}Ge_2Cl]$**: Calculated for **$PPh_4[Cx^{Et}Ge_2Cl]$** x 0.75 TlF [%]: C: 58.74; H: 5.59; N: 4.57. Found: C: 58.96; H: 5.51; N: 4.43.

ESI(–)-MS: Calculated for **$[Cx^{Et}Ge_2F]^-$**: 701.255. Found: 701.233 (dichloromethane).

^{1}H-NMR (400 MHz, 298 K, dichloromethane-*d2*): δ = 7.73 – 7.66 (m, 4H, *p*-PPh_4), 7.62 – 7.56 (m, 8H, *m*-PPh_4), 7.51 – 7.45 (m, 8H, *o*-PPh_4), 5.80 – 5.76 (m, 4H, β-C*H*), 5.67 – 5.63 (m, 4H, β-C*H*), 2.52 – 2.45 (m, 2H, CH_2-ethyl), 2.45 – 2.39 (m, 2H, CH_2-ethyl), 2.31 (q, ^3J = 7.3 Hz, 4H, CH_2-ethyl), 1.97 (q, ^3J = 7.1 Hz, 2H, CH_2-ethyl), 1.94 – 1.85 (m, 4H, CH_2-ethyl), 1.77 (q, ^3J = 7.4 Hz, 2H, CH_2-ethyl), 1.03 (t, ^3J = 7.3 Hz, 6H, CH_3-methyl), 0.89 (t, ^3J = 7.1 Hz, 6H, CH_3-methyl), 0.78 – 0.72 (m, 3H, CH_3-methyl), 0.59 – 0.54 (m, 6H, CH_3-methyl), 0.51 (t, ^3J = 7.4 Hz, 3H, CH_3-methyl) ppm.

^{13}C{^{1}H} NMR (151 MHz, 298 K, dichloromethane-*d2*): δ = 144.7 (C_q, α-*C*), 142.8 (C_q, α-*C*), 139.3 (C_q, α-*C*), 138.8 (C_q, α-*C*), 136.1 (d, $^3J(^{31}P,^{13}C)$ = 3.0 Hz, *p*-PPh_4), 134.7 (d, $^3J(^{31}P,^{13}C)$ = 10.2 Hz, *m*-

PPh_4), 130.9 (d, $^3J(^{31}P,^{13}C)$ = 12.9 Hz, *o*-PPh_4), 117.7 (d, $^3J(^{31}P,^{13}C)$ = 89.4 Hz, C_q, PPh_4), 105.4 (*C*H, β-C), 105.3 (*C*H, β-C), 105.1 (*C*H, β-C), 104.4 (*C*H, β-C), 44.9 (C_q, *meso*-C), 44.9 (C_q, 2C, *meso*-C), 44.5 (C_q, *meso*-C), 40.5 (CH_2-ethyl), 30.3 (CH_2-ethyl), 30.1 (CH_2-ethyl), 28.4 (CH_2-ethyl), 27.6 (CH_2-ethyl), 27.4 (CH_2-ethyl), 10.5 (CH_3-methyl), 9.8 (CH_3-methyl), 9.4 (CH_3-methyl), 9.4 (CH_3-methyl), 9.4 (CH_3-methyl), 9.4 (CH_3-methyl) ppm.

$^{31}P\{^1H\}$ NMR (162 MHz, 298 K, dichloromethane-*d2*): δ = 21.3 ppm.

^{19}F NMR (376 MHz, 298 K, dichloromethane-*d2*): δ = −145.2 ppm.

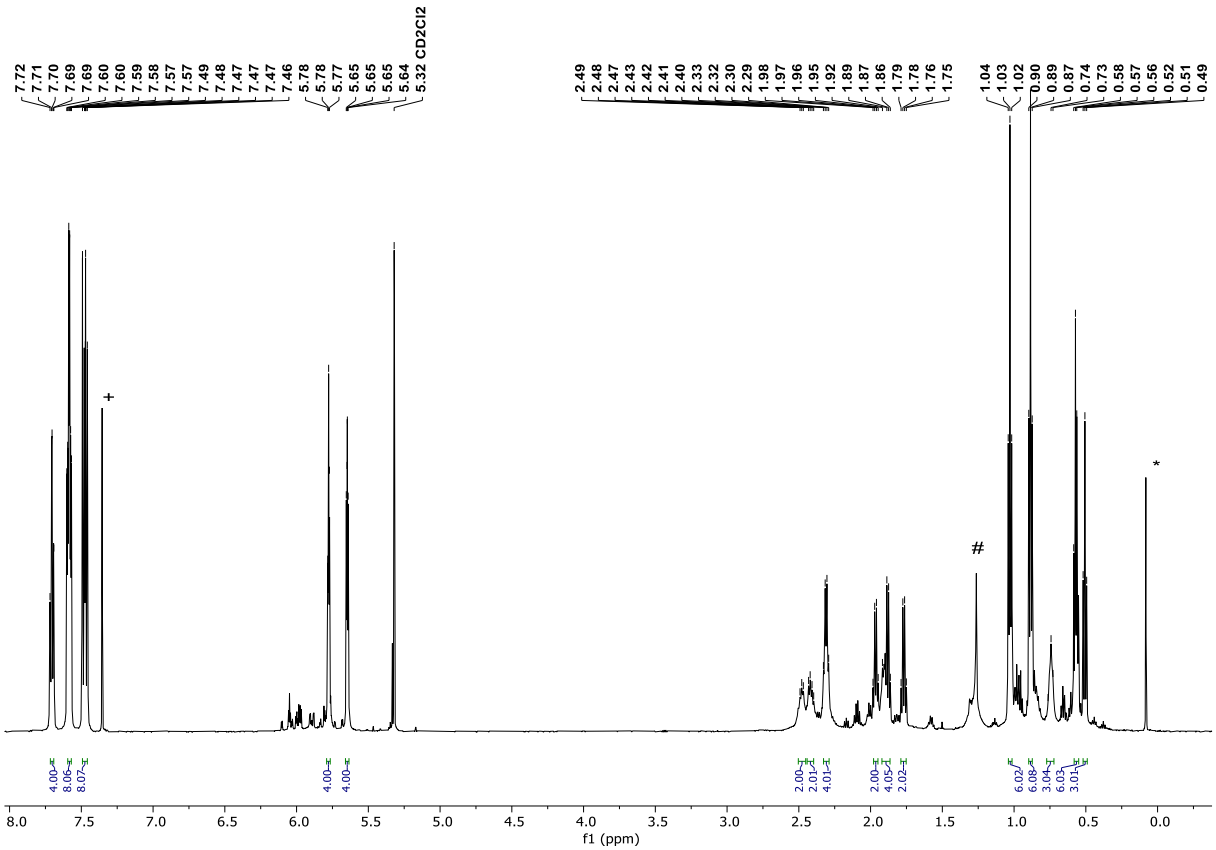


Figure S 1-78. ^1H NMR (600 MHz, 298 K, dichloromethane-*d2*) spectrum of **$PPh_4[Cx^{Et}Ge_2F]$. *** = Silicon grease, + = benzene, # = hexane.

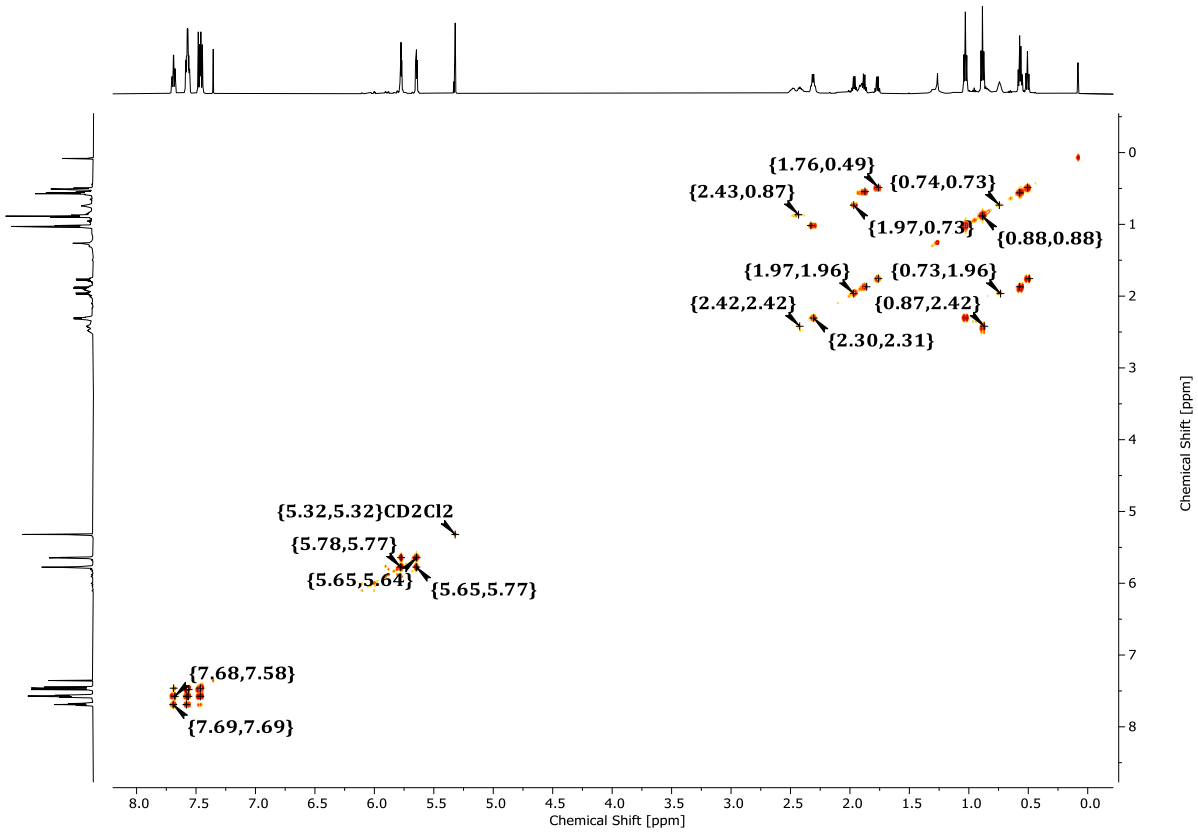


Figure S 1-79. ^{1}H-^{1}H COSY NMR (600 MHz, 298 K, dichloromethane-*d2*) spectrum of **PPh_4[Cx^{E}-$^{t}Ge_2F$].**

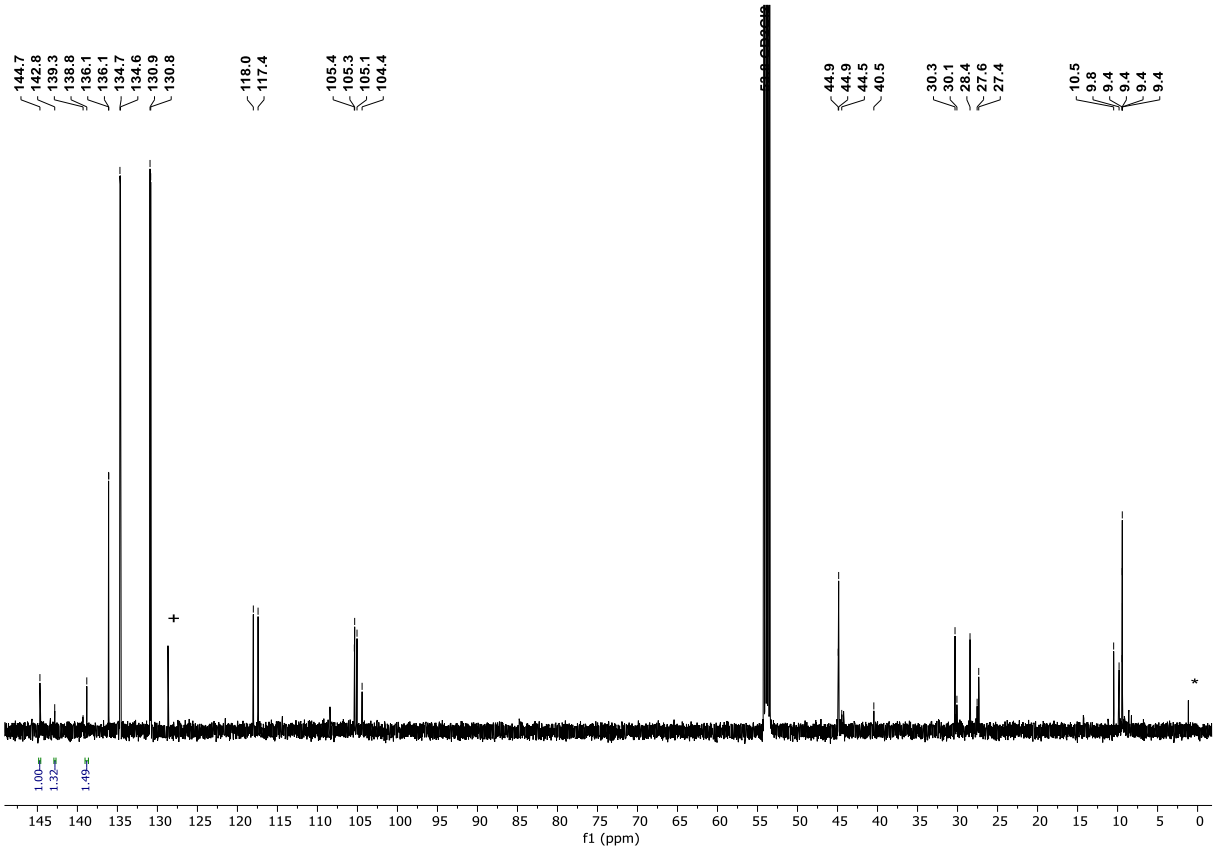


Figure S 1-80. ^{13}C{^{1}H} NMR (151 MHz, 298 K, dichloromethane-*d2*) spectrum of **PPh_4[$Cx^{Et}Ge_2F$].** + = Benzene, = silicon grease.

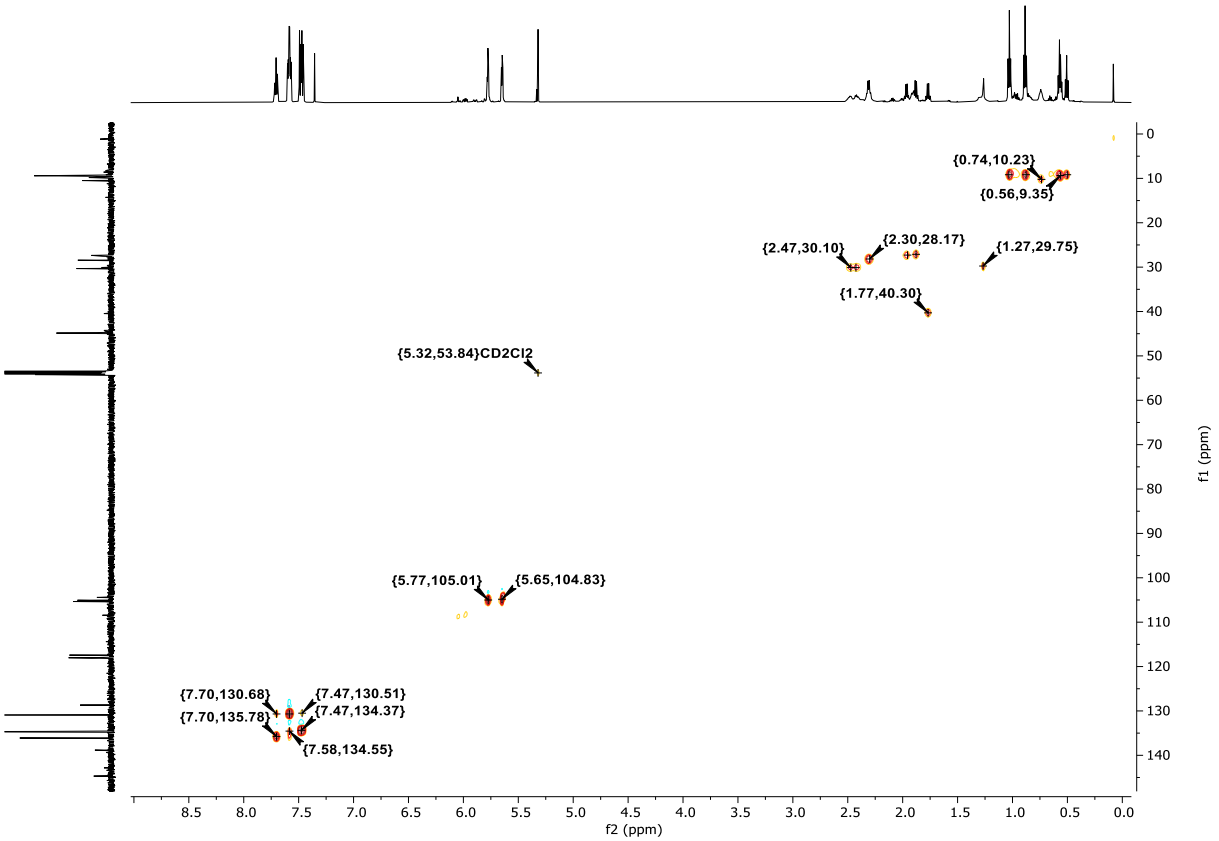


Figure S 1-81. ^{1}H-^{13}C HSQC NMR (600 MHz, 298 K, dichloromethane-*d2*) spectrum of **PPh$_4$[Cx^{E}-^{t}Ge$_2$F]**.

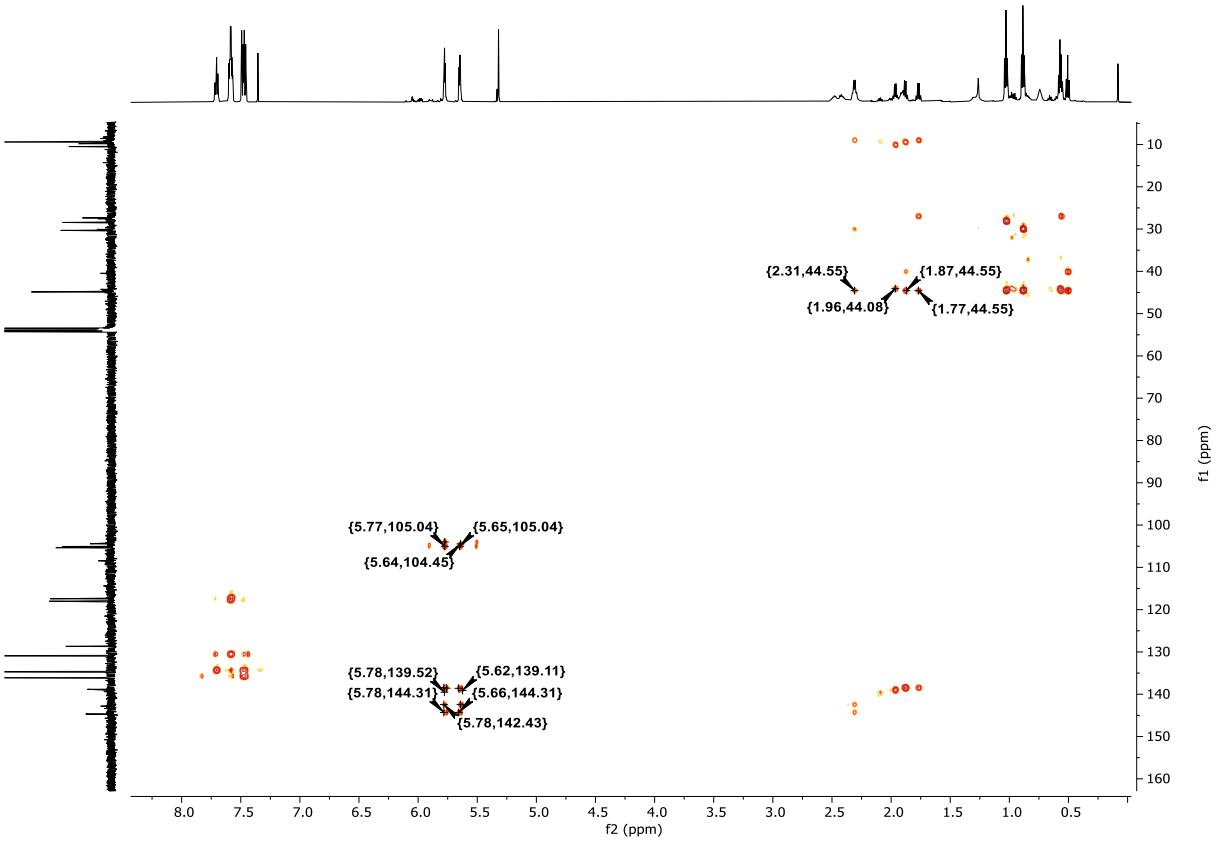


Figure S 1-82. ^{1}H-^{13}C HMBC NMR (600 MHz, 298 K, dichloromethane-*d2*) spectrum of **PPh$_4$[Cx^{E}-^{t}Ge$_2$F]**.

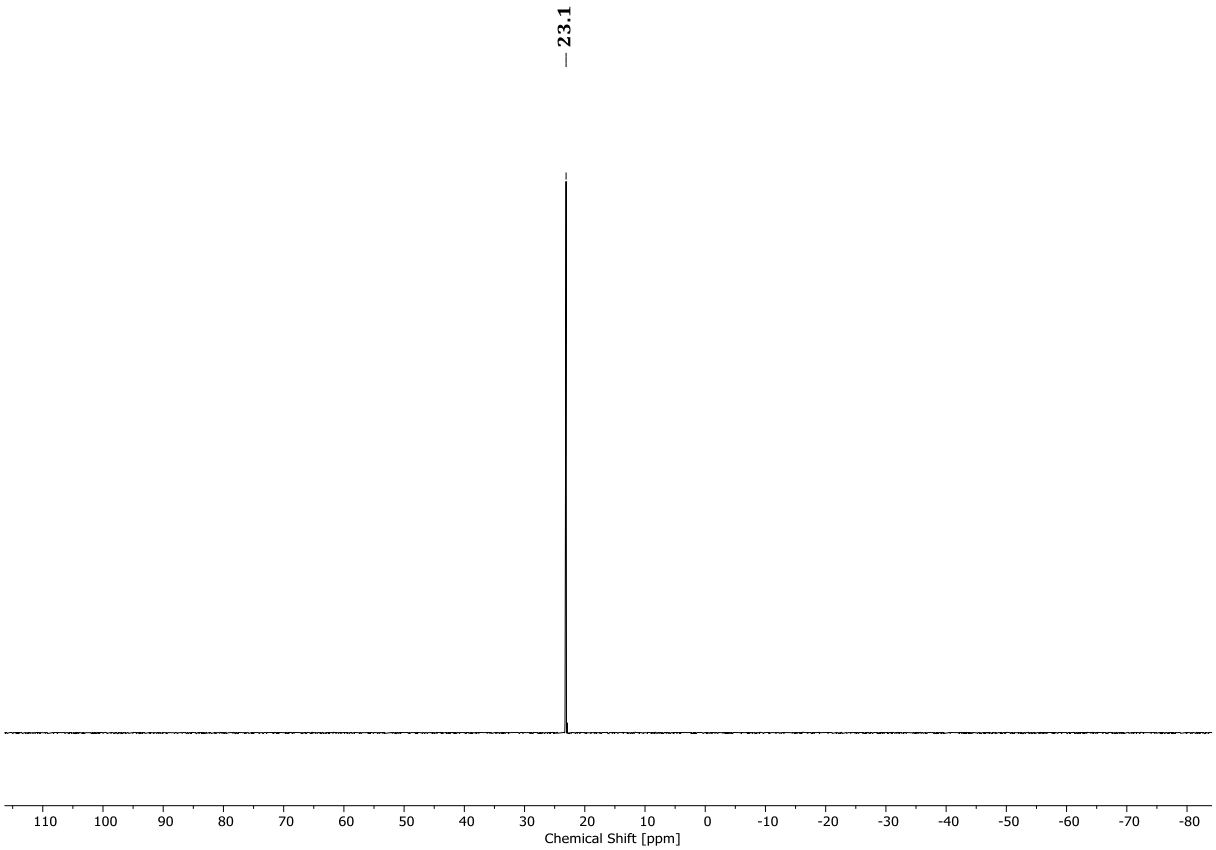


Figure S 1-83. $^{31}P\{^{1}H\}$ NMR (121 MHz, 298 K, dichloromethane-*d2*) spectrum of **$PPh_4[Cx^{Et}Ge_2F]$.**

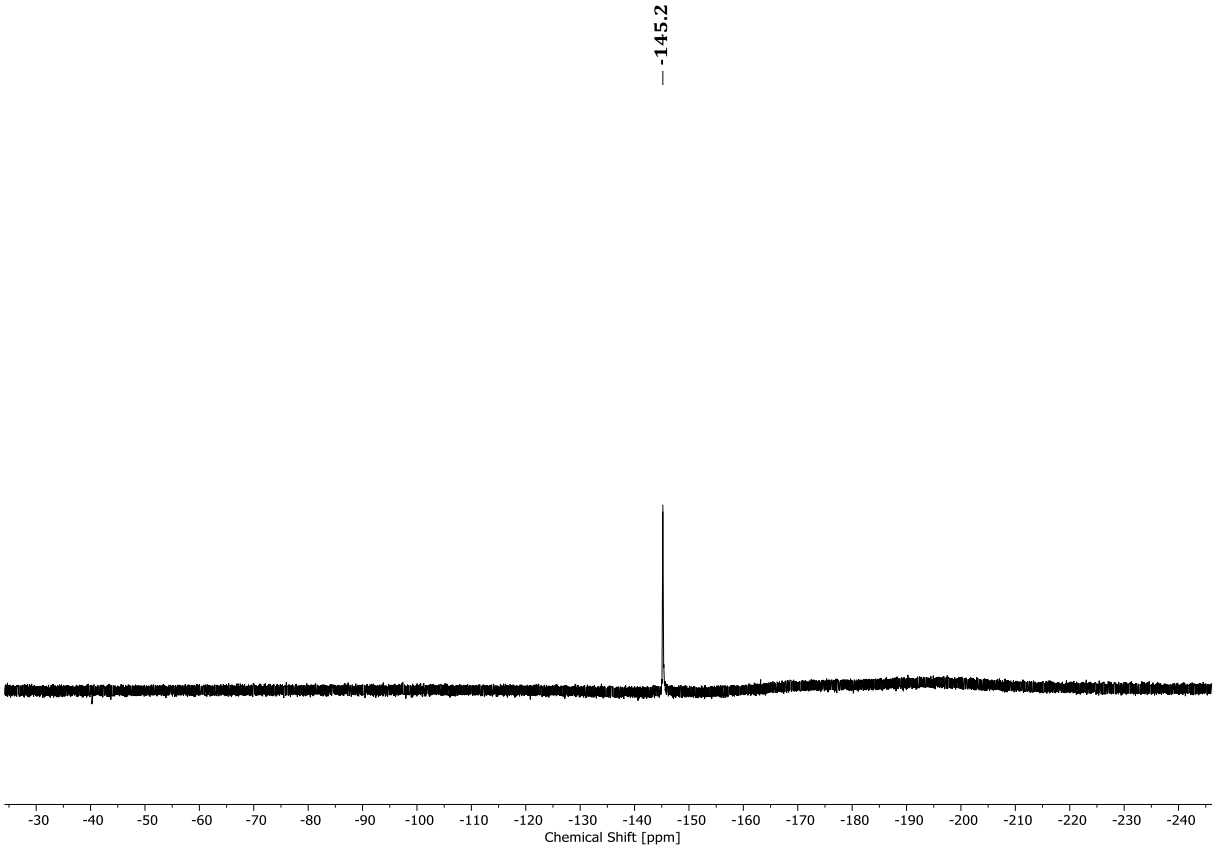
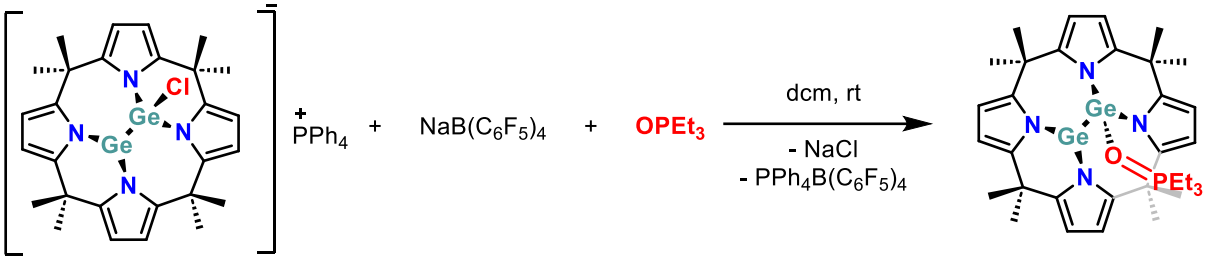


Figure S 1-84. ^{19}F NMR (376 MHz, 298 K, dichloromethane-*d2*) spectrum of **$PPh_4[Cx^{Et}Ge_2F]$.**

1.5.2 Gutmann-Beckett-Method: Synthesis of *meso*-Octamethylcalix[4]pyrrolato-1-triethylphosphineoxide-digermane $Cx^{Me}Ge_2(OPEt_3)$



Reactants				*Products*	
Formula	$C_{52}H_{52}ClGe_2N_4P$	$C_{24}BF_{20}Na$	$C_6H_{15}OP$	Formula	$C_{34}H_{47}Ge_2N_4OP$
MW	944.70	702.03	134.16	MW	704.01
Limiting?	***Yes***	No	No	Equivalents	
Equivalents	***1.00***	***1.00***	***1.00***	%Completion	
Sample Mass	***20.00mg***	14.86mg	2.84mg	Expected Mass	14.90mg
%Weight				Expected Moles	21.17µmol
Molarity				Measured Mass	
Density				Purity	
Volume				Product Mass	
Reactant Moles	21.17µmol	21.17µmol	21.17µmol	Product Moles	
Reactant Mass	20.00mg	14.86mg	2.84mg	%Yield	

$PPh_4[Cx^{Me}Ge_2Cl]$, $NaB(C_6F_5)_4$ and triethylphosphine oxide ($OPEt_3$) were suspended in dichloromethane-*d2* (0.45 mL). The mixture turned turbid due to the precipitation of NaCl. The mixture was stirred for 15 minutes. Further work-up was not performed.

^{1}H NMR (400 MHz, 298 K, dichloromethane-*d2*): δ = 5.95 (d, *J* = 3.4 Hz, 1H), 5.89 (d, ^3J = 3.3 Hz, , 2H, β-C*H*), 5.86 (d, *J* = 3.3 Hz, , 2H, β-C*H)*, 5.78 (d, *J* = 3.3 Hz, , 2H, β-C*H*), 2.03 (s, 6H, *C*H_3-methyl), 2.01 – 1.89 (m, 6H, *C*H_2-$OPEt_3$), 1.87 (s, 6H, *C*H_3-methyl), 1.63 (s, 3H, *C*H_3-methyl), 1.60 (s, 3H, *C*H_3-methyl), 1.44 (s, 3H, *C*H_3-methyl), 1.42 (s, 3H, *C*H_3-methyl), 1.06 (t, ^3J = 7.7 Hz, 3H, *C*H_3-$OPEt_3$), 1.02 (t, ^3J = 7.7 Hz, 6H, *C*H_3-$OPEt_3$) ppm.

^{31}P{^{1}H} NMR (162 MHz, 298 K, dichloromethane-*d2*): δ = 79.3 ppm.

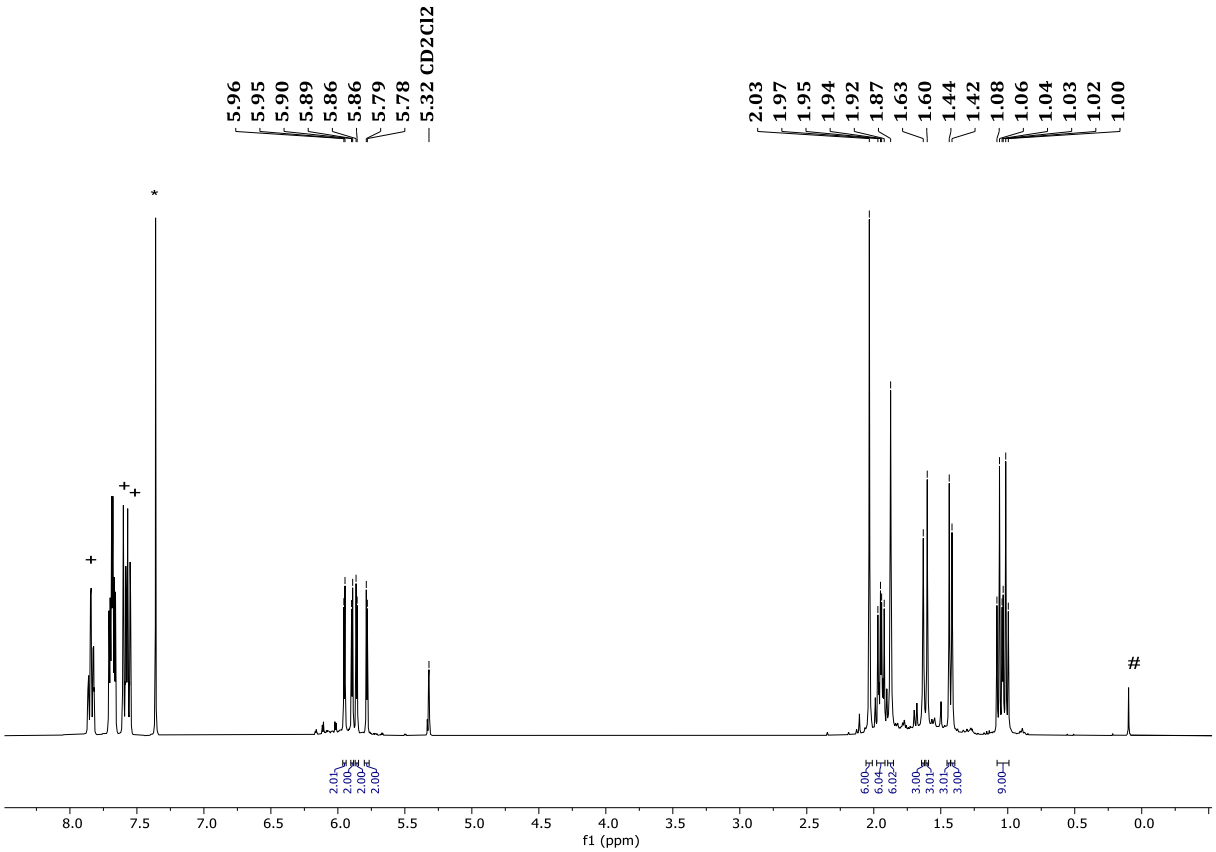


Figure S 1-85. ^{1}H NMR (600 MHz, 298 K, dichloromethane-*d2*) spectrum of **Cx^{Me}Ge$_2$(OPEt$_3$).** * = Benzene, + = $PPh_4B(C_6F_5)_4$, # = silicon grease.

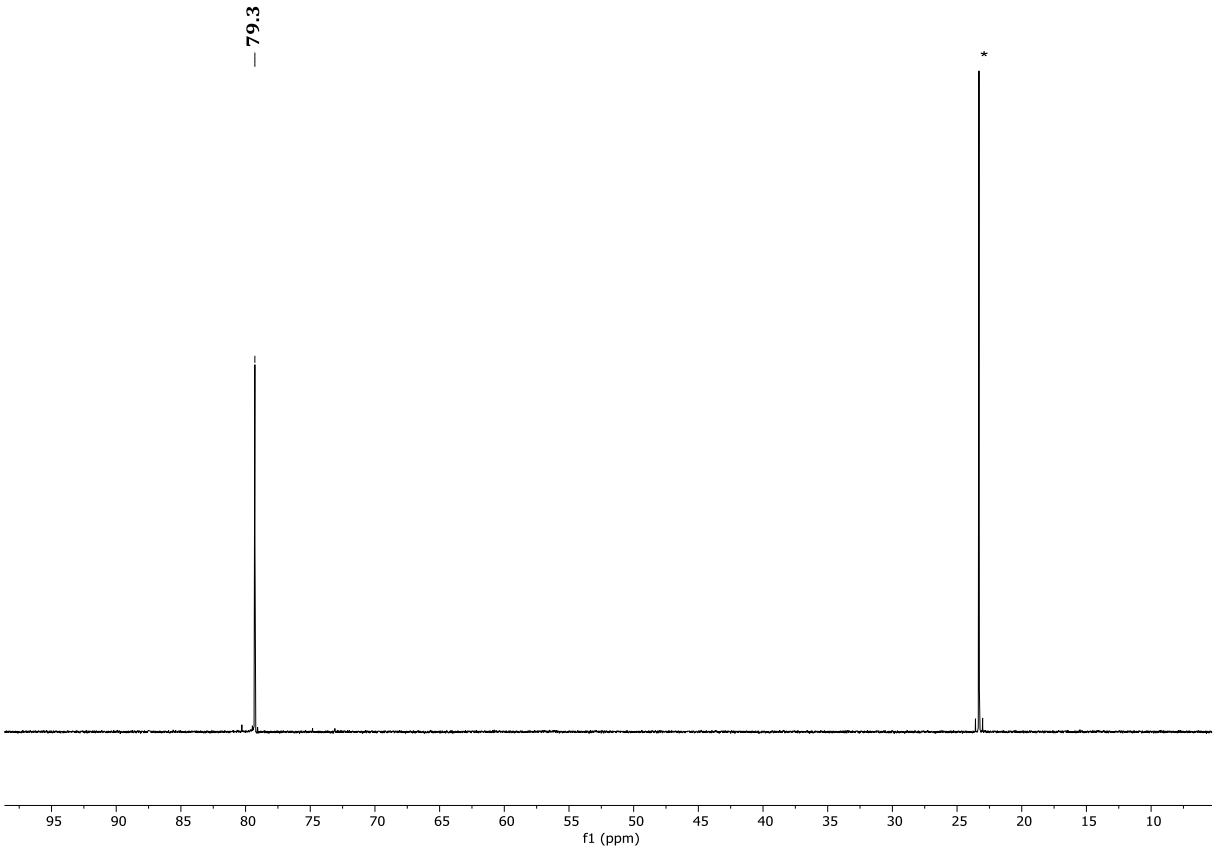
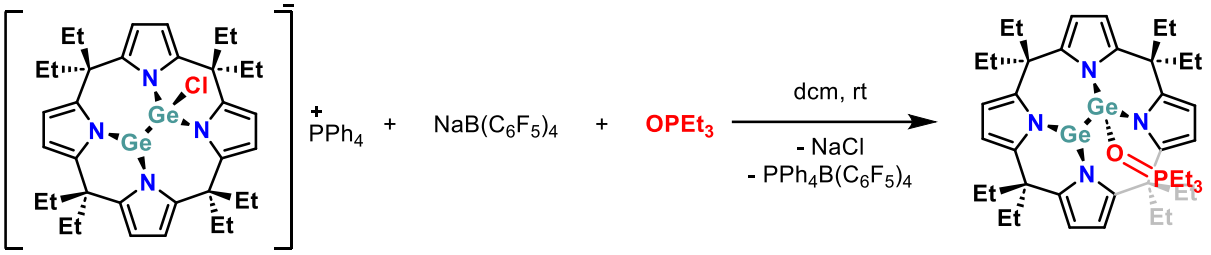


Figure S 1-86. ^{31}P{^{1}H} NMR (162 MHz, 298 K, dichloromethane-*d2*) spectrum of **Cx^{Me}Ge$_2$(OPEt$_3$).** * = $PPh_4B(C_6F_5)_4$.

1.5.3 Gutmann-Beckett-Method: Synthesis of *meso*-Octaethylcalix[4]pyrrolato-1-triethylphosphineoxide-digermane $Cx^{Et}Ge_2(OPEt_3)$



Reactants				*Products*	
Formula	$C_{60}H_{68}ClGe_2N_4P$	$C_{24}BF_{20}Na$	$C_6H_{15}OP$	Formula	$C_{42}H_{63}Ge_2N_4OP$
MW	1056.92	702.03	134.16	MW	816.23
Limiting?	***Yes***	No	No	Equivalents	
Equivalents	***1.00***	***1.00***	***1.00***	%Completion	
Sample Mass	***15.00mg***	9.96mg	1.90mg	Expected Mass	11.58mg
%Weight				Expected Moles	14.19µmol
Molarity				Measured Mass	
Density				Purity	
Volume				Product Mass	
Reactant Moles	14.19µmol	14.19µmol	14.19µmol	Product Moles	
Reactant Mass	15.00mg	9.96mg	1.90mg	%Yield	

$PPh_4[Cx^{Et}Ge_2Cl]$, $NaB(C_6F_5)_4$ and triethylphosphine oxide ($OPEt_3$) were suspended in dichloromethane-*d2* (0.45 mL). The mixture turned turbid due to the precipitation of NaCl. The mixture was stirred for 15 minutes. Further work-up was not performed.

*Note: **$Cx^{Et}Ge_2(OPEt_3)$** decomposes readily in solution (dichloromethane or benzene) over the period of 24 hours at room temperature forming $Cx^{Et}H_4$. Attempts to isolate the title compound led to unselective decomposition.*

^{1}H NMR (400 MHz, 298 K, dichloromethane-*d2*): δ = 5.93 (d, ^3J = 3.4 Hz, 1H), 5.89 (d, ^3J = 3.3 Hz, 2H, β-C*H*), 5.83 (d, *J* = 3.4 Hz, , 2H, β-C*H)*, 5.76 (d, *J* = 3.4 Hz, 2H, β-C*H*), 2.59 – 2.50 (m, 4H, CH_2-ethyl), 2.21 – 2.14 (m, 4H, CH_2-ethyl), 2.06 – 1.85 (m, 10H, 2xCH_2-ethyl, 3xCH_2-$OPEt_3$), 1.71 – 1.62 (m, 4H, CH_2-ethyl), 1.18 – 1.06 (m, 18H, 3xCH_3-methyl, 3xCH_3-$OPEt_3$), 1.00 (t, ^3J = 7.2 Hz, 3H, CH_3-methyl), 0.92 – 0.88 (m,3H, CH_3-methyl), 0.66 (t, *J* = 7.5 Hz, 3H, CH_3-methyl), 0.63 – 0.56 (m, 6 H, CH_3-methyl) ppm.

^{31}P{^{1}H} NMR (162 MHz, 298 K, dichloromethane-*d2*): δ = 76.9 ppm.

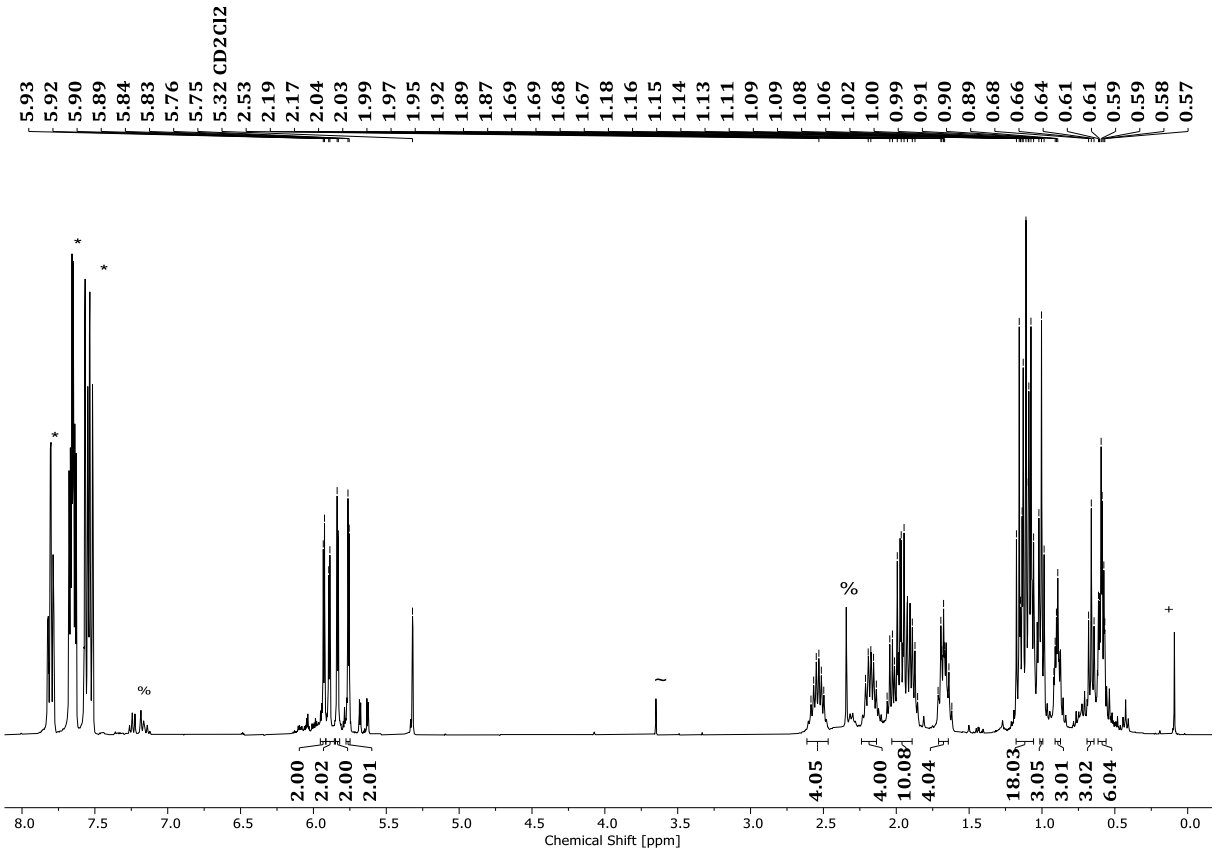


Figure S 1-87. ^{1}H NMR (600 MHz, 298 K, dichloromethane-*d2*) spectrum of **Cx^{Et}Ge$_2$(OPEt$_3$).** * = $PPh_4B(C_6F_5)_4$, + = silicon grease, % = toluene, ~ 1,4-dioxane.

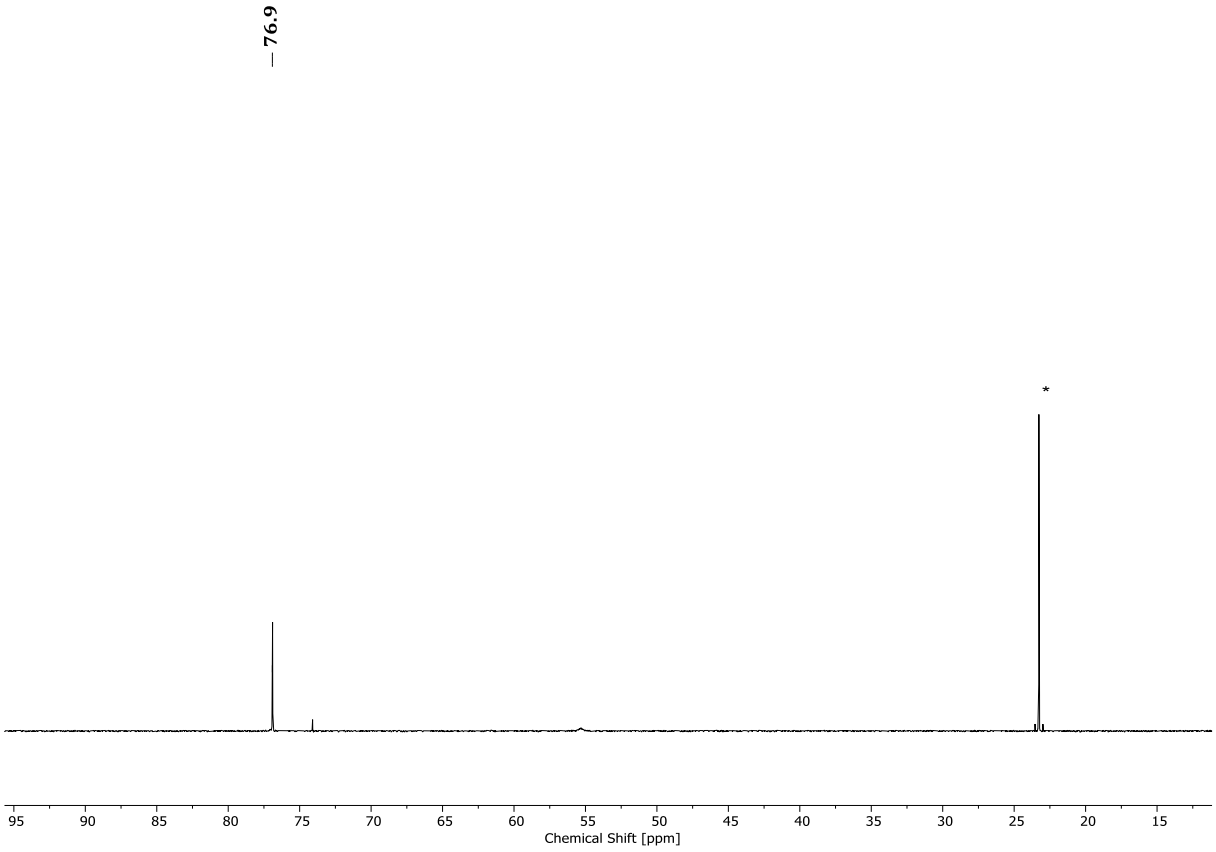


Figure S 1-88. ^{31}P{^{1}H} NMR (162 MHz, 298 K, dichloromethane-*d2*) spectrum of **Cx^{Et}Ge$_2$(OPEt$_3$).** * = $PPh_4B(C_6F_5)_4$.

Note: For $B(C_6F_5)_3$ a shift of $\delta(^{31}P)$ = 77.0 ppm and therefore, a difference of $\Delta\delta(^{31}P)$ = 26.5 ppm is reported.[6]

2 X-Ray Diffraction

2.1 General Information

Single crystal X-ray diffraction data were collected using Bruker D8 VENTURE with PHOTONIII detector, D8 Goniometer and INCOATEC Mo/Cu micro source. Crystals were selected under perfluoropolyether oil, mounted on 0.1 to 0.3 mm diameter CryoLoops and quench-cooled using an Oxford Cryostream 800 open flow N_2 cooling device.[7] Data were collected at 100 K using monochromated Cu Kα or Mo Kα radiation (λ = 1.5418/0.71073 Å). Data processing was done with SHELXS/XL, solved by direct method using SHELXT and refined by least squares on weighted F^2 values for all reflections by SHELXL, SHELXLE, disordering of fragments was done with the help of the implemented DSR tool.[8-9] Finalisation of gathered data was done using final cif tool.[10]

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+(44)1223-336-033; email: deposit@ccdc.cam.ac.uk).

2.2 Crystal Data and Refinement

Table S 2-1: Crystal data and structural refinements.

Name	$Cx^{Et}Ge_2Cl_2$	$Cx^{Et}Ge_2I_2$	K@18-c-6[$Cx^{Et}Ge_2I$]	PPh4[Cx^{Me}Ge2Cl]
CCDC number	2499817	2499816	2499829	2499824
Empirical formula	$C_{37}H_{50}Cl_{3.94}Ge_2I_{0.06}N_4$	$C_{40}H_{56}Ge_2I_2N_4O$	$C_{52}H_{80}Cl_{0.27}Ge_2I_{0.73}KN_4O_7$	$C_{53}H_{54}Cl_3Ge_2N_4P$
Formula weight	843.55	1007.86	1159.47	1029.50
Temperature [K]	100(2)	100.00	100(2)	100(2)
Crystal system	triclinic	triclinic	monoclinic	monoclinic
Space group (number)	$P\bar{1}$ (2)	$P\bar{1}$ (2)	(15)	(14)
a [Å]	10.782(4)	11.3938(6)	47.485(3)	11.1398(6)
b [Å]	11.301(4)	11.4590(6)	12.1551(8)	23.5832(11)
c [Å]	17.138(4)	15.8680(9)	24.9506(17)	18.5946(10)
α [°]	84.468(11)	82.263(2)	90	90
β [°]	87.777(7)	71.339(2)	119.561(2)	93.118(2)
γ [°]	63.21(2)	86.998(2)	90	90
Volume [Å^3]	1855.4(11)	1944.87(18)	12526.5(14)	4877.8(4)
Z	2	2	8	4
ρ_{calc} [gcm^{-3}]	1.510	1.721	1.230	1.402
μ [mm^{-1}]	1.989	3.170	1.442	1.470
F(000)	869	1004	4818	2120

Crystal size [mm^3]	0.105×0.119×0.121	0.168×0.231×0.427	0.11×0.18×0.32	0.055×0.148×0.213
Crystal colour	colourless	clear yellow	colourless	colourless
Crystal shape	block	block	block	block
Radiation	MoK_α (λ=0.71073 Å)	MoK_α (λ=0.71073 Å)	MoK_α (λ=0.71073 Å)	MoK_α (λ=0.71073 Å)
2θ range [°]	4.05 to 57.58 (0.74 Å)	3.90 to 54.37 (0.78 Å)	3.73 to 61.02 (0.70 Å)	4.05 to 57.59 (0.74 Å)
Index ranges	−14 ≤ h ≤ 14 −15 ≤ k ≤ 15 −23 ≤ l ≤ 23	−13 ≤ h ≤ 14 −14 ≤ k ≤ 14 0 ≤ l ≤ 20	−67 ≤ h ≤ 67 −17 ≤ k ≤ 17 −33 ≤ l ≤ 35	−15 ≤ h ≤ 15 −31 ≤ k ≤ 31 −25 ≤ l ≤ 25
Reflections collected	105380	8651	437112	321535
Independent reflections	9670 R_{int} = 0.0563 R_{sigma} = 0.0257	8651 R_{int} = 0.0671 R_{sigma} = 0.0193	19038 R_{int} = 0.0730 R_{sigma} = 0.0305	12688 R_{int} = 0.0802 R_{sigma} = 0.0222
Completeness to θ = 25.242°	100.0 %	99.9 %	99.9 %	100.0 %
Data / Restraints / Parameters	9670 / 0 / 440	8651 / 150 / 484	19038 / 1429 / 832	12688 / 26 / 604
Absorption correction T_{min}/T_{max} (method)	0.6948 / 0.7458 (multi-scan)	0.4785 / 0.7455 (multi-scan)	0.6435 / 0.7461 (multi-scan)	0.6740 / 0.7458 (multi-scan)
Goodness-of-fit on F^2	1.047	1.076	1.100	1.118
Final R indexes [I≥2σ(I)]	R_1 = 0.0299 wR_2 = 0.0733	R_1 = 0.0297 wR_2 = 0.0757	R_1 = 0.0582 wR_2 = 0.1451	R_1 = 0.0484 wR_2 = 0.1048
Final R indexes [all data]	R_1 = 0.0367 wR_2 = 0.0769	R_1 = 0.0321 wR_2 = 0.0769	R_1 = 0.0854 wR_2 = 0.1607	R_1 = 0.0550 wR_2 = 0.1078
Largest peak/hole [eÅ^{-3}]	0.83/−0.38	0.90/−1.01	1.20/−1.12	1.51/−1.12

Table S 2-2: Crystal data and structural refinements.

Name	$PPh_4[Cx^{Et}Ge_2Cl]$	$CxEtGe_2(NH_3)$	$Cx^{Et}Ge_2$(pip-CN)	$Cx^{Et}Ge_2$(pyridine)
CCDC number	2499828	2499827	2499823	2499822
Empirical formula	$C_{61}H_{70}Cl_3Ge_2N_4P$	$C_{36}H_{51}Ge_2N_5$	$C_{47}H_{70}Ge_2N_6$	$C_{46}H_{65}Ge_2N_5$
Formula weight	1141.71	698.99	864.27	833.21
Temperature [K]	100(2)	100(2)	100(2)	100(2)
Crystal system	Triclinic	monoclinic	triclinic	monoclinic
Space group (number)	$P\overline{1}$ (2)	(14)	$P\overline{1}$ (2)	(14)
a [Å]	11.3256(4)	19.116(4)	11.1727(10)	12.3991(7)
b [Å]	12.5180(5)	6.8224(17)	11.6755(10)	14.9407(7)
c [Å]	20.4239(9)	25.135(7)	19.2313(17)	22.6663(11)
α [°]	87.596(2)	90	95.877(4)	90
β [°]	79.208(2)	90.124(7)	99.533(4)	99.797(2)
γ [°]	74.705(2)	90	115.171(3)	90
Volume [Å^3]	2743.53(19)	3278.1(15)	2196.7(3)	4137.7(4)
Z	2	4	2	4
ρ_{calc} [gcm^{-3}]	1.382	1.416	1.307	1.338
μ [mm^{-1}]	1.314	1.867	1.408	1.491
F(000)	1188	1464	916	1760
Crystal size [mm^3]	0.159×0.089×0.037	0.15×0.10×0.08	0.112×0.158×0.583	0.176×0.170×0.052
Crystal colour	colourless	colourless	colourless	yellow
Crystal shape	block	block	block	block
Radiation	MoK_α (λ=0.71073 Å)	MoK_α (λ=0.71073 Å)	MoK_α (λ=0.71073 Å)	MoK_α (λ=0.71073 Å)
2θ range [°]	3.92 to 57.58 (0.74 Å)	4.56 to 59.46 (0.72 Å)	4.11 to 57.61 (0.74 Å)	4.06 to 57.60 (0.74 Å)
Index ranges	−15 ≤ h ≤ 15 −16 ≤ k ≤ 16 −27 ≤ l ≤ 27	−26 ≤ h ≤ 26 −9 ≤ k ≤ 9 −34 ≤ l ≤ 34	−15 ≤ h ≤ 15 −15 ≤ k ≤ 15 −26 ≤ l ≤ 26	−16 ≤ h ≤ 16 −20 ≤ k ≤ 20 −30 ≤ l ≤ 30
Reflections collected	204192	190248	194682	162906
Independent reflections	14270 R_{int} = 0.0878 R_{sigma} = 0.0350	9279 R_{int} = 0.1053 R_{sigma} = 0.0348	11417 R_{int} = 0.0760 R_{sigma} = 0.0258	10776 R_{int} = 0.0691 R_{sigma} = 0.0254
Completeness to θ = 25.242°	100.0 %	99.9 %	99.8 %	100.0 %
Data / Restraints / Parameters	14270/947/686	9279/3126/771	11417 / 0 / 506	10776/0/488
Absorption correction T_{min}/T_{max} (method)	0.65/0.7458 (multi-scan)	0.5877/0.7459 (multi-scan)	0.6044 / 0.7458 (multi-scan)	0.6676/0.7458 (multi-scan)
Goodness-of-fit on F^2	1.322	1.106	1.115	1.024
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0751 wR_2 = 0.1668	R_1 = 0.0531 wR_2 = 0.1227	R_1 = 0.0335 wR_2 = 0.0782	R_1 = 0.0289 wR_2 = 0.0677
Final *R* indexes [all data]	R_1 = 0.0807 wR_2 = 0.1689	R_1 = 0.0567 wR_2 = 0.1246	R_1 = 0.0376 wR_2 = 0.0806	R_1 = 0.0368 wR_2 = 0.0718
Largest peak/hole [eÅ^{-3}]	0.94/−1.59	1.06/−2.04	0.71/−1.05	0.57/−0.32

Table S 2-3: Crystal data and structural refinements.

Name	$PPh_4[Cx^{Et}Ge_2ClS]$	$PPh_4[Cx^{Et}Ge_2ClSe]$	$PPh_4[Cx^{Et}Ge_2ClNi(CO)_3]$
CCDC number	2499821	2499819	2499826
Empirical formula	$C_{42}H_{44}Ge_2N_4$	$C_{42}H_{44}Ge_2N_4$	$C_{52}H_{54}ClGe_2N_4P$
Formula weight	749.99	749.99	946.59
Temperature [K]	100(2)	100(2)	100(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group (number)	(14)	(14)	(14)

a [Å]	9.7110(9)	9.7110(9)	10.8756(5)
b [Å]	16.7873(14)	16.7873(14)	19.3147(7)
c [Å]	21.351(2)	21.351(2)	21.5382(10)
α [°]	90	90	90
β [°]	99.318(4)	99.318(4)	96.082(2)
γ [°]	90	90	90
Volume [Å^3]	3434.7(5)	3434.7(5)	4498.8(3)
Z	4	4	4
ρ_{calc} [gcm^{-3}]	1.450	1.450	1.398
μ [mm^{-1}]	1.788	1.788	1.472
F(000)	1552	1552	1960
Crystal size [mm^3]	0.044×0.079×0.094	0.044×0.079×0.094	0.098×0.178×0.251
Crystal colour	colourless	colourless	colourless
Crystal shape	block	block	block
Radiation	MoK_α (λ=0.71073 Å)	MoK_α (λ=0.71073 Å)	MoK_α (λ=0.71073 Å)
2θ range [°]	4.56 to 59.39 (0.72 Å)	4.56 to 59.39 (0.72 Å)	4.55 to 60.27 (0.71 Å)
Index ranges	−13 ≤ h ≤ 13 −23 ≤ k ≤ 23 −29 ≤ l ≤ 29	−13 ≤ h ≤ 13 −23 ≤ k ≤ 23 −29 ≤ l ≤ 29	−15 ≤ h ≤ 15 −27 ≤ k ≤ 27 −30 ≤ l ≤ 30
Reflections collected	107515	107515	404114
Independent reflections	9708 R_{int} = 0.0906 R_{sigma} = 0.0401	9708 R_{int} = 0.0906 R_{sigma} = 0.0401	13247 R_{int} = 0.0687 R_{sigma} = 0.0183
Completeness to θ = 25.242°	99.9 %	99.9 %	99.7 %
Data / Restraints / Parameters	9708 / 0 / 441	9708 / 0 / 441	13247 / 390 / 604
Absorption correction T_{min}/T_{max} (method)	0.6163 / 0.7459 (multi-scan)	0.6163 / 0.7459 (multi-scan)	0.6794 / 0.7460 (multi-scan)
Goodness-of-fit on F^2	1.084	1.084	1.114
Final *R* indexes [I≥2σ(I)]	R_1 = 0.0398 wR_2 = 0.0872	R_1 = 0.0398 wR_2 = 0.0872	R_1 = 0.0367 wR_2 = 0.0876
Final *R* indexes [all data]	R_1 = 0.0536 wR_2 = 0.0925	R_1 = 0.0536 wR_2 = 0.0925	R_1 = 0.0405 wR_2 = 0.0896
Largest peak/hole [eÅ^{-3}]	0.68/−0.84	0.68/−0.84	0.82/−0.97

Table S 2-4: Crystal data and structural refinements.

Name	$Cx^{Me}Ge_2(SMe)_2$	$Cx^{Me}Ge_2(PhCCH)$	$Cx^{Me}Ge(Cl)Ge(PPh_2)$
CCDC number	2499820	2499818	2499825
Empirical formula	$C_{31}H_{40}Cl_2Ge_2N_4S_2$	$C_{64}H_{76}ClGe_2N_4OPSe$	$C_{72.81}H_{88}ClGe_2N_4Ni_{0.94}O_{5.31}P$
Formula weight	748.87	1207.84	1370.65
Temperature [K]	100(2)	100(2)	100(2)
Crystal system	triclinic	triclinic	monoclinic
Space group (number)	$P\bar{1}$ (2)	$P\bar{1}$ (2)	(15)
a [Å]	9.5721(7)	11.674(3)	38.123(3)
b [Å]	12.9117(10)	12.597(3)	12.6709(11)
c [Å]	15.7082(12)	23.374(6)	29.096(3)

α [°]	83.625(3)	96.224(9)	90
β [°]	79.820(3)	101.076(9)	99.909(3)
γ [°]	83.824(3)	104.174(8)	90
Volume [Å^3]	1891.3(2)	3226.6(13)	13845(2)
Z	2	2	8
ρ_{calc} [gcm^{-3}]	1.315	1.243	1.315
μ [mm^{-1}]	1.865	1.602	1.229
F(000)	768	1252	5740
Crystal size [mm^3]	0.045×0.135×0.165	0.099×0.205×0.326	0.082×0.193×0.231
Crystal colour	colourless	colourless	colourless
Crystal shape	block	plate	plate
Radiation	MoK_α (λ=0.71073 Å)	MoK_α (λ=0.71073 Å)	MoK_α (λ=0.71073 Å)
2θ range [°]	3.95 to 58.52 (0.73 Å)	3.72 to 50.70 (0.83 Å)	4.30 to 50.05 (0.84 Å)
Index ranges	−13 ≤ h ≤ 13 −17 ≤ k ≤ 17 −21 ≤ l ≤ 21	−14 ≤ h ≤ 14 −15 ≤ k ≤ 15 −28 ≤ l ≤ 28	−45 ≤ h ≤ 43 −15 ≤ k ≤ 15 −34 ≤ l ≤ 34
Reflections collected	133434	122466	234304
Independent reflections	10294 R_{int} = 0.0743 R_{sigma} = 0.0300	11627 R_{int} = 0.0596 R_{sigma} = 0.0285	12204 R_{int} = 0.1114 R_{sigma} = 0.0339
Completeness to θ = 25.242°	100.0 %	98.5 %	99.9 %
Data / Restraints / Parameters	10294 / 65 / 408	11627 / 30 / 716	12204 / 865 / 930
Absorption correction T_{min}/T_{max} (method)	0.6389 / 0.7458 (multi-scan)	0.6477 / 0.7453 (multi-scan)	0.6268 / 0.7458 (multi-scan)
Goodness-of-fit on F^2	1.056	1.011	1.101
Final R indexes [I≥2σ(I)]	R_1 = 0.0401 wR_2 = 0.0977	R_1 = 0.0623 wR_2 = 0.1661	R_1 = 0.0573 wR_2 = 0.1377
Final R indexes [all data]	R_1 = 0.0465 wR_2 = 0.1010	R_1 = 0.0686 wR_2 = 0.1698	R_1 = 0.0660 wR_2 = 0.1432
Largest peak/hole [eÅ^{-3}]	1.05/−0.78	0.72/−1.10	1.71/−1.01

2.3 Single Crystal Structures

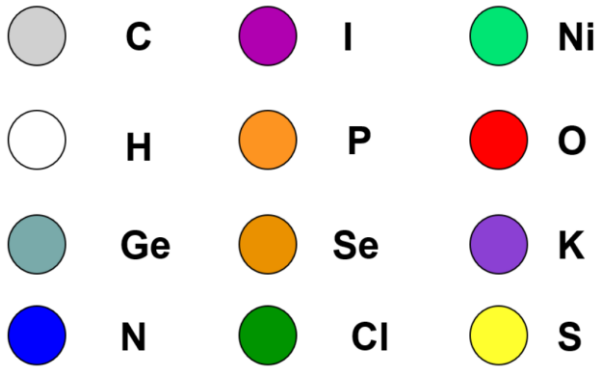


Figure S 2-1. Colour coding.

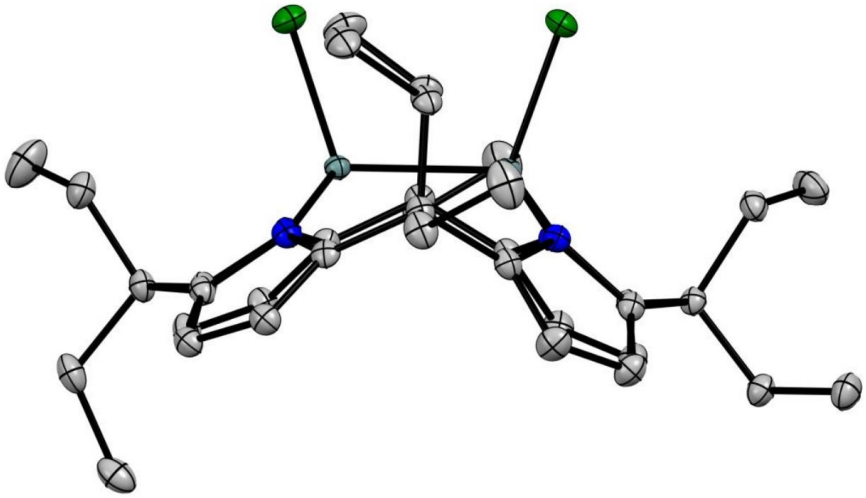


Figure S 2-2. Molecular structure of complex $\mathbf{Cx^{Et}Ge_2Cl_2}$ in the solid state with thermal ellipsoids at 50% probability. The hydrogen atoms and non-coordinated solvent (dichloromethane) are omitted for clarity.

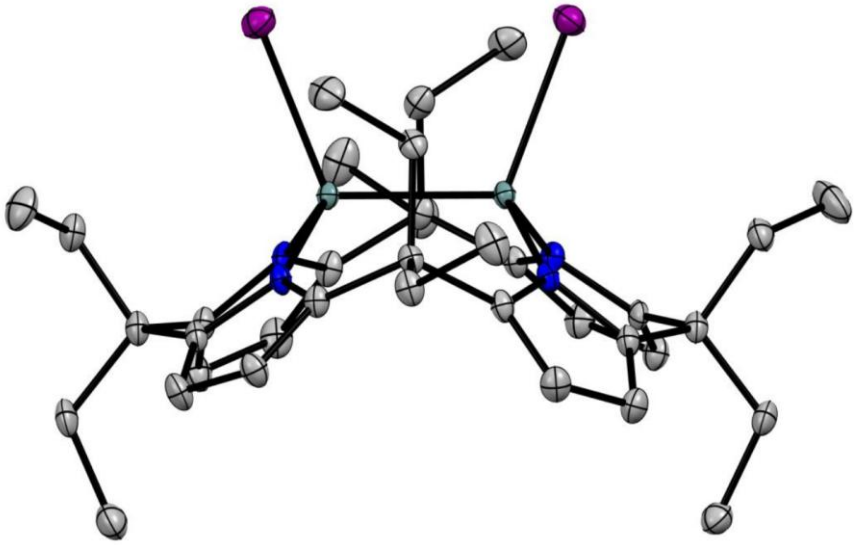


Figure S 2-3. Molecular structure of complex $\mathbf{Cx^{Et}Ge_2I_2}$ in the solid state with thermal ellipsoids at 50% probability. The hydrogen atoms and non-coordinated solvent (tetrahydrofuran) are omitted for clarity.

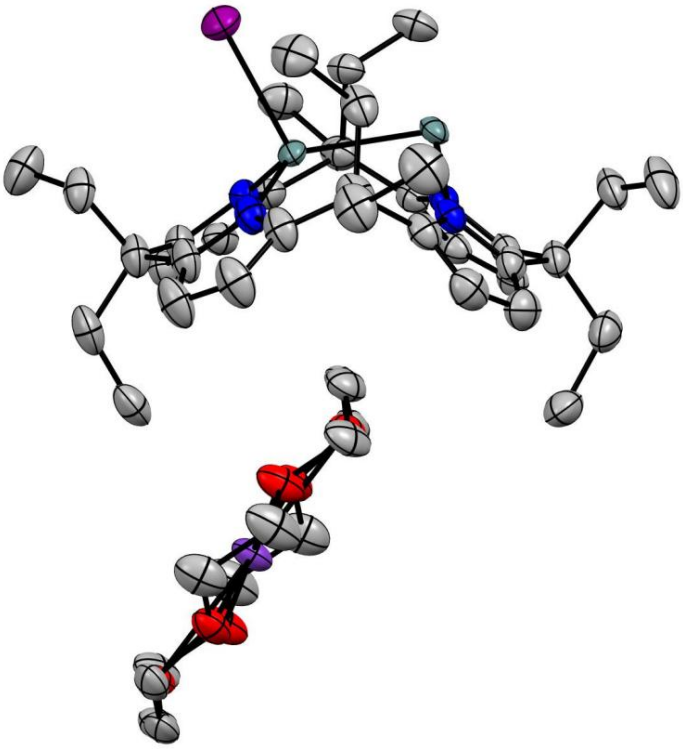


Figure S 2-4. Molecular structure of complex **K@18-crown-6[Cx^{Et}Ge$_2$I]** in the solid state with thermal ellipsoids at 50% probability. The hydrogen atoms and non-coordinated solvent (tetrahydrofuran) are omitted for clarity.

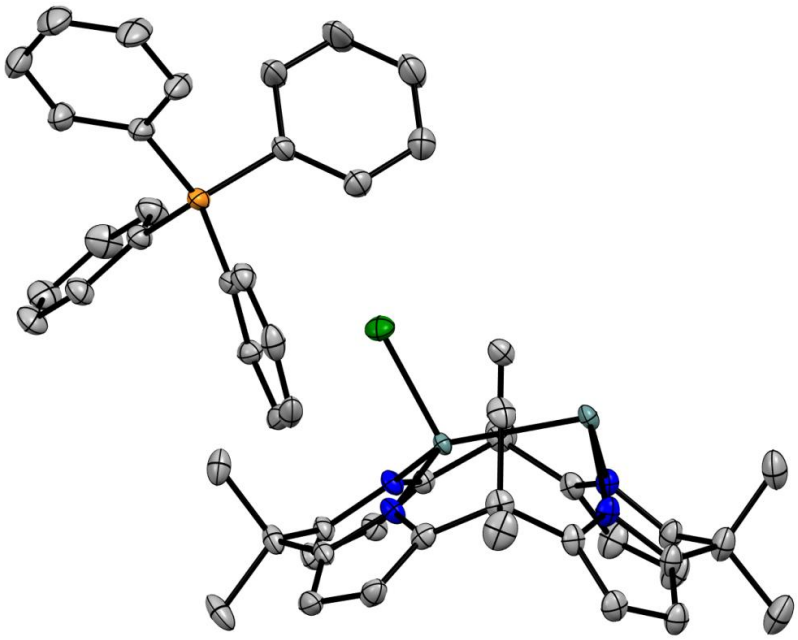


Figure S 2-5. Molecular structure of complex **PPh$_4$[Cx^{Me}Ge$_2$Cl]** in the solid state with thermal ellipsoids at 50% probability. The hydrogen atoms and non-coordinated solvent (dichloromethane) are omitted for clarity.

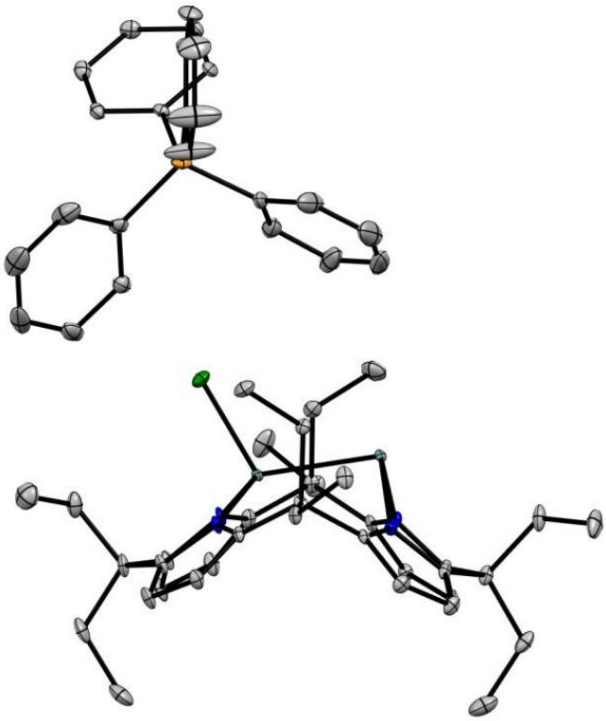


Figure S 2-6. Molecular structure of complex **$PPh_4[Cx^{Et}Ge_2Cl]$** in the solid state with thermal ellipsoids at 50% probability. The hydrogen atoms and non-coordinated solvent (dichloromethane) are omitted for clarity.

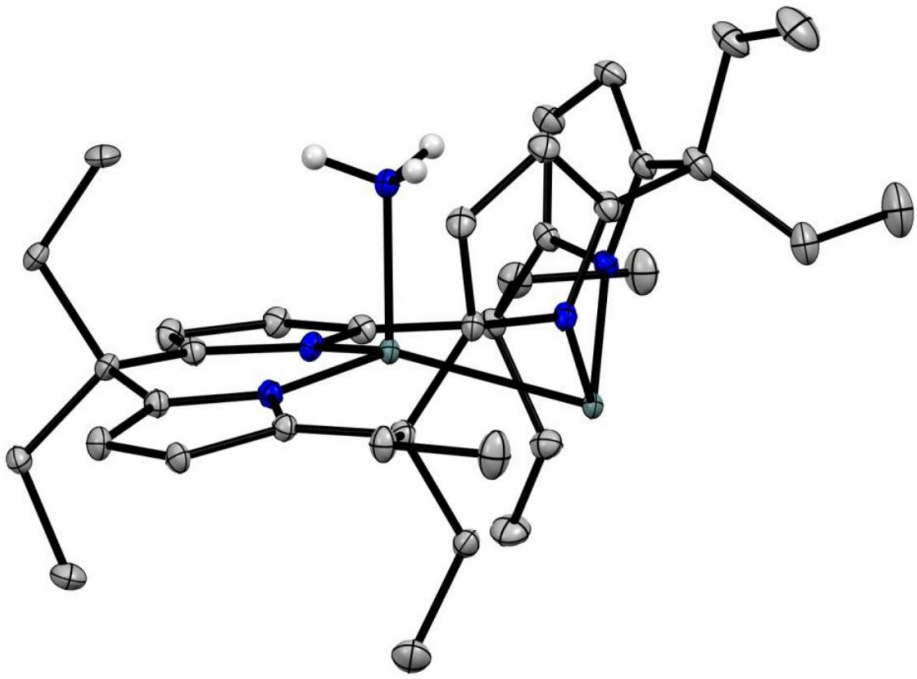


Figure S 2-7. Molecular structure of complex **$Cx^{Et}Ge_2(NH_3)$** in the solid state with thermal ellipsoids at 50% probability. A disorder and hydrogen atoms are omitted for clarity.

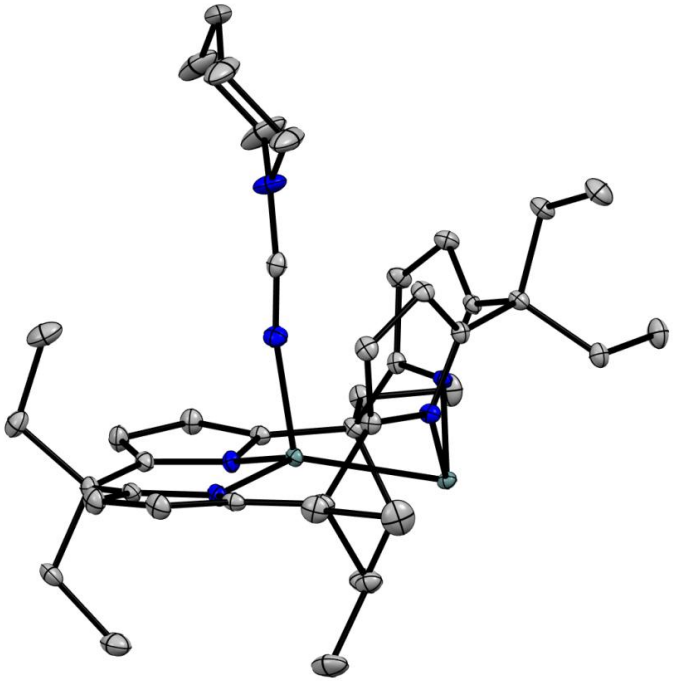


Figure S 2-8. Molecular structure of complex **Cx^{Et}Ge$_2$(NC-pip)** in the solid state with thermal ellipsoids at 50% probability. The hydrogen atoms are omitted for clarity. The hydrogen atoms and non-coordinated solvent (pentane) are omitted for clarity.

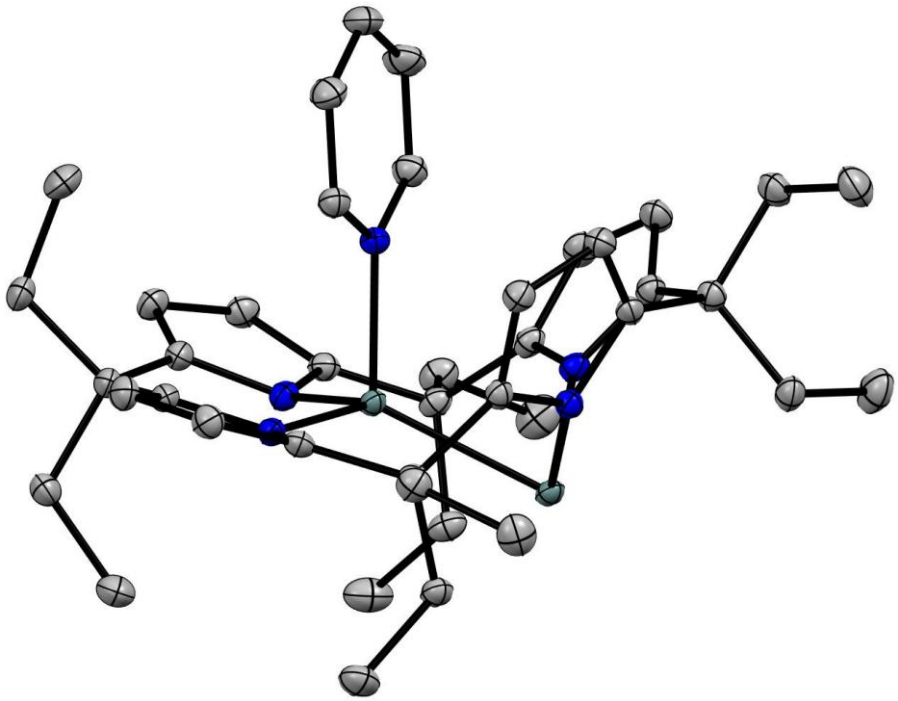


Figure S 2-9. Molecular structure of complex **Cx^{Et}Ge$_2$(pyridine)** in the solid state with thermal ellipsoids at 50% probability. The hydrogen atoms and non-coordinated solvent (pentane) are omitted for clarity.

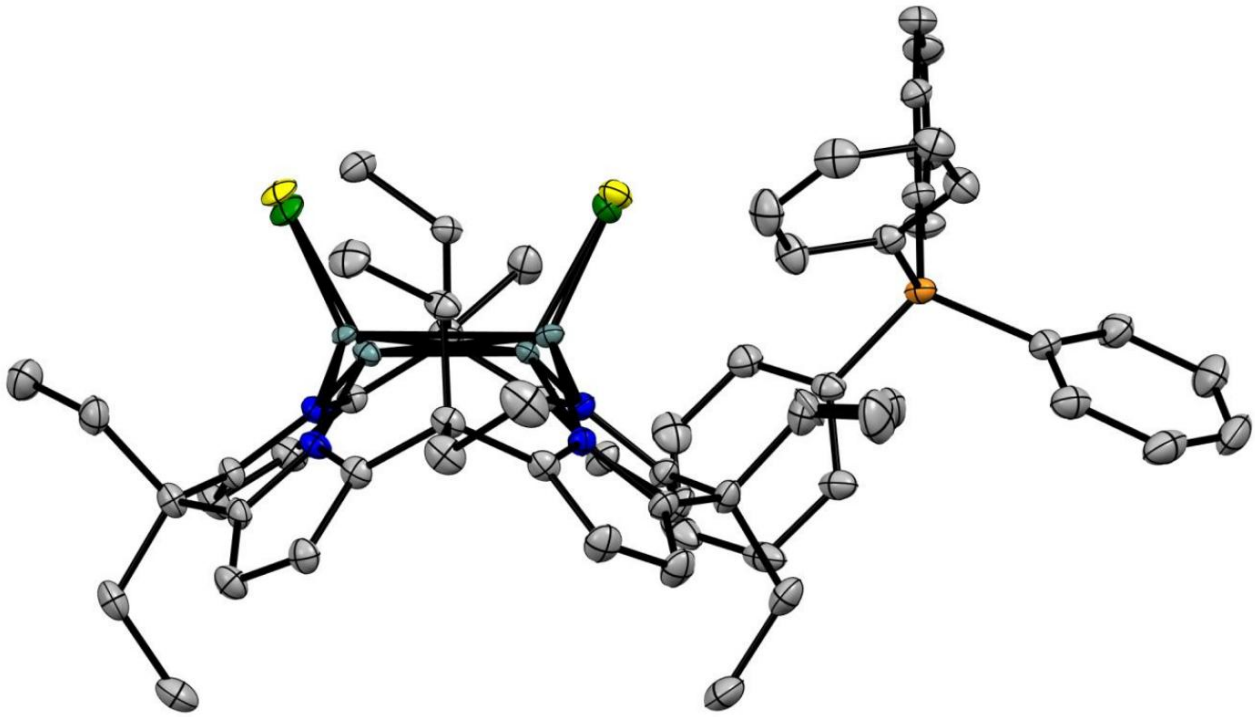


Figure S 2-10. Molecular structure of complex **$PPh_4[Cx^{Et}Ge_2ClS]$** in the solid state with thermal ellipsoids at 50% probability. The hydrogen atoms and non-coordinated solvent (tetrahydrofuran) are omitted for clarity.

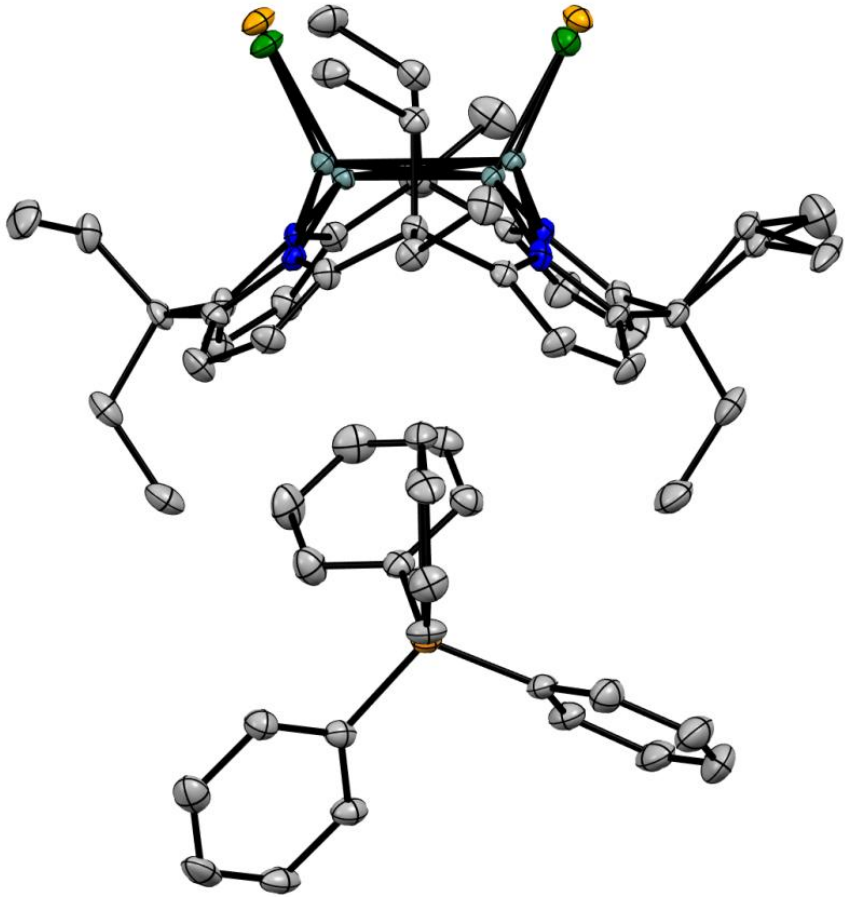


Figure S 2-11. Molecular structure of complex **$PPh_4[Cx^{Et}Ge_2ClSe]$** in the solid state with thermal ellipsoids at 50% probability. The hydrogen atoms and non-coordinated solvent (tetrahydrofuran) are omitted for clarity.

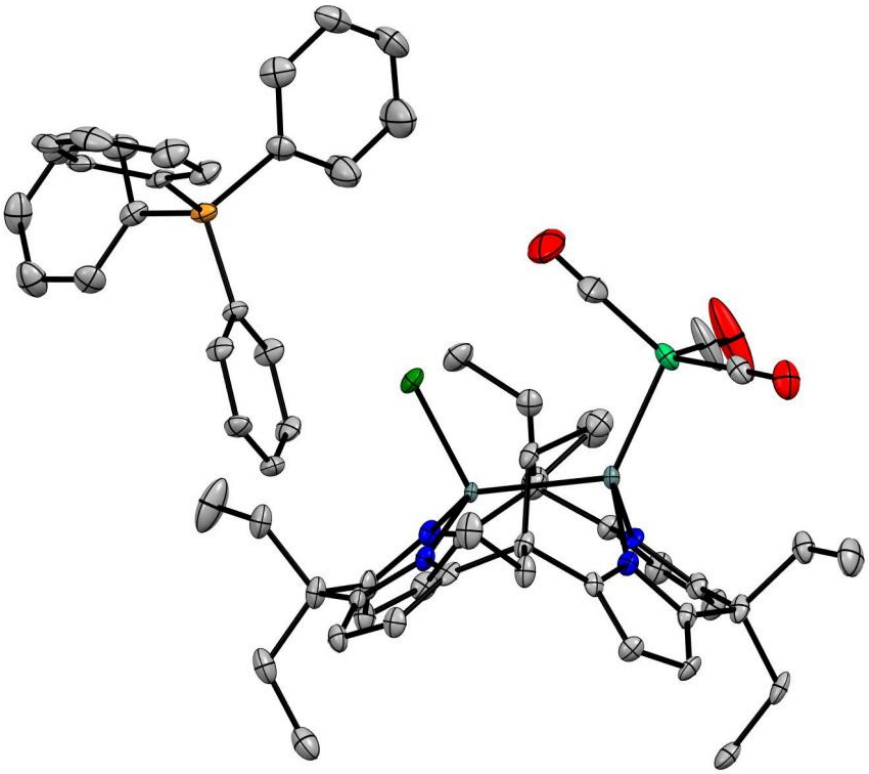


Figure S 2-12. Molecular structure of complex **$PPh_4[Cx^{Et}Ge_2ClNi(CO)_3]$** in the solid state with thermal ellipsoids at 50% probability. The hydrogen atoms and non-coordinated solvent (3 x tetrahydrofuran) are omitted for clarity.

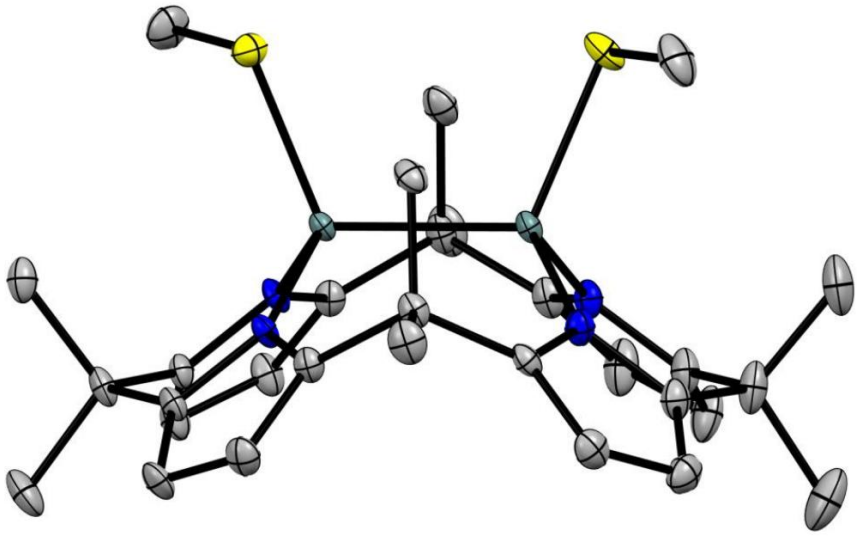


Figure S 2-13. Molecular structure of complex **$Cx^{Me}Ge_2(SMe)_2$** in the solid state with thermal ellipsoids at 50% probability. The hydrogen atoms and non-coordinated solvent (dichloromethane) are omitted for clarity.

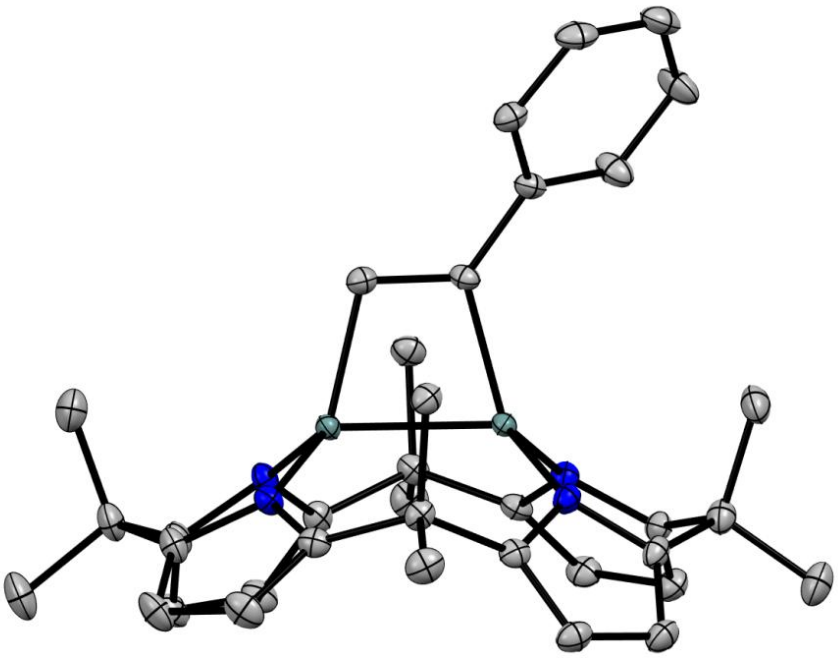


Figure S 2-14. Molecular structure of complex **Cx^{Me}Ge$_2$(PhCCH)** in the solid state with thermal ellipsoids at 50% probability. The hydrogen atoms and non-coordinated solvent (benzene) are omitted for clarity.

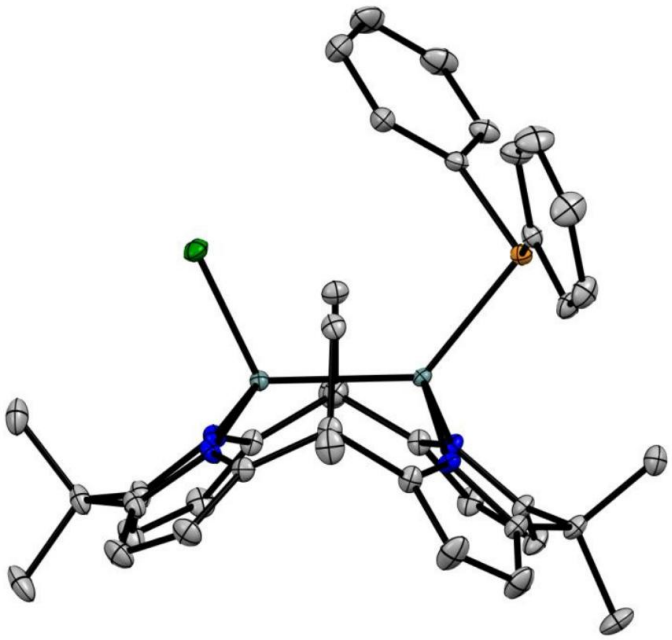


Figure S 2-15. Molecular structure of complex **Cx^{Me}Ge(Cl)Ge(PPh$_2$)** in the solid state with thermal ellipsoids at 50% probability. The hydrogen atoms and non-coordinated solvent (3 x benzene) are omitted for clarity.

3 Computational Details

3.1 General Remarks

All computations have been performed using the Orca 5.0.3 program package.[11-12] As starting geometries, VSEPR structures preoptimized with UFF or data obtained from the respective crystal structure were used. Geometry optimizations for structures in the presented reaction pathways were carried out using the r^{2}SCAN-3c method including the def2-mTZVPP basis set, geometrical counter-poise correction scheme (gCP) and the atom-pairwise dispersion correction (D4).[13] Calculated geometries were confirmed as energetic minima by frequency calculations at the same level of theory as the optimization calculation. Structures with imaginary frequencies >10 cm^{-1} have been reoptimized with defgrid3, TightOPT and VeryTightSCF settings. Enthalpies at 298 K were computed at the same level of theory using the rigid-rotor harmonic oscillator (RRHO) approximation.[14] For the Coulomb Integral, the RI approximation (RIJCOSX) was applied along with the corresponding auxiliary basis sets.[15-18] Graphics of calculated geometries were created by the program CYLview20.[19]

For all computational approaches regarding the calculation of thermodynamic data (binding affinities and mechanistical studies of the comproportionation reaction), more precise single point energies were calculated after successful geometry optimization using the RI-DSD-PBEP86/2013 spin-component-scaled-double hybrid functional,[20-21] including the D3(BJ) correction.[14, 22] The def2-QZVPP set of basis functions was used.[15] Solvation corrected energies (DCM) were calculated using the SMD solvation module with the conductor-like polarizable continuum model, CPCM.[23]

Cartesian coordinates are reported in Å.

3.2 Frontier Molecular Orbitals

Orbital energies for the calculation of the frontier molecular orbitals were calculated at PBE0 level of theory,[24] including the atom-pairwise dispersion correction (D4).[14, 22] The def2-TZVPP set of basis functions was used.[15] Plots of frontier molecular Kohn-Sham orbitals were created by the program IboView.[25]

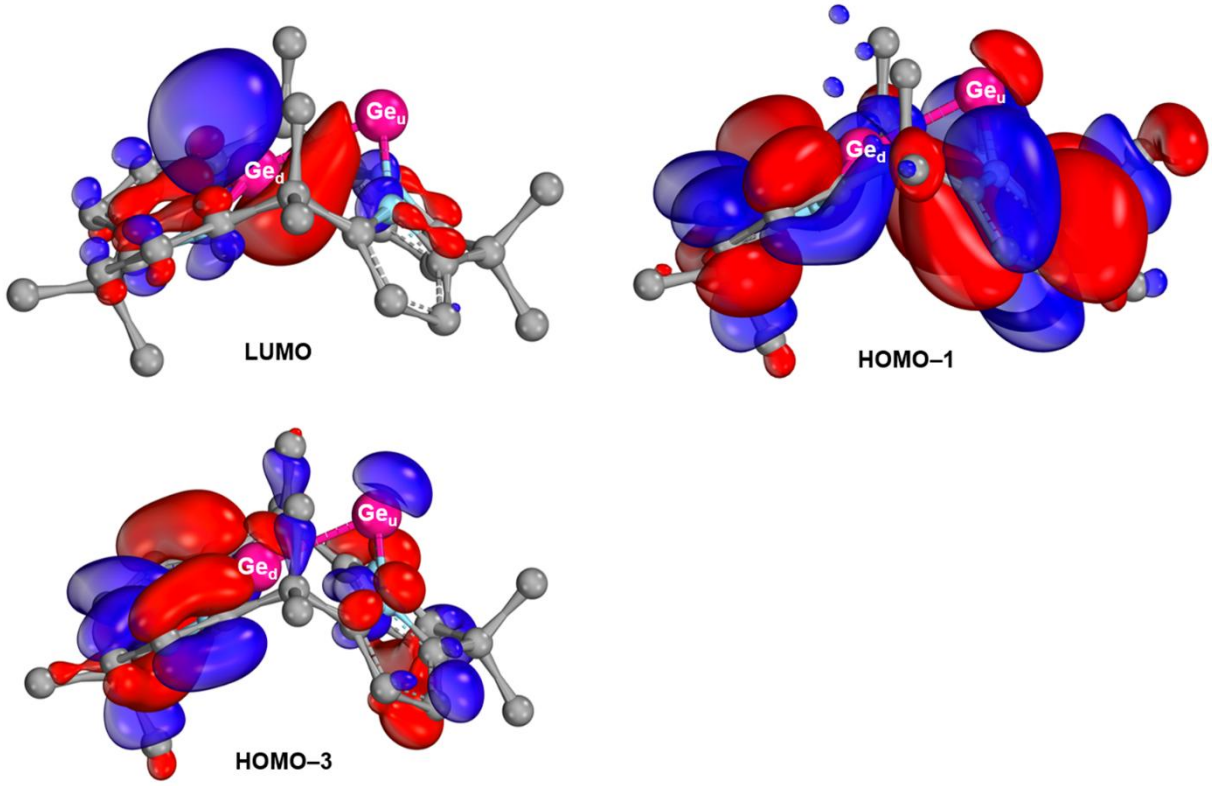


Figure S 3-1. Plotted frontier molecular orbitals of **Cx^{Me}Ge$_2$**. Threshold for LUMO and HOMO–3: 65; HOMO–1: 90.

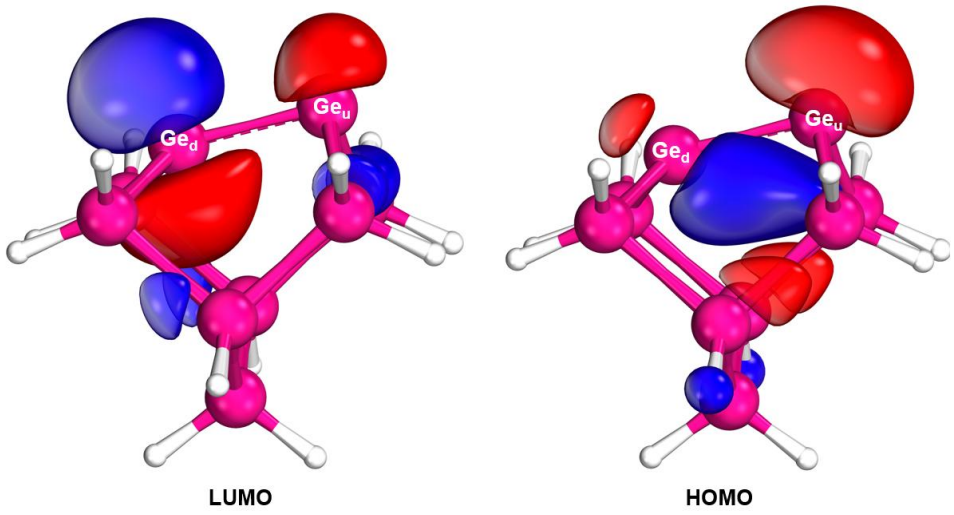


Figure S 3-2. Plotted frontier molecular orbitals of **Ge$_9$H$_{12}$**. Threshold for LUMO and HOMO: 50.

3.3 NBO Calculations

Natural Bond Orbital (NBO) calculations were conducted on PBE0/def2-TZVPP level of theory,[15, 26-27] using NBO 6.0.18a as included in Orca 5.0.3.[28] Wiberg bond indices were calculated using the BNDIDX keyword. NBOs were rendered and plotted using Chemcraft.[29]

Table S 3-1. Result for the NBO analysis of **Cx^{Me}Ge$_2$**.

NBO	Occupation	Type	Hybridization
65	1.93799	LP (Ge$_{up}$/Ge2)	4s (83 %), 4p (17 %)

146	1.89888	BD (Ge_{down}/Ge1-Ge_{up}/Ge2)	74 % Ge1: (4s (56 %); 4p (43 %) 26 % Ge2: (4s (4%); 4p (95 %)

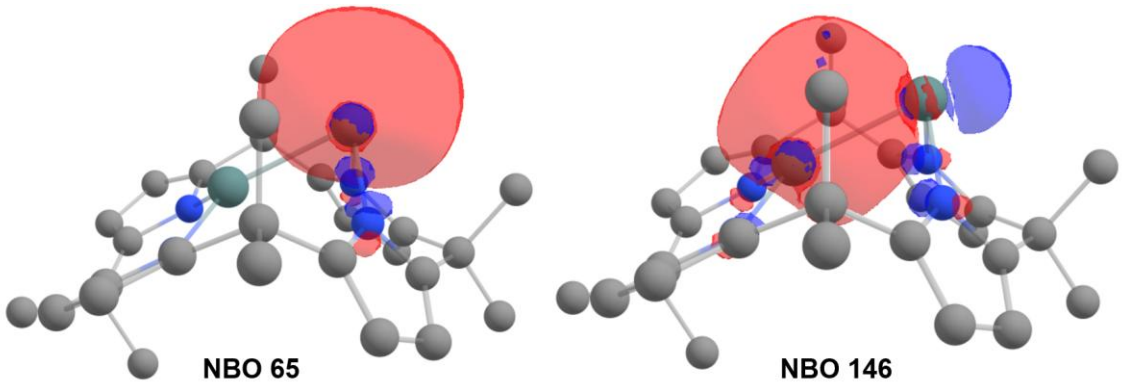


Figure S 3-3. Selected NBOs (PBE0/def2-TZVPP//PBEh-3c) of $Cx^{Me}Ge_2$, displayed at 0.07 e/Å3. Hydrogen atoms are hidden for clarity.

Table S 3-2. Result for the NBO analysis of Ge_9H_{12}.

NBO	Occupation	Type	Hybridization
127	1.72222	LP (Ge_{up}/Ge2)	4s (80 %), 4p (20 %)
128	1.93753	BD (Ge_{down}/Ge1-Ge_{up}/Ge2)	61 % Ge1: 4s (42 %); 4p (57 %) 39 % Ge2: 4s (9%); 4p (90 %)

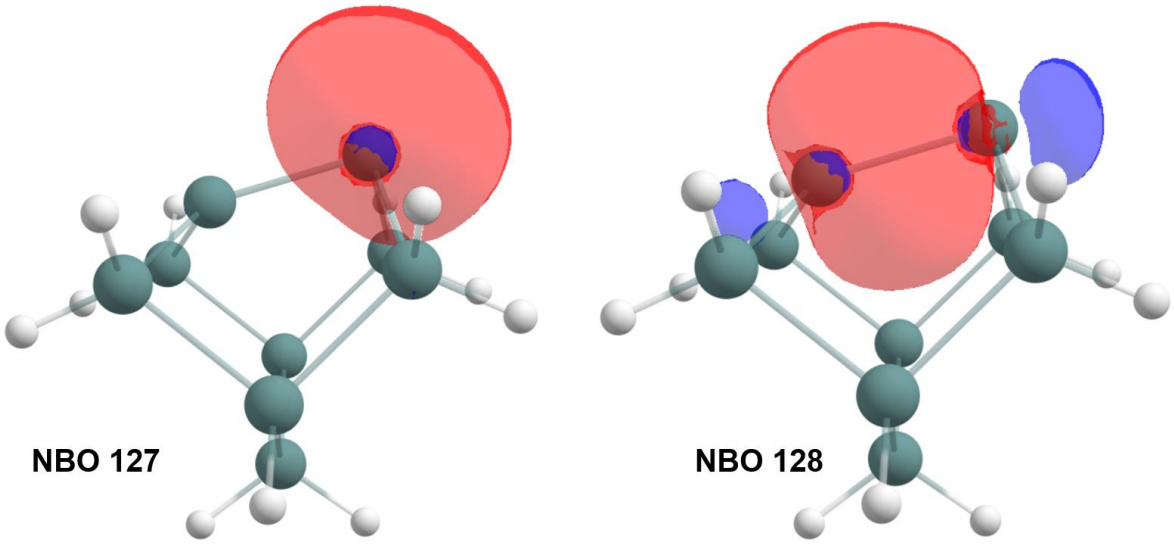


Figure S 3-4. Selected NBOs (PBE0/def2-TZVPP//PBEh-3c) of Ge_9H_{12}, displayed at 0.07 e/Å3. Hydrogen atoms are hidden for clarity.

Table S 3-3. Result for the NBO analysis of $Cx^{Et}Ge_2(NH_3)$.

NBO	Occupation	Type	Hybridization
62	1.94314	LP (Ge_{up}/Ge2)	4s (82 %), 4p (18 %)
63	1.73433	LP (N_{NH3})	4s (16 %), 4p (84 %)
72	1.94386	BD (Ge_{down}/Ge1-Ge_{up}/Ge2)	69 % Ge1: 4s (68%); 4p (32 %) 31 % Ge2: 4s (8 %); 4p (91 %)

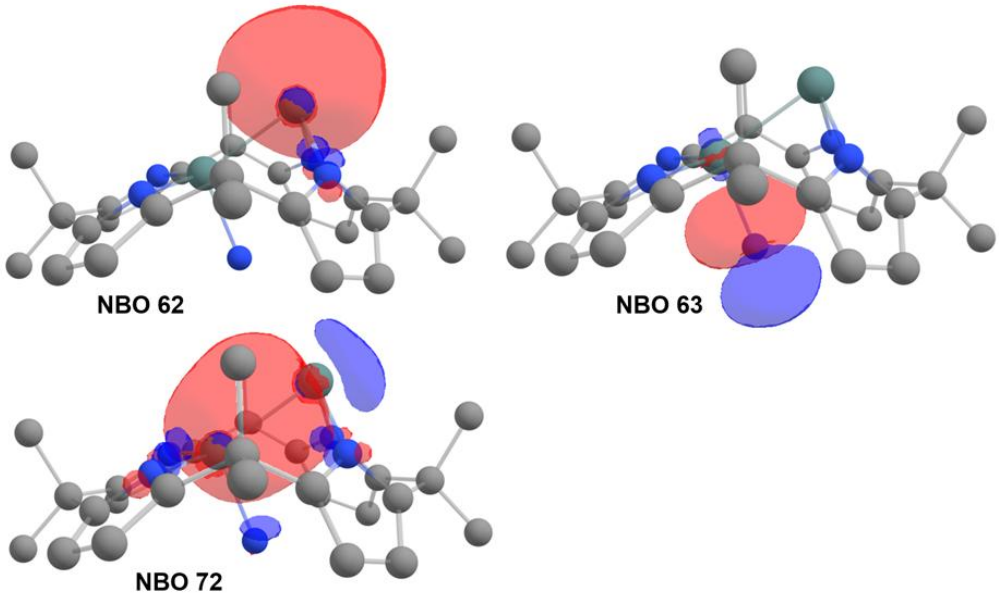


Figure S 3-5. Selected NBOs (PBE0/def2-TZVPP//PBEh-3c) of **$Cx^{Me}Ge_2(NH_3)$**, displayed at 0.07 e/Å3. Hydrogen atoms are hidden for clarity.

Table S 3-4. Result for the NBO analysis of **$[Cx^{Et}Ge_2I]^-$.**

NBO	Occupation	Type	Hybridization
78	1.92947	LP (Ge_{up}/Ge2)	4s (79 %), 4p (21 %)
90	1.91720	BD (Ge_{down}/Ge1-Ge_{up}/Ge2)	68 % Ge1: 4s (59 %); 4p (41 %) 32 % Ge2: 4s (9%); 4p (91 %)
93	1.96225	BD (Ge_{down}/Ge1-I)	29 % Ge1: 4s (21 %); 4p (78 %) 71 % I: 5s (13 %); 5p (86 %)

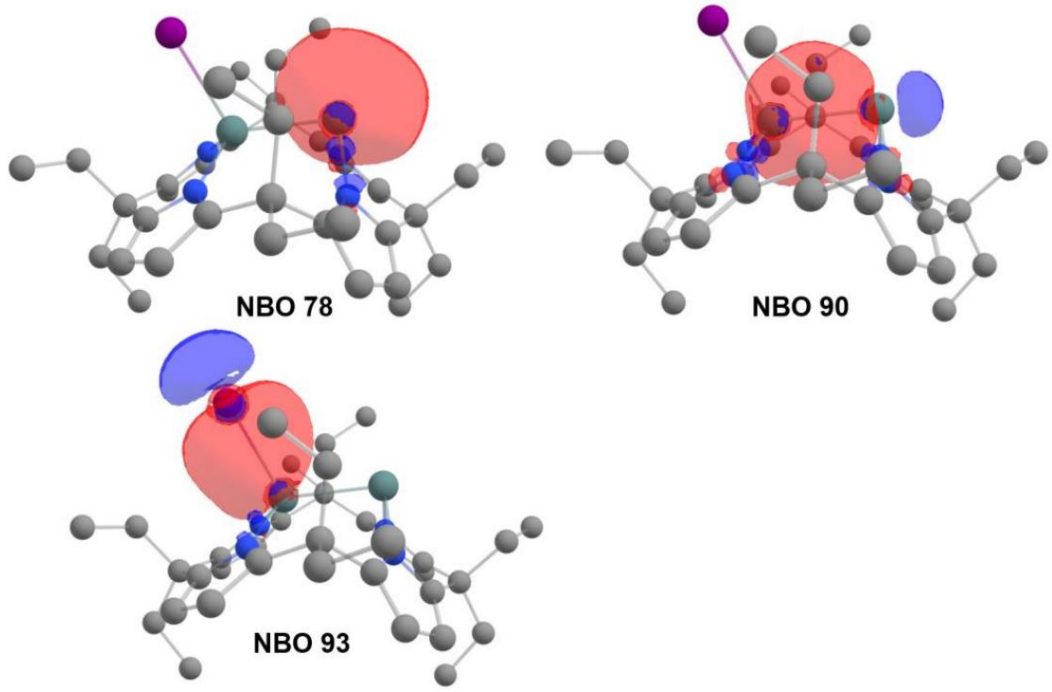


Figure S 3-6. Selected NBOs (PBE0/def2-TZVPP//PBEh-3c) of **$[Cx^{Et}Ge_2I]^-$**, displayed at 0.07 e/Å3. Hydrogen atoms are hidden for clarity.

The Ge–Ge bond (252.4(2) pm) in the solide-state structure of K@18-crown-6[CxEtGe2I] is markedly elongated compared to a regular Ge–Ge single bond observed in digermanes, being in line with the computed structure of [CxEtGe2I]–. The Ge–I bond is also lengthened by 8.3 pm relative to **$Cx^{Et}Ge_2I_2$**, and falls within the range observed for germylene iodide adducts (d_{av}(Ge-I) = 259.0).[30-31] Accordingly, Ge1 can be described as a germylene iodide adduct (NBO 93), while Ge2 functions as the adjacent coordination partner (NBO 90), consistent with the description as a germanide-substituted germylene (NBO 78 for the free electron pair). DFT calculations and natural bond orbital (NBO) analysis support this assignment.

3.3.1 Cartesian Coordinates for the NBO Analysis

The cartesian coordinates for **$Cx^{Me}Ge_2$** and **Ge_9H_{12}** can be found below.

$Cx^{Me}Ge_2(NH_3)$

Ge	4.79918866254001	8.61562486380118	12.52182398260532
Ge	3.37997402146656	10.53060815614258	13.21024375071534
N	4.65111847848210	11.73367943198602	14.30570380603620
N	5.29803665195875	8.74826787363881	14.48657754881129
N	2.71749396441481	11.85899924047609	12.09271532968118
N	6.02072076675165	10.16419745210396	12.03833422228242
N	2.00654361124963	10.47926529698071	14.46206106635077
C	6.56757844625011	9.17634984193994	14.82196531114953
C	2.12909476480124	9.74600810790455	15.64233129083282
C	1.20021426042915	11.59476480384060	14.69389672172012
C	1.82681802959379	12.82723374745141	12.55679027973245
C	7.64823127803939	9.32059618845111	13.77152489342885
C	3.47923872117445	12.39238214312574	11.05404564488468
C	3.00298681005342	8.50046915404810	15.72853165839045
C	7.62728388942908	11.64776398932494	12.57078039539516
C	6.58063067607829	9.55579264054595	16.15039243369878
C	6.73700246115510	12.26018354125074	11.65531728645437
C	7.16496182971115	10.36292422443365	12.78500825589875
C	2.56898637376622	7.46196182100687	14.67523986623431
C	5.27164177491552	9.35220652101956	16.65141898266564
C	4.48971237228525	8.85627215031730	15.62151122471899
C	4.58403536456173	11.59298605005632	10.37571149571446
C	0.78920578701067	11.53777818959420	16.00458145398228
C	4.01736506725985	10.28817097353199	9.78173834819369
C	7.94262460435950	7.97487340020686	13.07512694150085
C	5.75212754416530	11.34176395484591	11.33470903901510
H	5.91799962832784	11.86787600890563	8.68910937925283
C	3.04325996479332	13.67891623943221	10.84513760611937
H	1.54657995216208	7.13591668939875	14.89054586800559
C	0.73507380886813	12.48155700691165	13.55350575386822
C	2.77128960429760	7.84534095795114	17.10458425301168
C	1.37193797666099	10.37932818120311	16.59872189219224
C	2.00706550080531	13.95181411238645	11.78637762855159
H	7.06645106626884	7.55402331331522	12.56731900462229
C	8.94650787291592	9.79759381839399	14.43017378184742
H	4.14747847483358	12.57036009987659	14.59481476031089
C	0.13522827929142	13.77214424184561	14.12208417761584
C	-0.37852605269960	11.71691467916435	12.78439068693642
C	5.11437355537320	12.41757963020901	9.18684691056661
H	9.72514310296861	9.92629992594965	13.67233058989332
H	5.50964696244224	13.38477542423476	9.50402432652847
H	-0.76066368926422	12.33678420638552	11.96643618236043
H	8.72400141830932	8.10770091711510	12.31963978883368
H	8.51930759708842	12.08914994450622	12.99178321043146
H	7.43470536651102	9.90936311023252	16.71007028989724
H	6.82602675728517	13.25992521081726	11.25397365651566
H	3.40004860697290	6.95549525795263	17.19565438519222
H	3.01725437382357	8.52127610246216	17.92602741421791
H	4.94649632834740	9.52279024946287	17.66821648393232
H	0.11251296561276	12.22512675692417	16.49271367240729
H	-0.25189629633787	14.39776030282274	13.31334826784291
H	-0.70184562607503	13.54079084863131	14.78653496783044
H	5.46864696519600	12.01022009922018	13.74827099549664
H	4.97965407542593	11.23350640029389	15.14125976210282
H	0.01327026416592	10.78839970608832	12.35876220583131
H	4.30909622964905	12.59886797839145	8.46746547419369
H	8.80794832335996	10.75016671962202	14.94860019088814
H	3.40973587398820	14.36272139814315	10.09308615058652
H	1.72140949276544	7.55272395030515	17.20788215934088
H	2.56293763231982	7.85216412792299	13.65331648853305
H	3.23193570133360	6.59089566372890	14.70301524146191
H	9.29071779816081	9.05597791699317	15.15724304353886
H	8.27467505428220	7.23882712905503	13.81445690776631
H	1.22859477160049	10.05286226876995	17.61872464577465
H	1.44065017383619	14.86998175026462	11.85378697735514
H	-1.19949556343597	11.46574139726464	13.46432220569804
H	0.88044961470407	14.34494706885812	14.68221747925496
H	3.49265691964627	9.66877379446785	10.51506935822104
H	3.28965286866296	10.53342256243149	9.00202384126725
H	4.82081009285321	9.68803073366288	9.34205070381000

$[Cx^{Et}Ge_2I]^-$

Ge	10.39040943041604	9.19403328102589	2.66553842666982
N	9.53677356668751	10.36671644455278	4.02231994383682
Ge	11.31767863530902	7.72810808515024	4.49504876885586
N	8.75957157089969	8.07204723455711	2.60741050174982
N	10.47272494683435	6.08348664453205	4.81242550398024
N	11.23706390183563	8.38636502488744	6.25099099621821
C	11.27974530525799	9.72404064485871	6.64903607305725
C	9.92113846817931	5.23322734908120	3.85316655286437
C	10.44954706077500	5.45794905616527	6.05259137840401
C	10.96967425579168	7.58407730768842	7.35497261764371
C	8.56128410737171	6.71635514036468	2.36748585332226
C	7.52890855816086	8.70646004693017	2.57818255134269
C	10.08424791871205	11.17618754662838	5.01069855169811
C	11.04842798287448	9.74314871415107	8.00843557086899
H	10.99421761512599	10.62158888533381	8.63456530578883
C	9.63803715930769	5.63136298062436	2.40565302300453
C	9.89055196306097	4.21259463347931	5.87588730325741
H	9.71144656654227	3.47841537032124	6.64923214254178
C	9.56105779365079	4.07264678072181	4.50423030182344
H	9.07182009056230	3.21798646810525	4.06133069231106
C	10.92290344857072	6.05137201810371	1.64336282137764
H	10.62891698009478	6.40192039059584	0.64645960828088
H	11.39298089421758	6.92084629947432	2.11604967533450
C	7.20230510284528	6.51462743997391	2.19760856050305
H	6.71137953300738	5.56775449982421	2.02534076927626
C	12.49339807174291	5.65246364728816	7.54582421034644
H	13.09996682867757	6.17192106122220	6.79687266689885
H	12.79149592086809	6.06012372602644	8.52147615916157
C	10.99660709803606	6.06826351294861	7.32697063670274
C	8.25758134242582	10.82107603362071	3.74866804788053
C	11.73631184153627	12.17045734841853	6.57557139492354
H	11.63592545322612	13.05371515781066	5.93555558759759
H	10.96055220645589	12.27024371169493	7.34000184576801
C	5.89601771433580	10.55247730747739	2.98688149588701
H	5.78656767313314	11.64239683113431	2.96810610404435
H	5.28984499630774	10.17610916743025	2.15210473771966
C	12.80163371401199	11.96646299080653	3.78917231050108
H	13.51850827921523	11.71806474278792	2.99989993886672
H	13.19400676014550	12.82700414289592	4.34071711914104
H	11.86180275232091	12.26968500842158	3.31394378719963
C	12.57819523573035	10.75551219655628	4.69315733544196
H	13.49436159172468	10.49557020930320	5.23586679054271
H	12.39860594503395	9.89744250228289	4.03842545496090
C	7.37560817293835	10.21108989600010	2.67981528035924
C	11.98616052889249	4.95986818157984	1.54123785287153
H	11.67892613799807	4.14839449440380	0.87323080471852
H	12.19647663089346	4.53339872502702	2.52795993550311
H	12.92141023294652	5.37967435755817	1.15852741414229
C	13.11128351489603	12.17391595685938	7.24470870216040
H	13.92027793682411	12.32069671148210	6.52158309040361
H	13.29978320131059	11.23530116620499	7.77441668815837
H	13.17153969536138	12.99227757378992	7.97141432717344
C	6.55552273178428	7.76293620568244	2.31558741827368
H	5.49282064135760	7.94014504401385	2.22837289171980
C	10.86151696151547	8.41061637034118	8.44986042810050
H	10.66227658293358	8.10192875397670	9.46660628641314
C	11.41847329831549	10.92218442577157	5.70793746177647
C	9.07441696109224	4.36956448750133	1.69377005585395
H	9.77235699737160	3.54394974581511	1.87146582947139
H	8.14093259026790	4.08341283580712	2.18626322380477
C	7.73027267292321	10.80408071817156	1.27240578514839
H	8.72987814639516	10.44123005473494	0.99384886210551
H	7.03485406441472	10.35641822446104	0.54889828132292
C	8.83540686831723	4.51549152489755	0.19123640118649
H	9.77463928275431	4.58182525696120	-0.36738395144691
H	8.24385701586438	5.40863482472257	-0.03056807217635

H	8.29146801051146	3.64258383183990	-0.18760258438764
C	7.99786361898961	11.91468949712703	4.55126291903772
H	7.08047841772905	12.48632037477303	4.58050260841652
C	9.14290868082257	12.13301774592058	5.34826552601831
H	9.24132641574334	12.88669821738150	6.11601479461611
C	10.16338051656856	5.53343722216951	8.52052532806465
H	10.26422285572667	4.44298935017838	8.54604589014036
H	10.63217903159582	5.89556025751054	9.44457087723156
C	5.34540072863202	10.01967996794522	4.31054157563130
H	4.28919742862317	10.29486981835039	4.41925584556950
H	5.89741431451622	10.43266401395183	5.15865418900006
H	5.42602804038821	8.93148710828956	4.36605786473120
C	8.68126130528985	5.90300711149356	8.50358722146283
H	8.19610911175756	5.51892933403557	7.60137059665598
H	8.54476197259209	6.98777405404041	8.51871541722699
H	8.17083358554400	5.47792681306259	9.37581684144041
C	7.71859392374692	12.32641628692880	1.16050498529823
H	8.04896684690552	12.63311578435172	0.16150991394994
H	8.39001717387402	12.77525964139457	1.89973221389487
H	6.71897483131827	12.74478621964834	1.31992289776473
C	12.80548902873793	4.16029087230184	7.47865092939916
H	12.52874934154105	3.74516511750095	6.50497518834628
H	12.28063920281905	3.58796278343066	8.25190664093049
H	13.88029665992355	4.00244526863823	7.62286872046703
I	13.89240180771519	7.09558018671325	4.12219948445281

3.4 QTAIM Analysis

QTAIM analyses were performed on the PBE0/def2-TZVP level of theory.[15, 26-27] Electron densities were analyzed using the AIMAll software with default integration.[32] Descriptors in the context of Bader's theory of AIM to describe and compare the nature of chemical bonds have been used according to the literature.[33-36] Analysis of electron density: $\rho(\mathbf{r}_{BCP})$ and Laplacian of the density, $\nabla^2\rho(\mathbf{r}_{BCP})$ at the bond critical points (bcp's) (positive Laplacians: closed shell (ionic) interactions, negative Laplacians: covalent); total electronic energy density $H(\mathbf{r}_{BCP}$, negative values for shared-type (covalent) atomic interactions (typical covalent single bonds ≈ -0.35) and positive values in closed-shell bonds);[37] the ratio of $G(\mathbf{r}_{BCP})/\rho(\mathbf{r}_{BCP})$ (*Lagrangian kinetic energy per electron,* <1 for shared interaction and >1 for closed-shell (ionic) bonding);[38-39] ellipticity ($\varepsilon=\lambda_1/\lambda_2-1$) of a bond quantifies the anisotropy of the electron density, with deviations from a cylindrical distribution leading to values larger than zero. The delocalization index is yet another indicator for covalent bonding.

Table S 3-5. Result for the QTAIM analysis of **$Cx^{Me}Ge_2$** and **Ge_9H_{12}**.

QTAIM								**Bader charge analysis**	
$CxGe_2$	$\rho(\mathbf{r}_{BCP})$	$\nabla^2\rho(\mathbf{r}_{BCP})$	$H(\mathbf{r}_{BCP})$	$G(\mathbf{r}_{BCP})$	$G(\mathbf{r}_{BCP})/\rho(\mathbf{r}_{BCP})$	$\varepsilon=\lambda_1/\lambda_2-1$	DI		**Q**
Ge-Ge	0.06604	**-0.00892**	-0.02773	0.02550	0.386	0.08480	0.534	Ge-up	1.07
								Ge-down	1.29
Ge_9H_{12}	$\rho(\mathbf{r}_{BCP})$	$\nabla^2\rho(\mathbf{r}_{BCP})$	$H(\mathbf{r}_{BCP})$	$G(\mathbf{r}_{BCP})$	$G(\mathbf{r}_{BCP})/\rho(\mathbf{r}_{BCP})$	$\varepsilon=\lambda_1/\lambda_2-1$	DI		**Q**
Ge-Ge	0.08194	**-0.03302**	-0.03956	0.00267	0.0325	0.14622	1.176	Ge-up	0.03
								Ge-down	-0.07

3.5 Anion Affinities

For the final fluoride anion affinities, single point energies were calculated at DSD-BYLP(D3BJ)/def2-QZVPP[40-41] level of theory using the protocol proposed by Krossing,[42-43] anion affinities were determined by an isodesmic reaction scheme using CCSD(T)/CBS anchor points, thus by subtraction of the anchor enthalpies for the reaction $Me_3Si^+ + X^- \rightarrow Me_3SiX$ from the column [(B) − (A)] in the tables below.

Table S 3-6. Computed energies [kJ mol^{-1}] for the *vacuum* fluoride ion affinities at r^{2}SCAN/def2-TZVPP level of theory.

Compound	E	Total therm. correc.	Enthalpy	LA + Me_3SiY	Me_3Si^+ + A-Y	(B)-(A)	FIA
$Cx^{Me}Ge_2$	-14332550.0	1503.3	-15155879.9	-15667422.9	/	516.1	442.3
$Cx^{Et}Ge_2$	-15158006.6	2126.7	-9702634.9	-16492256.0	/	506.6	451.8
Ge_9H_{12}	-49097619.2	56.2	-9965210.2	-50433939.2	/	513.9	444.5
$B(C_6F_5)_3$	-5797674.8	480.7	- 5797194.1	- 7133570. 3	/	508.0	450.4
$[Cx^{Me}Ge_2F]^-$	-14595121.5	1510.7	-14593610.9	/	-15666906.8	/	/
$[Cx^{Et}Ge_2F]^-$	-10577548.8	2455.2	-9704482.1	/	-11648389.4	/	/
$[Ge_9H_{12}F]^-$	-49360189.2	59.9	-49360129.3	/	-50433425.2	/	/
$[B(C_6F_5)_3]^-$	-6060252.6	486.3	- 6059766.3	/	-7133062.2	/	/

Table S 3-7. Computed energies for the *vacuum* fluoride affinities at DSD-BYLP(D3BJ)/def2-QZVPP level of theory.

Compound	E [kJ mol^{-1}]	Enthalpy [kJ mol^{-1}]	LA + Me_3SiY	Me_3Si^+ + A-Y	(B)-(A)	XIA [kJ mol^{-1}]
$Cx^{Me}Ge_2$	-14328331.7	-14326828.5	-15662573.69	/	522.5	436
$Cx^{Et}Ge_2$	-15153347.5	-15151220.8	-16486966.01	/	530.5	427.9
Ge9H12	-49086458.3	-49086402.1	-50422147.38	/	537.1	421.3
$B(C_6F_5)_3$	-5795524.56	-5795043.9	-7130789.13	/	526.4	431.9
$[Cx^{Me}Ge_2F]^-$	-14590850.3	-14589339.6	/	-15662043.21	/	/
$[Cx^{Et}Ge_2F]^-$	-15415874.5	-15413739.9	/	-16486443.56	/	/
$[Ge_9H_{12}F]^-$	-49348966.5	-49348906.6	/	-50421610.26	/	/
$[B(C_6F_5)_3]^-$	-6058045.32	-6057559.1	/	-7130262.68	/	/

3.5.1 Cartesian Coordinates for the Calculation of Fluoride Ion Affinities

The cartesian coordinates (reported in Å) for $\mathbf{Cx^{Me}Ge_2}$, $\mathbf{Cx^{Et}Ge_2}$ and $\mathbf{Ge_9H_{12}}$ were also used for NBO and QTAIM calculations as well as for the calculation of biding affinities of neutral Lewis bases.

$\mathbf{Cx^{Me}Ge_2}$

C	-24.059712	-2.417633	-6.770128
C	-24.756896	-1.273537	-7.056888
C	-25.791153	-1.597651	-7.990218
C	-25.718102	-2.937740	-8.260231
N	-24.652355	-3.451170	-7.508807
C	-22.906894	-2.667589	-5.805365
C	-26.683795	-3.852693	-8.984068
C	-26.019395	-5.011884	-9.697150
C	-23.191329	-3.892617	-4.943308
C	-23.876580	-3.900822	-3.747613
C	-24.046786	-5.246813	-3.340207
C	-23.467696	-6.041099	-4.301185
C	-26.386881	-5.693521	-10.826098
C	-25.570503	-6.863798	-10.926283
C	-24.710071	-6.882653	-9.860259
C	-23.671836	-7.913380	-9.434217
C	-23.318964	-7.544657	-4.354812
C	-23.766475	-8.064374	-5.702430
C	-23.827733	-8.243980	-7.953944
C	-24.610850	-9.104784	-6.009328
C	-24.651549	-9.211931	-7.421312
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C	-21.552725	-2.760098	-6.546351
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C	-27.644115	-4.452548	-7.917088
C	-27.508248	-3.038838	-9.987288
C	-22.238130	-7.463836	-9.800182
C	-23.928640	-9.198279	-10.245945
C	-21.845867	-7.948485	-4.088875
C	-24.173667	-8.182049	-3.253443
Ge	-23.757746	-4.978061	-7.972913
Ge	-21.891059	-6.094317	-6.754586
H	-25.640136	-7.614198	-11.700454
H	-27.176812	-5.416504	-11.509722
H	-21.512444	-8.216004	-9.472158
H	-21.948533	-6.505658	-9.358513
H	-22.159794	-7.345654	-10.885664
H	-28.381471	-5.100099	-8.402735
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H	-27.091447	-5.049482	-7.185140
H	-25.244339	-9.918709	-7.983414
H	-25.142782	-9.727615	-5.304921
H	-26.521075	-0.906457	-8.387110
H	-24.575169	-0.295514	-6.635196
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H	-25.231812	-7.937977	-3.383702
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H	-22.021592	-1.610741	-4.129842
H	-23.740711	-1.233182	-4.370437
H	-22.526742	-0.554113	-5.464315
H	-20.745945	-2.959161	-5.832638
H	-21.350448	-1.812569	-7.055795
H	-21.521690	-3.541167	-7.311683
H	-24.537934	-5.585862	-2.439745
H	-24.241029	-3.030959	-3.220917
H	-28.254544	-3.677286	-10.467863
H	-26.870128	-2.597958	-10.758669
H	-28.047539	-2.238073	-9.473765
H	-21.743042	-9.038109	-4.126850
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H	-23.756931	-9.010310	-11.310240
H	-24.954416	-9.552906	-10.125512
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Ge	-0.756419	-0.010467	0.174997
N	1.855235	-1.374151	-0.020676
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N	-1.774729	1.368453	-0.455554
C	-1.499936	2.720276	-0.205162
C	-1.308229	-2.765036	-0.397855
C	-2.887989	-1.328939	-1.235287
C	-3.004240	1.246818	-1.107228
C	1.184921	-2.538927	-0.417159
C	2.863641	-1.123646	-0.938396
C	0.985495	2.559737	-0.335293
C	-2.560964	3.434195	-0.696648
H	-2.666314	4.509262	-0.682924
C	-0.010853	-3.194009	0.277268
C	-3.274814	-2.611145	-1.521446
H	-4.170671	-2.899718	-2.054297
C	-2.290672	-3.505170	-1.000859
H	-2.317162	-4.581687	-1.083237
C	-0.046518	-2.886835	1.801431
H	0.939686	-3.113653	2.223540
H	-0.192473	-1.812062	1.964988
C	1.788125	-2.990521	-1.573398
H	1.508897	-3.873103	-2.131217
C	-5.066958	-0.140078	-1.097714
H	-5.616129	0.736507	-1.462507
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C	-3.603836	-0.047906	-1.616671
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H	-0.161779	4.968158	-0.772121
H	-1.002637	5.153189	0.749587
C	4.712757	0.159665	-2.001383
H	5.219649	-0.810551	-2.050645
H	4.133596	0.245255	-2.927594
C	-1.214334	3.515236	2.793021
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C	-0.154043	2.816355	1.945034
H	-0.292772	1.736399	2.079494
H	0.849770	3.034819	2.328359
C	3.717618	0.122265	-0.822554
C	-1.143165	-3.612315	2.577804
H	-2.119401	-3.470528	2.100678
H	-1.202598	-3.222939	3.598835
H	-0.955374	-4.687598	2.648338
C	1.140103	5.338910	0.905455
H	2.046128	4.862688	0.517287
H	1.150049	5.254712	1.996986
H	1.186632	6.404822	0.660754
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H	3.512293	-2.198299	-2.744095
C	-3.500662	2.515145	-1.257436
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H	0.120701	-4.959900	-0.968421
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H	5.035852	1.083836	0.605929
H	3.788449	0.143580	1.369428
C	1.333913	-5.357670	0.769273
H	1.409880	-6.414649	0.494658
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H	2.254455	-4.858622	0.451251
C	2.574992	2.219925	-1.911610
H	3.171695	2.330575	-2.805458
C	1.455051	3.003890	-1.554367
H	1.048229	3.825983	-2.126661
C	-3.632029	0.030867	-3.174659
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Ge	-0.58841246654205	-3.92423654014774	-2.16501609533332
Ge	1.04391378731919	-4.05494996302126	-3.98604724188003
Ge	1.04468267178729	0.07659734945414	-3.97670158585319
Ge	2.34842325396779	-1.98931917104807	-4.03208743502267
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C -4.45985016391251 1.93286623017136 -0.78762602046728

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C 0.54209910545296 1.70312707253105 0.04417903804557

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C 1.89403536143510 3.62613320615564 -0.63959626044394

C 2.96350524507952 3.15941768118478 0.11691214264610

C 2.84171230496151 1.97579970089534 0.83699675501339

C 1.65109755349651 1.26912519300460 0.77925908246980

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H -23.87782634185524 -9.06445293680138 -11.26329056229624

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$[Cx^{Et}Ge_2F]^-$

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N -1.68620212810862 -1.43421147486752 -0.44876749928961

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C -2.84582692758240 -1.33393525325222 -1.19964610296300

C -2.95192141441767 1.24929678883708 -1.08945882529955

C 1.20681389833693 -2.58616335335058 -0.38617826734913

C 2.83065450907579 -1.13497074064874 -0.94385753990685

C 1.02914868338440 2.64244698490115 -0.30176523575783

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C -0.00401006252461 -3.22350937883081 0.29901831539220

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H -5.50713213504329 -1.01845465582304 -1.45757879392410

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H 0.82262203911581 3.18903502309006 2.36028600153013

C 3.67393291417562 0.12268615794814 -0.85250625808236

C -1.17931850053667 -3.60388208719658 2.58068679858590

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H 1.06117280844385 6.50620759684518 0.68384520804124

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H -4.29770321467768 2.77065855734657 -1.92834618035983

C -0.18162843843657 3.21011638716819 0.44073584480200

C 0.08726890186800 -4.76245605936869 0.10859646070417

H -0.84433030543875 -5.20555343892126 0.47786288651896

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H 1.34250958582735 -6.48395704619898 0.48468916691508

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H 3.30940682365106 2.48606567670232 -2.69057610543968

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H 1.26502588257897 4.06480596618380 -1.96480370081544

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H -4.25970460648507 0.88195680273625 -3.39302093516118

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H 6.24569271507023 1.29768418920236 -2.96435008388760

H 6.50865000239402 0.96328744772448 -1.25147892963855

H 5.34690246671180 2.20409072592969 -1.73478706197409

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H -2.37405828979964 0.16285869368696 -4.87240856502597

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C -5.10201978671230 -0.21057364917432 0.50545608027127

H -6.14336065096012 -0.26227305829388 0.84311423029993

H -4.63281578875507 0.66697214198155 0.96203801702476

H -4.57359080855721 -1.09444430593776 0.87739889018733

F -2.10161493340091 -0.08811594106173 2.00777732299979

$[Ge_9H_{12}F]^-$

Ge -2.30028747700207 -1.97619792497903 -2.50917727133844

Ge -1.90546427655822 -1.96714420764915 -4.99066380399289

Ge -0.57547659754304 -3.86625341479893 -5.81659911296821

Ge -0.58038622420692 -0.20173664888460 -2.10987583647675

Ge -0.55559525861412 -0.07455840630478 -5.80005591559775

Ge -0.59296728863883 -3.76648002718826 -2.12503444209058

Ge 1.00413367509586 -3.98128554071232 -3.96883715288565

Ge 1.02168428839257 0.01486880606377 -3.94913703926557

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H 3.30627370382285 -1.98626648461451 -5.29717912471859

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H 0.19241242016215 -3.59491522250890 -0.80090399354862

H -1.23396449977530 -5.17451538123839 -2.00027879643445

H -1.21171776281418 1.20999617489873 -1.97765964277749

H 0.20080557208889 -0.38700017888857 -0.78509952197509

H 1.92524658530118 1.27169897206412 -3.98379720371762

F -3.44682965608186 -1.95427414572753 -5.91380557147440

$[B(C_6F_5)_3]^-$

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C -2.32050957129494 1.99834670925956 0.91750884144898

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C -4.33989455873825 3.19913239527618 0.48314368366120

C -4.24058630302364 2.82359590565114 -0.84649223537746

C -3.17157051935732 2.03436307385406 -1.26660344522656

C 0.45998412462742 1.67375581611250 0.43619451220067

C 0.68668021088616 2.84601790107137 -1.15509338435530

C 1.73927864792623 3.71643278949682 -0.89956412204633

C 2.61943957443940 3.43184379828359 0.13364877256092

C 2.42608809845260 2.28742640999998 0.89116991958317

C 1.35826096701488 1.44546652617541 0.59964618618514

C -0.78325432443833 -0.78774051121747 -0.22062847687327

C -1.78121636721998 -1.43495662089560 0.49647627939626

C 0.32119011582347 -1.58334507409988 -0.52210010510665

C -1.69044056470994 -2.75897830810225 0.91888600688309

C 0.45660594659376 -2.90483637571877 -0.12340073426613

C -0.56389543116269 -3.50012131802385 0.60506736676333

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F -0.45988944441334 -4.78046218916142 0.99833032175292

F -2.92828859540481 -0.80513937403809 0.83108913518736

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F 1.35274313469749 -1.06557421251093 -1.21698816912973

F -0.15085859300588 3.20721599647574 -2.14590336422797

F 3.64368703390836 4.25938160152992 0.40137857122236

F 1.91183773563145 4.83478232362579 -1.62801712641736

F 1.23629068790883 0.36659688127738 1.40101679097897

F 3.27230576551098 2.01140601574333 1.90047315440049

F -5.18491156319652 3.22617702654918 -1.71719917542308

F -5.36705559794506 3.95827807756352 0.90121217599758

F -3.46014757562834 3.13234624705057 2.67567519372438

F -1.41684558969215 1.59632464319617 1.83804114788244

F -3.17031844327925 1.71146079654936 -2.57139511782285

F -0.80708938634260 0.55192540314069 -2.26977961356385

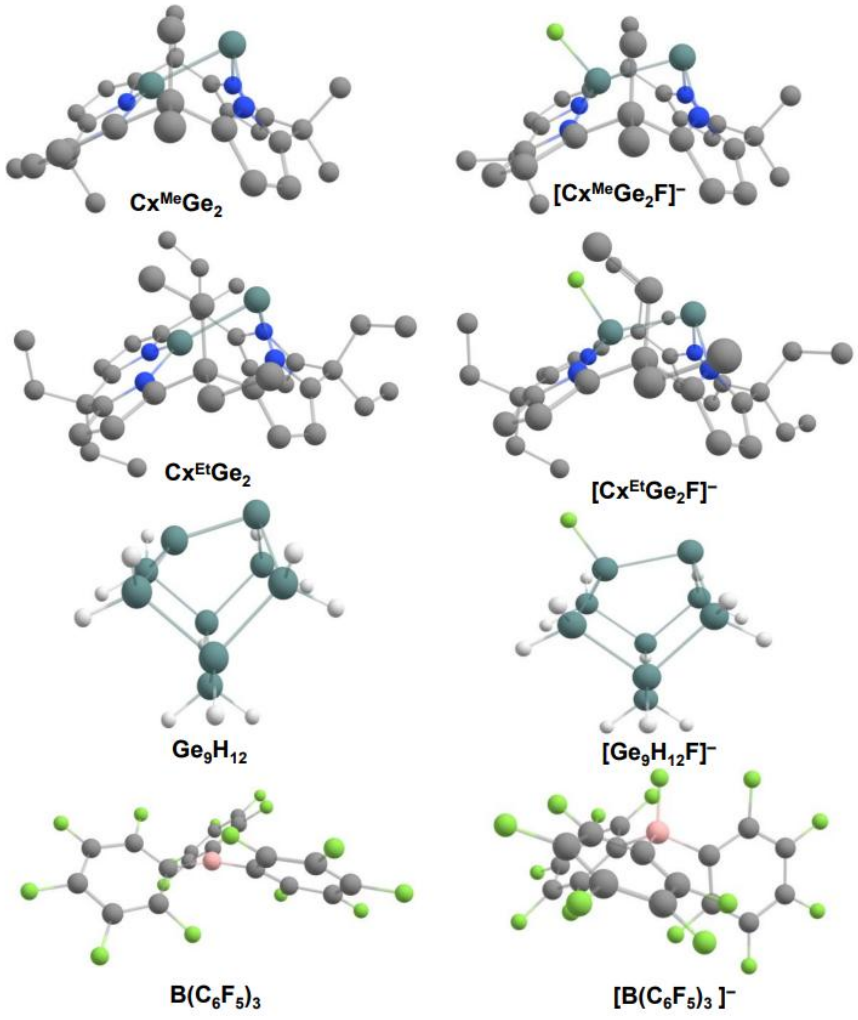

Figure S 3-7. Structures for the calculation of Fluoride Ion Affinities.

3.6 Mechanistic Considerations and Thermodynamic Data for the Comproportionation Reaction of $Cx^{Et}Ge(thf)_2$ and GeX_2 (X = Cl)

Transition states were found by first performing relaxed surface scans along a potential reaction coordinate (starting from the geometric structure of the starting material) and by then optimizing a reasonable input geometry close to the actual transition state with the exact hessian. The surface scans and optimizations were carried out at the same level of theory as the optimization of the local minima. Transition states were confirmed as saddle points of the potential surface by frequency calculations at the same level of theory. More precise single-point energies were calculated as described above.

For a deeper understanding of the comproportionation reaction between **$Cx^{Et}Ge(thf)_2$** and Ge(II) halides, DFT calculations were carried out. Prior to the computational study, several methodological considerations were made:

(i) The *meso*-octamethylcalix[4]pyrrole ligand **(Cx^{Me})** was employed instead of Cx^{Et} to minimize conformational complexity. In our group it is well established that twisted ethyl substituents at the *meso*-positions can induce significant conformational energy differences of up to ~40 kJ mol^{-1} between isomers.

(ii) For reasons of computational simplicity, the donor-free species **$Cx^{Me}Ge$** was used as the initial model. The germanium center within this complex is denoted **Ge^1**, while the germanium atom of $GeCl_2$ is referred to as **Ge^2** in the following discussion.

(iii) The mechanism was investigated using **$GeCl_2$(dioxane)** as the Ge(II) precursor, as this avoids the computational cost associated with heavy-atom treatment of GeI_2. It is assumed that the mechanism for GeI_2 is analogous.

Figure **S107** shows a potential reaction pathway of the comproportionation reaction. The proposed pathway commences with the coordination of $GeCl_2$(dioxane) via its lone pair to the Lewis acidic Ge(IV) center **(Ge^1)** of **$Cx^{Me}Ge$**, which possesses a vacant p-orbital. This process is accompanied by dissociation of the dioxane ligand. The latter was not analyzed further, as $GeCl_2$(dioxane) is known to be polymeric, and the detailed mechanism of dioxane dissociation is beyond the scope of the present study.

Subsequent to coordination, the nucleophilic α-carbon atom of the calix[4]pyrrole framework attacks the coordinated Ge(II) center, affording a digerma-azetidine intermediate **(INT1)**. At this stage, the comproportionation event has effectively occurred, and both germanium centers are in the +III oxidation state. Notably, the simple σ-adduct **$CxMeGe^1 \leftarrow Ge^2Cl_2$** could not be located as a local minimum on the potential energy surface. The four-membered digerma-azetidine ring in **INT1** is associated with considerable ring strain. Consequently, ring opening and subsequent migration of the Ge^2Cl_2 fragment to a neighbouring pyrrole unit are feasible. This pathway involves a transition

state **(TS1*)** characterized by heterolytic cleavage of the Ge^1–N bond and concurrent formation of a Ge^2–N bond, leading to **INT1***.

From **INT1**, this next step is involving a heterolytic Ge^1-N bond cleavage and Ge^2-N bond formation (**TS1**) resulting in **INT2**. In this intermediate, Ge^2 adopts a pentacoordinate Ge(IV) configuration, while Ge^1 is reduced to tricoordinate Ge(II). The next step involves the transfer of one Cl atom from Ge^2 to Ge^1 (**TS2**), to form **INT3** in a strongly exergonic process, where Ge^2 is once again reduced to +III and Ge^1 is oxidized to +III. Finally, cleavage of the C–Ge^2 bond occurs concomitant with rearomatization of the pyrrole unit and formation of a new Ge^2–N bond via **TS3**. This furnishes the thermodynamically favoured product $\mathbf{Cx^{Me}Ge_2Cl_2}$, with the overall process being downhill in energy.

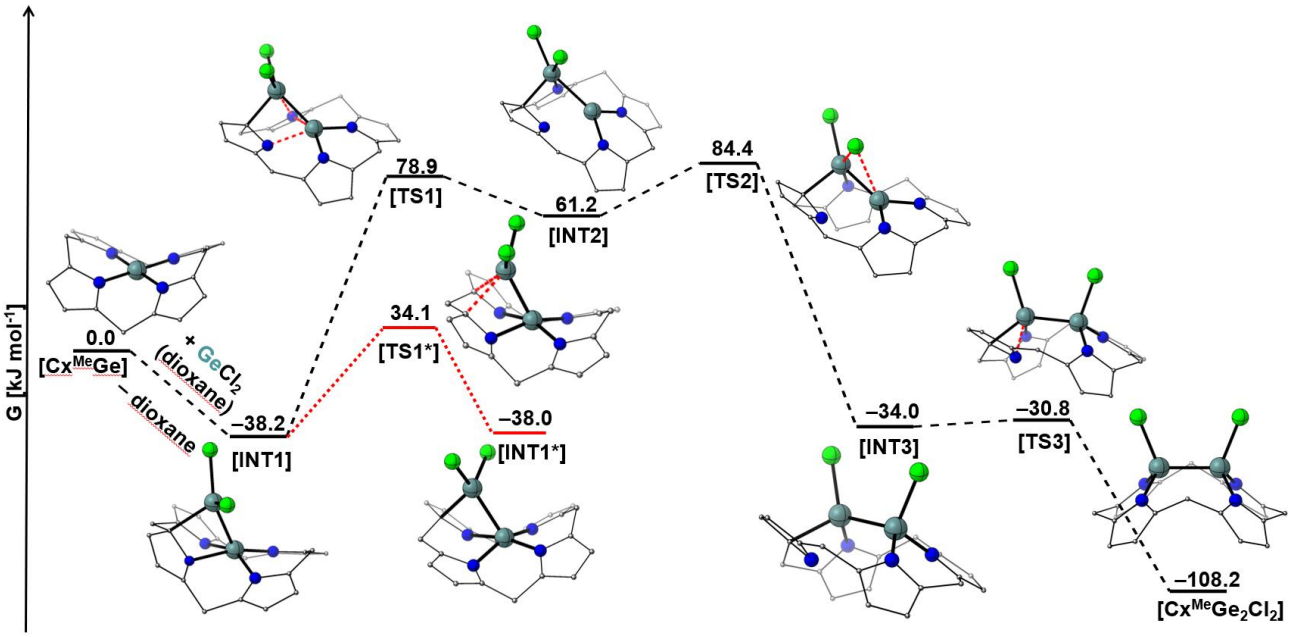

Figure S 3-8. Possible pathway for the comproportionation reaction of $\mathbf{Cx^{Me}Ge}$ and $GeCl_2$(dioxane).

Table S 3-8. Computed energies for the calculation of the thermodynamics for the reaction.

	r²scan/def2-TZVPP		DSD-PBEP86(D3BJ)/def2-QZVPP + SMD(DCM)	
Compound	**E^{r2scan} [a. u.]**	**G^{r2scan} [a. u.]**	**E^{PBEP86} [a. u.]**	**G (DCM) [kJ mol-1]**
$Cx^{Me}Ge$	-3381.956778	-3381.470467	-3379.951116	-8872785.521
$GeCl_2$ (dioxane)	-3305.058378	-3304.970773	-3303.618265	-8673420.409
Dioxane	-307.5936002	-307.5005105	-307.3173641	-806617.3939
INT1	-6379.442461	-6378.956712	-6376.271479	-16739626.71
TS1	-6379.40283	-6378.917137	-6376.226798	-16739509.55
TS1*	-6379.420494	-6378.935957	-6376.242745	-16739554.45
INT1*	-6379.442461	-6378.956711	-6376.271481	-16739626.71
INT2	-6379.408258	-6378.923343	-6376.23281	-16739527.37
TS2	-6379.4009	-6378.915401	-6376.224406	-16739503.78
INT3	-6379.441103	-6378.955263	-6376.269986	-16739622.55
TS3	-6379.441086	-6378.954244	-6376.269771	-16739619.36

$Cx^{Me}Ge_2Cl_2$	-6379.46929	-6378.981266	-6376.30043	-16739696.75

3.6.1 Cartesian Coordinates for Stationary Points in the Comproportionation Reaction of $Cx^{Me}Ge$ with $GeCl_2$(dioxane)

$Cx^{Me}Ge$

C	3.031055	-2.899109	2.120152
C	1.687000	1.272423	-2.865730
C	-3.381233	3.330303	0.894870
C	-1.506584	-1.961231	-2.647487
C	3.919708	-0.499457	0.598862
C	3.955469	0.632653	-0.268791
C	2.608323	-0.854624	0.767104
C	2.664050	0.952420	-0.591349
N	1.818337	0.037642	0.039789
Ge	-0.072987	0.006831	-0.078347
C	1.977135	-1.893382	1.649326
C	2.115061	1.971492	-1.548682
C	0.895908	-2.597247	0.879724
N	-0.056584	-1.872686	0.159870
N	-0.087267	1.885093	-0.326693
C	0.924992	2.640525	-0.921842
C	-2.292392	2.255067	0.838994
C	-1.109252	2.755234	0.059482
C	-0.999613	-2.771948	-0.341191
C	0.550508	-3.921090	0.831979
N	-1.963958	-0.022572	-0.189589
C	0.539375	3.953986	-0.913106
C	-1.859666	1.930073	2.293123
C	-0.638180	-4.032802	0.050999
C	-0.738079	4.027890	-0.282165
C	-2.823410	1.014022	0.180110
C	-2.740048	-1.082796	-0.663316
C	3.187322	3.010803	-1.886879
C	1.364061	-1.211344	2.900859
C	-3.137675	-3.412444	-1.437599
C	-4.109415	0.605669	-0.051407
C	-4.056090	-0.711906	-0.595731
H	-5.002973	1.176686	0.155587
H	-4.899856	-1.308013	-0.912134
H	-3.721239	3.596679	-0.110014
H	-2.999628	4.228274	1.389158
H	-4.236667	2.970027	1.473505
H	-1.074680	1.164494	2.319280
H	-2.711869	1.548809	2.865207
H	-1.462747	2.827035	2.779702
H	0.592634	-0.481419	2.625234
H	2.139208	-0.677045	3.459868
H	0.893110	-1.958877	3.547558
H	3.495726	-3.406202	1.269670
H	2.572034	-3.649455	2.770217
H	3.809037	-2.390194	2.696570
H	2.791748	3.745767	-2.593949
H	4.048119	2.526869	-2.357395
H	3.524582	3.532922	-0.986802
H	1.268430	2.004063	-3.564485
H	0.919746	0.508487	-2.688193
H	2.546382	0.774236	-3.326262
H	1.078301	-4.731632	1.313505
C	-2.096302	-2.304772	-1.254500
H	-3.928216	-3.078234	-2.115608
H	-3.587182	-3.689559	-0.479663
H	-2.672753	-4.298549	-1.879416
H	-1.155417	-4.947671	-0.199738
H	-2.298367	-1.608311	-3.316337
H	-1.025475	-2.843605	-3.082008
H	-0.749547	-1.169343	-2.584918
H	-1.307906	4.926426	-0.094265
H	1.098390	4.781790	-1.324994
H	4.771307	-0.983887	1.054405
H	4.841350	1.140777	-0.621658

$GeCl_2$(dioxane)

Ge	-0.467175391608	68	2.38194343244588	-0.42985112237502
Cl	0.68049154029069	3.50481844969091	1.13784662763518
Cl	-1.35406057649756	0.75365224451688	0.83210881275317
O	-2.25738679151012	3.65309428891639	-0.01235517264230
C	-3.51729876901260	3.15639979135727	-0.54467968766834
C	-2.10903147429411	5.07269939839242	-0.29554370430826
C	-3.27750997959602	5.81636985640805	0.31554618073389
H	-2.07670827259307	5.21604781285926	-1.38551558465855
H	-1.15949045260084	5.37438105849591	0.15451659252850
O	-4.51516103861650	5.33688827124432	-0.20371382902774
H	-3.21511796086838	6.87984271475145	0.06303646211055
H	-3.25396777395389	5.70639344868609	1.41247821739289
C	-4.65258078866586	3.94547615183691	0.07205143211471
H	-3.56706057604872	2.09892752209559	-0.27128669139741
H	-3.50905711402778	3.26706571854999	-1.63894174566802
H	-4.67694367873557	3.77116946771198	1.16054094868980
H	-5.60606090166088	3.62633037204060	-0.36115773621307

Dioxane

C	-2.84913705350607	1.99738392231858	-1.18227596999002
C	-2.74050215631361	2.43135636482667	0.26851371486012
O	-1.69358625448167	3.38885482184083	0.43064596402784
C	-0.45573433201269	2.84208886362670	-0.02554549053085
C	-0.56436927733673	2.40811652058446	-1.47633515538779
O	-1.61128511742509	1.45061793048680	-1.63846732985586
H	-3.13165850787512	2.86129304975666	-1.80910856488562
H	-3.60245789946005	1.21052701476712	-1.29930662840733
H	0.35982451346366	1.92289524301930	-1.80919440514299
H	-0.75798767978965	3.28801943311531	-2.11458327894845
H	-0.17321296525058	1.97817978526244	0.60128716319015
H	0.29758661301606	3.62894568538650	0.09148514766838
H	-2.54688397113371	1.55145351098477	0.90676196929351
H	-3.66469591189475	2.91657785402384	0.60137286410891

INT1

C	1.65648539963445	-2.32110977597797	-3.16229203672849
C	3.68840428928561	2.88956166176995	0.42825577707438
C	-1.55063285013900	1.18243136673460	-3.05315029719219
C	-2.09432041990136	-3.86600023448687	-1.05076559635876
C	4.30435704105343	-1.09124841436146	-1.08702805046779
C	4.35446704464731	0.17823205483552	-0.46193541751953
C	2.98101174967823	-1.44494378993728	-1.20573697825453
C	3.06262578729145	0.57231334582477	-0.20732110610011
N	2.19882666764993	-0.42312235394738	-0.67717081060252
Ge	0.32317629739884	-0.39089655267152	-0.19905528154553
C	2.40644367973031	-2.68153351938479	-1.85852068283274
C	2.59510586983523	1.81454514939481	0.52141423128136
C	1.42740774002759	-3.24411681289332	-0.87023939675562
N	0.42301225901848	-2.48998820494693	-0.49508073653370
N	0.27511952295474	1.48746387688689	-0.42820815299607
C	1.32914768187051	2.33613662106746	-0.09782574522973
C	-1.94631830560574	1.62277395634061	-1.61870863189534
C	-0.75361336196916	2.25765751377459	-0.95810634086992
C	-0.31419760056065	-3.15011577903950	0.55595638977517
C	1.40865853668322	-4.49412170875854	-0.15136577227377
N	-1.54297795361274	-0.66425585079384	-0.64477686293822
C	0.95281544901592	3.62207803507467	-0.39553993024275
C	-3.08880310189625	2.63794524276586	-1.72261734294935
C	0.35466921667542	-4.44256406235198	0.70789851977987
C	-0.35836334244434	3.57177693686333	-0.94212224629029
C	-2.39675626400204	0.41741454809594	-0.84412908417945
C	-2.27814260536020	-1.64941241889841	0.06003835882979
C	2.37190804216841	1.52160984988515	2.02875132073376
C	3.50708643242399	-3.69522968436997	-2.17822177443831
C	-2.62156306636009	-3.75091298130466	1.39066453633511
C	-3.62769676659896	0.12643131509179	-0.31343603108294
C	-3.54864424263179	-1.16789167687945	0.25903523136511
H	-4.50243319598504	0.75911958408075	-0.34562143516548
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C	3.78911729651107	0.79472979548139	-1.46685346737313
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C	-0.84146396449253	4.68374463829752	-0.00358560201893
C	-0.52499224532965	2.93671404518994	1.68230918916877
H	-2.59919202585722	3.90163400098642	-1.86942566491101
C	-0.57226440381674	3.17355233386429	0.15962571076365
C	-2.58163027058719	2.89734963081395	-1.47417492900469
H	1.04884884166898	4.53850974437917	-1.90605862375181
C	-1.72246611786599	2.42882580586334	-0.51073027434806
C	1.38873181291623	3.59771849416001	-1.50026683192969
C	-3.43139334004354	1.83617630428392	-1.88400972808063
C	0.75920265894088	2.87035565935083	-0.52026178001116
H	-4.20689187912441	1.89749055339276	-2.63305383441052
N	-2.04536291969990	1.07869166620531	-0.30778616312893
Cl	-1.96691047111035	-0.34958113269783	2.69561050723906
C	-3.08953640494276	0.72012050894477	-1.16666213313561
C	-4.62122999785687	-0.84075702508019	0.06996107111934
C	2.55540602519480	2.89968308281678	-1.90954974655994
N	1.54057714687775	1.72440748672488	-0.30659939413619
Cl	1.96618776725146	0.35020989725617	2.69585880205998
Ge	-1.17438942090826	-0.21097099720873	0.67392545462705
C	-3.70000214550700	-0.66643300826294	-1.16629705648842
H	3.25398122259375	3.22139520584984	-2.66770810530178
C	-4.57266039835938	-0.82207131029956	-2.41897960081585
Ge	1.17398147380629	0.21127331753489	0.67407297104398
C	2.63650352727437	1.74553637054163	-1.17579676751252
C	-2.63661743402564	-1.74548836066173	-1.17596520827699
C	4.62084433880566	0.84100676567859	0.07070171714216
N	-1.54083821177944	-1.72425358235627	-0.30657584002950
C	3.69990418183491	0.66650397692021	-1.16574525064750
N	2.04511407064349	-1.07852377437428	-0.30731931855875
C	4.57284433204111	0.82197531863793	-2.41825301181051
C	0.52455789453620	-2.93663604658912	1.68278285162422
C	-2.55543790469361	-2.89976569764233	-1.90950133131981
C	3.08944374634114	-0.72005379316219	-1.16605404093199
C	-0.75942851593271	-2.87024152730336	-0.51996210769853
H	-3.25389976030437	-3.22158934063064	-2.66771700549461
C	0.57197473382752	-3.17338797822537	0.16008823050459
C	1.72225697110916	-2.42868701562141	-0.51016183059058
C	-1.38878894767615	-3.59770687799227	-1.49999813126596
C	3.43144669992142	-1.83619912790419	-1.88319058146509
C	2.58151746429953	-2.89728694444049	-1.47348274055926
C	0.84119853825096	-4.68356479018284	-0.00314001514626
H	-1.04881944332235	-4.53852922618842	-1.90564998212427
H	4.20709338923015	-1.89760741865586	-2.63207350550601
H	2.59910263686898	-3.90159950115680	-1.86866461284296
H	-0.33547673636519	1.90760289956914	1.99671233427670
H	-1.48307598188002	3.22075376562027	2.12888991773562
H	0.27226292438701	3.54198348528702	2.12531719134375
H	-0.90227706955698	4.98333574242987	-1.05093857449821
H	-0.03361912536609	5.25179490270433	0.46605898622976
H	-1.78857326216917	4.94067838349634	0.47908178113900
H	0.90210922669938	-4.98311343472353	-1.05050133114278
H	0.03331248186477	-5.25163529244066	0.46640959901228
H	1.78826629953587	-4.94050808949229	0.47960478491868
H	0.33500868073429	-1.90755783052747	1.99723951322656
H	1.48260061158407	-3.22069671966266	2.12943845625719
H	-0.27273377990241	-3.54193755550255	2.12568122924637
H	-5.40169624992498	-0.07291516761759	0.05804656890032
H	-4.07547345244815	-0.75044521610600	1.01173207242250
H	-5.08768760271603	-1.83112710857359	0.04482670910983
H	-3.98181415569464	-0.70813715044861	-3.33221830078740
H	-5.36870885052777	-0.07255464411356	-2.41507500575597
H	-5.04786242723859	-1.80680783713358	-2.42304841761892
H	5.40133463589318	0.07318458317584	0.05906927692016
H	4.07486898036186	0.75080064462850	1.01235794017009
H	5.08728053517345	1.83138621748682	0.04554989776055
H	3.98220243274232	0.70792624890710	-3.33160938385536
H	5.36888405549341	0.07245140791270	-2.41406761260243
H	5.04805458832174	1.80670743406782	-2.42234338788675

3.7 Mechanistic Considerations and Thermodynamic Data for the Reaction of $Cx^{Me}Ge_2$ and PhCCH

DFT experiments were conducted following the same procedures described in Sections **3.1** and **3.6**. For the cycloaddition reaction between **$Cx^{Me}Ge_2$** and phenyl acetylene (PhCCH), three possible pathways can be considered: (i) zwitterionic, (ii) biradical, and (iii) concerted. For the latter case, no evidence could be found in the literature, and it was therefore not investigated further.

In the zwitterionic pathway, starting from the in situ generated digermene **$Cx^{Me}Ge_2$** and phenyl acetylene, a σ-adduct (**INT1**) was identified prior to the formation of the transition state (TS) (Fig.**S3-9**). In this structure, the α-carbon coordinates to the Lewis-acidic Ge-down atom. The observed configuration is more stable, since the positive charge on the phenylacetylene is better stabilized in this case. A σ-adduct **$INT1^{trans}$** analogous to those observed for neutral Lewis bases such as NH_3 and pyridine—where the alkyne binds from below—was found to be slightly less stable (ΔΔG = 3.7 kJ mol^{-1}). Furthermore, no corresponding transition state leading to the formation of **$Cx^{Me}Ge_2$(PhCCH)** as the respective product could be found. From **INT1**, the imaginary mode in **TS1** reveals a bond shortening between the Ge-up atom and the β-C atom, leading to the cycloaddition product **$Cx^{Me}Ge_2$(PhCCH)** in an exergonic reaction.

For the biradical pathway, optimization of **TS1** in the triplet state **(S = 3)** yielded both an intermediate (**$INT1^{S=3}$**) and a transition state (**$TS1^{S=3}$**). However, these structures were found to be significantly higher in energy than their closed-shell counterparts, (ΔG(dcm) = 173.4 kJ mol^{-1}, and ΔG(dcm) = 129.5 kJ mol^{-1} respectively). Attempts to identify open-shell singlet state structures (**S = 1**) using the “broken symmetry” or “spin-flip” approaches were unsuccessful. Single-point calculations in the open-shell singlet state, based on the optimized geometries of **$INT1^{S=3}$** and **$TS1^{S=3}$**, gave energies differing by less than 1 kJ mol^{-1}. These results strongly suggest that a biradical pathway can be ruled out.

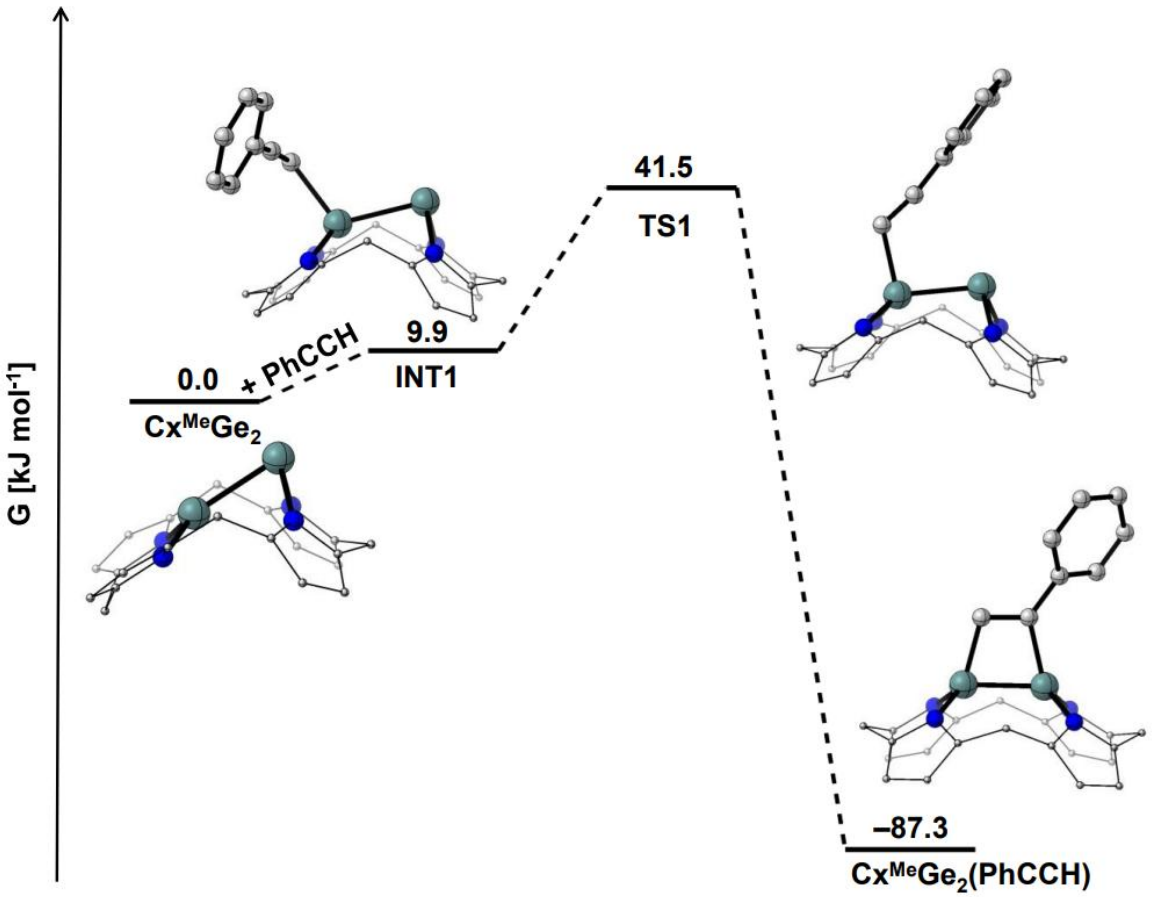

Figure S 3-9. Possible pathway for the comproportionation reaction of **Cx^{Me}Ge** and PhCCH.

Table S 3-9. Computed energies for the calculation of the thermodynamics for the reaction.

	r^{2}scan/def2-TZVPP		DSD-PBEP86(D3BJ)/def2-QZVPP + SMD(DCM)	
Compound	**E^{r2scan} [a. u.]**	**G^{r2scan} [a. u.]**	**E^{PBEP86} [a. u.]**	**G (DCM) [kJ mol-1]**
Cx^{Me}Ge$_2$	-5458.979251	-5458.494117	-5456.323979	-13784177.93
PhCCH	-308.3105074	-308.2322385	-307.9772905	-777906.9397
INT1	-5767.313732	-5766.724907	-5764.322775	-14562074.98
INT1^{trans}	-5767.326019	-5766.735726	-5764.322778	-14562071.28
TS1	-5767.307665	-5766.718759	-5764.310366	-14562043.42
CxMeGe2(PhCCH)	-5767.353093	-5766.7587	-5764.366817	-14562172.18
INT1$^{S=3}$	-5767.31365	-5766.726775	-5764.256093	-14561911.43
TS1$^{S=3}$	-5767.268877	-5766.686267	-5764.269231	-14561955.4

3.7.1 Cartesian Coordinates for Stationary Points in the Reaction of Cx^{Me}Ge$_2$ and PhCCH

PhCCH

C	-5.11912370169012	3.72928150344654	0.00685864879438
C	-5.12983297662478	2.33647612288449	0.00559577890309
C	-3.92721146908165	1.63396727514498	0.00399931191721
C	-2.71798624349315	2.31512084484958	0.00366033574600
C	-2.69942599475524	3.71904237353745	0.00492532927982
C	-3.91569419081565	4.42053066693565	0.00653172039881
H	-1.77706078198248	1.77438096647347	0.00241886376297
H	-3.89951670749282	5.50563444444598	0.00751142709179
H	-6.05478947557776	4.28070378012860	0.00810937092786
H	-3.93150174290559	0.54792766943573	0.00301018971435
H	-6.07372331409160	1.79950693016003	0.00585660571928
C	-1.46487607239163	4.42182235176593	0.00458455810452
C	-0.41765596067036	5.02199103673376	0.00427842490401
H	0.50695863157285	5.54670403405781	0.00401943473592

INT1

Ge	10.74633080931138	7.81725915388697	3.42395350978063
N	10.22556799370572	9.60096179433549	3.39877836136342
Ge	11.55162695012751	7.06007155571666	5.44963581924327
N	9.26525683695398	6.92758333239043	2.75173360913295
N	10.63760765785752	5.62191182480959	6.18173247362408
N	11.59996986178355	8.29655436300945	6.82672981294376
C	11.29690873028685	9.66828256317930	6.73784622771164
C	9.56161642296770	4.92862248355177	5.59055170903234
C	10.49416266349406	5.58939362830113	7.56686132807210

C	11.33017610081449	7.85027003457145	8.11720974008308
C	8.65806546787955	5.77679020945745	3.29249199286655
C	8.30798446441709	7.66999434144607	2.06453631518609
C	10.35247823500679	10.51822920041823	4.46255188304971
C	10.89902925203454	10.05685638447630	7.99732082295702
C	9.36206822661620	4.66476457692181	4.08753066693183
C	9.38038460042092	4.84714120367281	7.86102881745556
C	8.80680304269404	4.43201027776622	6.62931106175152
C	10.69191336733024	4.26927596571862	3.41442384801339
C	7.34648395858409	5.80212422908849	2.87523966689206
C	12.89629433271141	5.88612546110062	8.24994603310075
C	11.44231711089977	6.37494737930613	8.45391843954348
C	9.10214084878541	9.93605214907187	2.64495424258567
C	11.56329467222154	12.01515044223128	6.01309286888234
C	7.40366757967406	9.64100360658406	0.84987863799668
C	12.85054936142696	10.29529938224226	4.83067641034800
C	8.64802573979349	9.04081343090218	1.50864106896651
C	7.12343932472353	6.98234320267920	2.11634135159500
C	10.91211000474392	8.92542595302273	8.85744336134051
C	11.48670641521255	10.55944553734048	5.49987925634204
C	8.46502139972154	3.41117480816820	3.97792973876261
C	9.76149046883081	8.94082615446784	0.44062722620134
C	8.55133923233370	11.06995024329590	3.18160349191541
C	9.33619468465516	11.43332799709857	4.30834354224466
H	13.00000743080260	11.00648960862271	4.01140847348956
H	12.95219517794975	9.29457183110180	4.41389751296793
H	13.65110722764809	10.42439524159424	5.56697384545975
H	11.73116886657889	12.69047475277966	5.16979580441872
H	12.39265819126057	12.11041555897560	6.71947447073199
H	10.64768233911917	12.32534513741579	6.52011426056018
H	9.46315726429967	8.24924490960824	-0.35435779908502
H	10.71332476017689	8.58483887224221	0.85091146216122
H	9.95425576471402	9.92891481670374	0.01020953476353
H	13.24413089020617	6.01019279293833	7.21704740239949
H	12.97084795531237	4.82096727116206	8.49200742633899
H	13.57559472532602	6.45543151331955	8.89259351618914
C	11.06376984779507	6.15854492370918	9.92095979716322
H	11.13811326861343	5.09695328895661	10.17529994030071
H	10.04175237047804	6.49401094816432	10.11759414143850
H	11.74492110475106	6.71732113900688	10.56977120057944
H	7.07394812025098	9.00530609322256	0.02245317991148
H	7.63420399074885	10.63340681281906	0.45120502459177
H	6.58239605778476	9.73533611199979	1.56579501195047
H	10.50231083870641	3.97872767125551	2.37554285717375
H	11.13506461867014	3.42003306985664	3.94537213021879
H	11.43583142016908	5.06386194708665	3.39938252478535
H	8.32919980629323	3.14944106587079	2.92495303189620
H	7.47891738912949	3.56761676992200	4.41941577348550
H	8.94158648641394	2.57469489493587	4.49621988440359
C	13.07357140415326	6.80231660515365	4.20653592311965
C	12.60981767509442	7.22423134083577	3.00474626958689
C	13.35665704572724	7.22685212947184	1.74663614444851
C	12.74692865784275	6.77904232641343	0.56666791717815
H	7.68152495355628	11.59376280620964	2.81244733032788
H	9.17119395078152	12.30154706541581	4.92840665486986
H	6.60507005510456	5.04381500466478	3.07709452238267
H	6.18882285624428	7.28314182508323	1.66551178852619
H	7.93170735040314	3.80744927249527	6.53096267540258
H	9.00806844603135	4.61582167860631	8.84853046570519
H	10.64204288062528	8.91594063325470	9.90352631159494
H	10.63376364403308	11.06035406686327	8.29437434102848
H	14.68912926281007	7.65954887890037	1.66955183296840
H	15.39148395990130	7.64303345817529	0.50144971294741
C	14.78102900023043	7.18313550677771	-0.66274016424110
C	13.45932047201751	6.74619672357521	-0.62497618025882
H	11.71701851825012	6.43118380818071	0.59717499739443
H	15.33256338156874	7.16992914596055	-1.59812321274817
H	12.97981320335392	6.38248459109587	-1.52901961155048
H	15.15983544130839	8.02965785791995	2.60658771205636
H	16.41907124197750	7.99385035229644	0.47466432524979
H	14.07213786774742	6.38765492813767	4.34371899114353

INT1^{trans}

Ge	4.64755062033863	8.53956515156833	12.86579939351248
Ge	3.72805734486905	10.55003097301665	13.88876739349162
N	5.07301027520189	8.04506623092712	14.73697000085821
N	3.47410517861188	12.07054198463204	12.84330306685209
N	6.28170171896563	9.65384516777836	12.72678518956786
N	2.13356115000893	10.48456164074605	14.86417367426087
C	6.39849590707783	7.96315731511325	15.10726322262304
C	2.20451095086889	9.66102532608253	15.99441558178442
C	1.66962885391434	11.74604547802769	15.25516943659728
C	2.79324563087588	13.12259859811976	13.45726739852570
C	7.49260562107629	7.89584712014448	14.05876052143908
C	4.58005174441149	12.58012587564651	12.15374982043017
C	2.75651056504965	8.23288531266923	15.93586965151072
C	8.48119153637001	10.04203965146944	12.88771829850012
C	6.47795858440339	8.00747555237235	16.48546544466575
C	7.89562144635275	11.09739069447630	12.14681986865795
C	7.46286929730007	9.17006454853089	13.23336185136878
C	2.12154574563988	7.47635335716765	14.75287966215177
C	5.15424968575390	8.12823108659573	16.97371579796747
C	4.29391471768047	8.16300560648166	15.89076318545982
C	5.50169343735488	11.70429093710372	11.29450683230951
C	1.39041045032506	11.69626845774204	16.59730693368105
C	4.63773680627147	10.81238513986891	10.37661491597928
C	7.30085461161556	6.65655967952884	13.14936536157331
C	6.53675706168937	10.86141814620184	12.05593575021698
C	4.54725148367838	13.94931359986515	12.29654300360386
C	1.51002545519849	12.85702782620281	14.23083189784724
C	2.29784125572759	7.50852798722733	17.21715074652041
C	3.42991974193129	14.28991540568862	13.11810894232055
C	8.85870094637914	7.74439324886034	14.73596016702398
C	1.07020180973481	14.14083695231623	14.93891076303628
C	0.41186054311065	12.43773999051401	13.22108667320336
C	6.28272560331047	12.65385439266229	10.36538127054196
H	9.52855586958352	9.93357632104213	13.13011503589629
H	7.37532415084876	7.91927723396566	17.08236862758944
H	8.42502571595136	11.94675656054754	11.74111688648014
H	3.12518728851890	15.29096669222922	13.39022155159667
H	1.20456909198271	7.50799548638252	17.27456961018013
H	2.68484921270944	7.98842529816793	18.11881287680183
H	2.65814685963682	6.47637831324113	17.20296207420913
H	8.10750574592740	6.61016272728556	12.41034482889571
H	6.35233054007264	6.67719273242982	12.59975933911484
H	7.30786666895560	5.74435641778569	13.75530614233811
H	5.58181036048669	13.23832516231205	9.76278235957634
H	6.92647775867309	12.07392881487432	9.69853364392090
H	6.91163249957548	13.34852933992185	10.92918050308714
H	4.00482152249214	11.44340496537724	9.74371666281482
H	3.96844571303382	10.14462814014145	10.92678916608298
H	5.28106049928128	10.19550359874735	9.74056180838359
H	9.64749853019880	7.68221732796643	13.98028252634525
H	8.88075434017031	6.82434110384942	15.32789954867128
H	9.08558446219677	8.58409458225971	15.39845992588028
H	0.26445567113967	13.22842033219633	12.47770335811397
H	-0.53195237209793	12.25702348831379	13.74679219541413
H	0.69477822556563	11.52072291580235	12.69711859770477
C	1.72644716728479	10.38544260388312	17.06210662909914
H	1.59829945858690	10.02569737931874	18.07334962152300
H	0.90318569896441	14.93615825545208	14.20667916088083
H	1.82592873968368	14.47759770808587	15.65533408215536
H	0.12959077646283	13.97316197619001	15.47185415983100
H	2.28849131388891	7.96036828886907	13.78590115015414
H	1.03704469012123	7.42342056573196	14.89344461257666
H	2.52513463164475	6.46027810197612	14.69675758326881
H	0.97293939332115	12.49279143510731	17.19750517827726
H	5.21867123430133	14.65567512888326	11.82846188970075
H	4.86689986721551	8.15980847855195	18.01521418887484
C	4.82098301904982	11.31763294212268	15.46781063294721
C	5.97231939476042	11.78169221415635	15.29681008100897
C	7.24872659545588	12.27295339498111	15.11292360266140
C	8.35131498146515	11.48147481602463	15.50844612760668
C	7.46388628811060	13.57040529685824	14.58376488603009
C	8.74915745311967	14.05583892679451	14.47970456364750
C	9.63424040539550	12.00187932672173	15.42152850240072
C	9.83423244195590	13.27731646779103	14.90637040220273
H	8.15402074795988	10.49735064201077	15.91862632310955
H	6.60454570865759	14.14740677316105	14.25730493457533
H	8.92229854771514	15.04710960609036	14.07196790481091
H	10.48170439342972	11.40332169003870	15.74205357371165
H	10.84196221736931	13.67606039595460	14.83179939963410
H	4.18158069816752	11.28118159505382	16.35065182212613

TS1

Ge	10.65523727111755	7.96510469254432	2.95652878947737
N	9.91946641784239	9.65166900473152	3.50882064873231
Ge	11.39297919216824	7.15054899555023	5.12873620263033
N	8.94317781801694	7.09813244992559	2.87962290248440
N	10.49318527049803	5.73676479768688	5.92684878739674
N	11.47810871354910	8.32544455244892	6.56368781220845
C	11.48945322782225	9.72677976825945	6.50991937088803
C	9.60667176909392	4.84501949629339	5.30424691225769
C	10.33781584648046	5.64437443654423	7.30970293309500
C	11.22122674893991	7.91981933369650	7.87288540854549
C	8.53040623140631	5.79919727289966	3.20510796396636
C	7.84349612518361	7.80743713665526	2.41840546986447
C	10.36899390299376	10.62588490021638	4.41067875741610
C	11.27040970445171	10.17414938333869	7.79074747152850
C	9.41268073405183	4.70087751050014	3.79479772648771
C	9.39042228066317	4.68596992653084	7.55984766597284
C	8.93627995391283	4.18779116276696	6.30758468182881
C	10.75445101750422	4.59118240461563	3.04337220073885
C	7.17833416284554	5.72606852813086	2.95478814397993
C	12.62896803317726	5.88998241844169	8.28997582367487
C	11.18637718243277	6.45748941919461	8.26401674708094
C	8.70145862810064	10.06299056439357	2.98746932791841
C	11.99803127209029	11.99678803759910	5.67779481021886
C	6.57924945466329	9.82903803248028	1.71660664651090
C	12.84848425068258	10.09677307699166	4.38555766082447
C	7.97383214085011	9.23903702398951	1.94886107609024
C	6.74496738977871	6.98430736305050	2.45893116872690
C	11.10206274977681	9.04772461381801	8.64272748913347
C	11.65034982681402	10.55924674593922	5.23833733452486
C	8.70208440116451	3.35229425354322	3.55660051395272
C	8.73427916537815	9.29040400577285	0.59813231502483
C	8.36992232735007	11.27028923197826	3.55255830854006
C	9.41652339727222	11.61952900002299	4.44620274244064
H	13.01257678118091	10.81416864829047	3.57419417768230
H	12.71564974818415	9.12666849171966	3.91303262386609
H	13.75096671852431	10.03790298117939	5.00429198271394
H	12.11346473723957	12.63002394573221	4.79396494579291
H	12.93456244288747	11.99384696786905	6.24374055374530
H	11.22222163199174	12.43511366052127	6.30749320540521
H	8.19943344290576	8.70141270361503	-0.15454938204295
H	9.75027786945034	8.88188964611622	0.67614032018062
H	8.82150682899391	10.32731347182492	0.25643200733552
H	13.10360682262269	5.94701955334551	7.30700249192808
H	12.61265031342745	4.83759275981765	8.59226438417571
H	13.24463293901282	6.46135863481413	8.99265246227765
C	10.61221123562051	6.32970155264719	9.67993275696707
H	10.60924119775314	5.28089588215146	9.99004523113380
H	9.59018193902317	6.71570404662718	9.72790838007264
H	11.23334637207912	6.88432326534583	10.38901805585743
H	8.04867986532230	9.25273959004827	0.95286904944778
H	8.66248617994366	10.86051222348956	1.36145216784174
H	9.98888935412765	9.82056786043545	2.63748128415193
H	10.56281415952796	4.33584586020043	1.99552621445018
H	11.37820305655739	3.81269989632362	3.49682052530139
H	11.34067343887939	5.51301601485009	3.03404775115062
H	8.53902874562152	3.20891285944716	2.48499161193421
H	7.73258634297903	3.30488282126400	4.05489724144580
H	9.32181698789675	2.53598698266413	3.93968382384338
C	13.27997096461037	6.58254217227842	4.54950567907380
C	13.65048076699602	6.73046816651720	3.34355727861280
C	14.24644337000328	6.80122149449053	2.09287344744978
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H	7.47572545068646	11.84530938606306	3.36058625577178
H	9.44645009007953	12.50629379872373	5.06178752940253
H	6.54553903508788	4.86787427366814	3.12567151920681
H	5.73601366899856	7.24620377272634	2.17530928497189
H	8.17821222469077	3.43082952293257	6.17459573127786
H	9.04613550811750	4.36668181851338	8.53278631591603
H	10.90991426676555	9.07854420987107	9.70537657641869
H	11.21612084650851	11.20636379834618	8.10204592123069
C	14.98858749776800	7.94864167921597	1.71501049225994
C	15.60418937537898	7.99459644555127	0.47948226979702
C	15.50050079565106	6.91794181220464	-0.40434955817890
C	14.77689328359873	5.78046406649529	-0.03950661835758
H	13.58167593769333	4.83519867713405	1.48027175017025
H	15.98369673412793	6.96485135669158	-1.37526199799182
H	14.70089471072265	6.94324004272793	-0.72644944272793
H	15.05587386732478	8.78352243651908	2.40516884860144
H	16.17062804318265	8.87635032829945	0.19539826422462
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Cx^{Me}Ge$_2$(PhCCH)

Ge	4.83998527667763	1.26195262508983	6.05226917813864
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C	1.02850589977601	2.38333327163209	7.15758638846270
Ge	4.13353937772655	2.61700311797060	7.78289816691369
N	5.80657405416070	-0.24128880291322	6.53878356290291
C	0.66663016195140	3.70705524991756	7.44304260978454
H	1.43226261967104	4.47937015237863	7.44619363001217
N	4.72404941469414	4.37318546091632	7.74125362264989
C	-0.65981149393481	4.03723052056907	7.68779888037454
H	-0.92882804826284	5.06921507077747	7.89285919846539
N	4.60437501527271	2.04211208044886	9.48516740628843
C	-1.64045650548509	3.04843987008325	7.67700605880944
H	-2.67520312774121	3.30536577844874	7.88317928847516
C	-1.28908622849468	1.72793083520909	7.40798029750038
H	-2.04940631616095	0.95231453074183	7.40783707395406
C	0.03325558073926	1.39612879388415	7.14322558608635
H	0.31140084230177	0.36444666114435	6.94480013689731
C	2.42289793080125	2.05124939959984	6.86884137469903
C	2.86763162531527	1.24297713922802	5.87688327259524
H	2.20423131814720	0.76375457601078	5.15715226839947
C	8.84485757564453	-0.65050932231801	5.70746160018633

C	6.89756056099722	-0.18102314283092	4.26545186845746
C	6.95621876906246	1.33507966518092	4.23929191572821
C	7.93194232241813	2.19823161859532	3.81400914400316
H	8.85460244270615	1.92817557864609	3.32100069244474
C	7.50680249998202	3.51489796674513	4.13629207884536
H	8.05153140460016	4.41752631024104	3.90365592498722
C	6.28323120921056	3.45217718071327	4.76417943451993
C	5.01929213700935	4.99541831005678	8.95213449304363
C	4.47331256699710	4.44331638189414	10.25623724048838
C	4.94814681707906	3.01293376747150	10.42407330009413
C	5.46813702568482	4.98549998768560	6.71296524228301
C	6.16415591327133	6.01584189985469	7.30322828570114
H	6.80440178821350	6.71928933558090	6.79259840983236
C	5.89236026026300	6.02082207988809	8.69787769746024
H	6.30179649555267	6.70708066545074	9.42488100156824
C	6.05425832073807	-0.69681679952063	7.84745290336890
C	7.21750256144275	-1.43069818565814	7.78609108070761
H	7.67397550435382	-1.96136858622972	8.60802834144920
C	7.71621668216168	-1.39862530018601	6.45555033666011
H	8.61728838679597	-1.87741262122680	6.10037226011626
C	5.13620167548818	-0.49998985212144	9.06458315245204
C	5.27589300542725	0.84249277655638	9.80060831097823
C	5.77967033407053	2.43674090200118	11.34779084775461
H	6.20552722372863	2.92135113071741	12.21439051153943
C	5.97580314825121	1.08424230146544	10.96045938661710
H	6.56370617624966	0.36058224216441	11.50488258599148
C	8.14683218761362	-0.75122997053040	3.59001462809928
H	8.19611479285311	-0.41733173791497	2.54923728036135
H	8.11183908397675	-1.84474932652776	3.60059382887343
H	9.05627494843057	-0.42694215340615	4.10339802153611
C	5.65525149748366	-0.68360407511726	3.49212025602076
H	5.69728693306628	-0.34099906510760	2.45317917943297
H	4.71311955551900	-0.31678500467394	3.91773565391883
H	5.61795201303630	-1.77751801792970	3.51505677109790
C	5.41002625577451	4.63562295264990	5.21696571215234
C	3.95132885558888	4.45450796700596	4.75236565082767
H	3.37474150372921	5.35266233236562	4.99856334155515
H	3.44172155364119	3.60581339174408	5.20558372826318
H	3.92753296441018	4.30443810328726	3.66771431795740
C	2.92803105299562	4.49081272179406	10.26750818272043
H	2.57964099713310	5.51303973350179	10.08558653196867
H	2.55136920062961	4.14543242743336	11.23582253248923
H	2.47667034908854	3.84593875566794	9.50493279880097
C	4.98881418272851	5.29336128909367	11.42001650076523
H	6.08177734246405	5.29678071580298	11.45466382359811
H	4.61098344708036	4.89790580965904	12.36749522829433
H	4.63998559219002	6.32506854106300	11.31351441801926
C	3.66399936788498	-0.77315862664428	8.69692317114770
H	3.25109349425831	-0.07215302899159	7.97305567117550
H	3.04348128247262	-0.71542115545445	9.59746831552322
H	3.57474428156274	-1.77569086467503	8.26499623324849
C	5.51102886960131	-1.60163117274429	10.08138245718849
H	5.38155430811794	-2.58437358089616	9.61958498341910
H	4.86024765052914	-1.52750727048160	10.95681135430601
H	6.54592534754011	-1.51917226393485	10.41887829040047
C	5.92502800128512	5.87779080894257	4.45537124658137
H	5.86542176748323	5.69647993883804	3.37877682600621
H	6.96119106431135	6.11619538711500	4.70300390695532
H	5.30660029175038	6.74379748500445	4.70714412999655

INT1$^{S=3}$

Ge	10.52586660637330	9.151435485583555	2.54017503612260
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Ge	11.72420658295606	7.96241193266497	4.42902056390207
N	9.01246417469573	7.82351801488875	2.51641009076212
N	11.12781996490170	6.21364248183677	4.85893969839775
N	11.50730320657615	8.68305168280847	6.17593785871722
C	11.22789684178078	9.99716501191216	6.52269855845176
C	10.57212076439552	5.26860929253343	4.00743839627275
C	11.18380573591496	5.68451046509904	6.13811461548600
C	11.38892421223546	7.89056278227568	7.30576499033371
C	8.98210297331527	6.45009164591038	2.59890402593690
C	7.71073732635045	8.27776058450629	2.57630859083103
C	9.76886381585630	11.04806320459548	4.90120643988687
C	10.92496159751513	10.02027518161167	7.87818028462912
C	10.19106317752068	5.53398846183252	2.56269857527143
C	10.66645130738036	4.39981045292463	6.09191628626691
C	10.28529802496105	4.14025695526308	4.76282967451825
C	11.33441967533948	6.07627800947116	1.69065232945801
C	7.64658968890207	6.04467922263711	2.75851577926196
C	13.30870650277178	6.28370911116771	7.35929481951929
C	11.76602585034476	6.42427409464564	7.32683839706937
B	8.07598214275124	10.40783408904329	3.60490910724622
C	11.23903974494459	12.47332034958773	6.31696218304641
C	5.86114481041353	9.94369566199028	2.56850895857985
C	12.29909507229171	11.18856452265433	4.52250420820660
C	7.37619591870241	9.74166485467661	2.44750616513473
C	6.85274855911865	7.18914347157110	2.75330663215466
C	11.02367391524420	8.70504837520720	8.36555364967993
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C	9.78030859587151	4.19971269772188	1.90912243238165
C	7.81764891605828	10.32075886138308	1.08697260966473
C	7.53194282658146	11.20100646298601	4.61763213127051
C	8.59048975112210	11.61156625130455	5.42246540153206
H	12.19030945674780	12.06474043406103	3.87514237986024
H	12.36919891566009	10.32109180217548	3.86045453710511
H	13.25161990785582	11.26307899729561	5.05752108719851
H	11.12304274487506	13.31461739884421	5.62714865173449
H	12.21715805075249	12.54203755915723	6.80278211798693
H	10.47473858818858	12.56315156689035	7.08923065533403
H	7.29980191982354	9.79524854958660	0.27722706383423
H	8.89477455898898	10.22416831076872	0.91415713656717
H	7.56645642706860	11.38600770378643	1.04179435060372
H	13.77484264456033	6.70676397149301	6.46809939123203
H	13.58150468383923	5.22380363211014	7.42059602891390
H	13.70652217389472	6.80291645129342	8.23829429167822
C	11.22380782630995	5.78916875415745	8.61734894030454
H	11.51501782038342	4.73681150674919	8.66917975468496
H	10.13353085673051	5.85787171253448	8.66971027868410
H	11.65499065549067	6.28689901428542	9.49012439265560
H	5.35102204782104	9.42696615341155	1.75037278263729
H	5.62032213264165	11.00838400468138	2.49822007731315
H	5.47695928270106	9.56073675065226	3.51826281175383
H	10.94931279001460	6.34628828899805	0.70164572796763
H	12.09834070575256	5.30358098428336	1.57409895470150
H	11.84779509742967	6.95566636671458	2.09149664206315
H	9.47952007203078	4.37891378896575	0.87272182938167
H	8.94903688440216	3.71670730845409	2.42447366516363
H	10.63393691906682	3.51410635359599	1.91832140404092
C	13.71119530219240	7.79709123490194	4.25866489320548
C	14.27296432720436	6.77130364774438	3.70261366401137
C	14.35719573155212	5.52121055387598	3.11207689809506
C	14.00863350736360	4.35397142806722	3.84752919884276
H	6.49134675355143	11.46715973826053	4.72916349520645
H	8.52372794860989	12.25006299897342	6.29052508856654
H	7.30227240814518	5.02556197021710	2.85278651780045
H	5.77624286779642	7.23188094649917	2.82865400928559
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H	10.56581981023511	3.72298872834173	6.92748312380078
H	10.86594931550944	8.39026565860134	9.38634543917011
H	10.66324429418448	10.89319678020954	8.45709866976645
C	14.79083424206761	5.36727732004370	1.76633282058308
C	14.84345369542744	4.11286001357576	1.18961672624426
C	14.47974770415651	2.97569174707115	1.91793867302021
C	14.06446190854235	3.11104215197755	3.24589205973908
H	13.65521327063806	4.46034305901209	4.86861317090895
H	14.52140190187782	1.99452432750132	1.45541035316373
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H	15.16915042523092	4.01307696965049	0.15792935178327
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C	11.43346994727142	9.68691851435998	6.38436172945504
C	9.57812887502593	4.79977767678500	5.32112203287834
C	10.34585769011135	5.62018035367928	7.29340321620100
C	11.16113824268068	7.91585403607793	7.78118158146531
C	8.44852656084705	5.77818253267831	3.30137249315171
C	7.74243505959973	7.80602547035019	2.59955270500459
C	10.51503867068627	10.68133566163295	4.23204700138397
C	11.00766749544862	10.15808099084919	7.61625553180876
C	9.34235349810481	4.65575271714171	3.82130955634514
C	9.37162431534306	4.68727171769923	7.57688855583917
C	8.89833248932245	4.17344463825080	6.34594321918602
C	10.65179862296913	4.53964161050466	3.01589952672255
C	7.06353794312379	5.75035608041984	3.19317930687740
C	12.65471987219605	5.95020858695472	8.23274648657868
C	11.19486070558893	6.46681716193075	8.21909984429898
C	8.71441942340105	10.07563743780536	3.00271517962167
C	12.17083265036175	11.91836803156588	5.60732322842350
C	6.47754333113872	9.83708238943165	1.92898875207224
C	12.94777304283738	9.96725444990496	4.34584949860091
C	7.87282041287400	9.21627666863586	2.07615819298240
C	6.62344680433114	7.02151556338834	2.75051595411138
C	10.83510040573195	9.05288648795583	8.48757275388068
C	11.73612099380371	10.51384358962167	5.13337664724908
C	8.60505904897901	3.31890098187498	3.59479656025678
C	8.52584306922594	9.19919220670524	0.66497055202066
C	8.65948052997257	11.46854414344195	3.19722393372427
C	9.78884955610909	11.84223210328974	3.98015749481700
H	13.23780861080345	10.70555308052741	3.58545592969343
H	12.74137998399146	9.03688527328311	3.80530836697134
H	13.79833285042989	9.78318583405156	5.01952772843963
H	12.40525679803304	12.54670115977903	4.73924007803262
H	13.06344517340275	11.83315952602196	6.23915988056541
H	11.38689491992843	12.41637700826267	6.18387319086721
H	7.92640830422587	8.58973288153145	-0.02154988939557
H	9.53963606070130	8.77981933910803	0.68485120224189
H	8.59629515062001	10.22217855861938	0.27866200745425
H	13.12618892258752	6.03534549331964	7.25094834578965
H	12.67772723415987	4.89605479589338	8.53089607958058
H	13.25262040238017	6.54006729561409	8.93634801971687
C	10.64495826096741	6.35495938046592	9.64577191493826
H	10.68744458137787	5.31416055952149	9.98244977022194
H	9.60766358841586	6.69990686163073	9.70034462830247
H	11.25360602332932	6.95524990148372	10.32894893858547
H	5.86330301773774	9.23012473006334	1.25425615898592
H	6.55664703898705	10.83733706911338	1.49140950520348
H	5.97372113263707	9.91554974120112	2.89962893341002
H	10.41427371124120	4.28698242278953	1.97670788146060
H	11.28598821635888	3.75307741233145	3.43993132428709
H	11.24976269448024	5.45408958902533	2.98443487606729
H	8.39647001324279	3.19332418678735	2.52803717041670
H	7.65540225578803	3.27322272578368	4.13039964552953
H	9.22951341582726	2.48867415894038	3.94034157727797
C	13.26243955734846	6.37411744545016	4.52074176543338
C	13.69062401250525	6.73524032868041	3.35058892419595
C	14.34970383433042	6.91361970877161	2.15138805648204
C	14.20726935102368	5.93773809803794	1.11196894354578
H	7.87989133450052	12.15487147734872	2.86327617750949
H	9.97662082089303	12.84536992302597	4.37452406901679
H	6.42483418609855	4.91101441711264	3.42881361516451
H	5.60026451364973	7.31568717529932	2.56096632511693
H	8.12061926614514	3.43280786319018	6.23297692036160
H	9.03356911393165	4.39773100902337	8.56149009924366
H	10.52266054071423	9.10061608979215	9.52391390598621
H	10.84120892229794	11.19468778279547	7.88152393815157
C	15.19934495528212	8.04762251894485	1.93222413392442
C	15.86441362928903	8.18493932321886	0.72823115099422
C	15.72024709983587	7.21661771085872	-0.28107976776508
C	14.89333190944053	6.09586717324328	-0.07642968982034
H	13.55704879704887	5.07370973112074	1.27436038505464
H	16.24982760154657	7.33587253207993	-1.22240591689290
H	14.78659259975071	5.33857313543226	-0.85672402563282
H	15.30421347341166	8.80053839188241	2.71552401843920
H	16.50798301843713	9.05455628102560	0.56723123613223
H	13.82435158427655	5.71758445381395	5.22635962151178

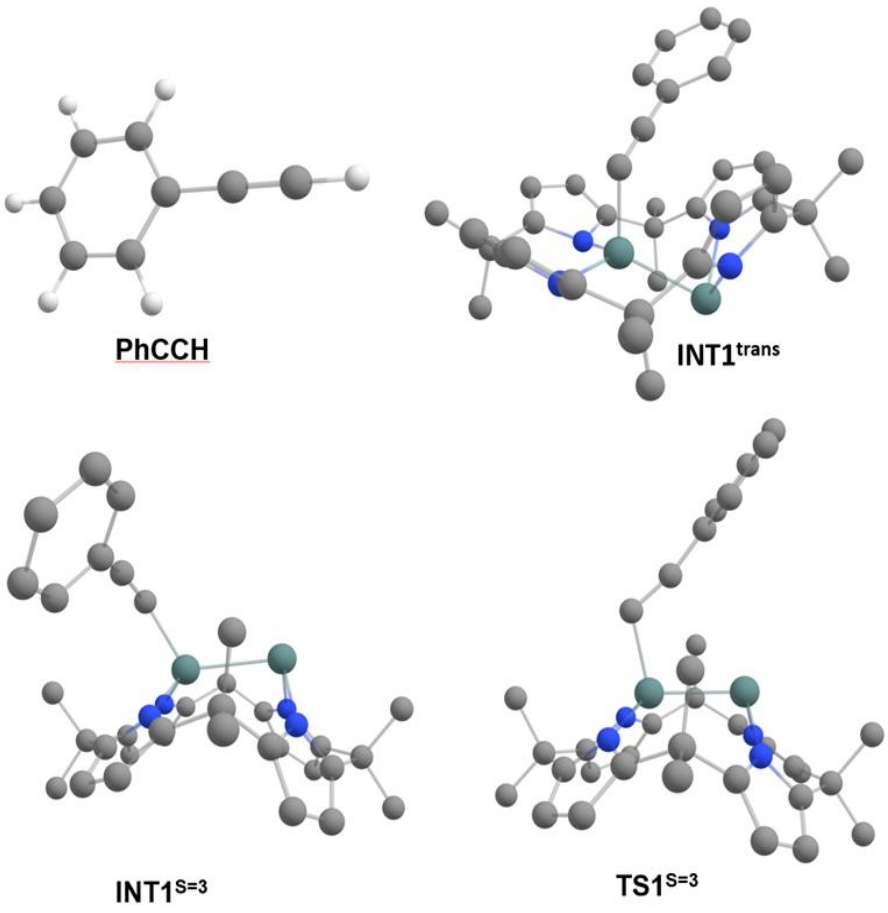

Figure S 3-10. Structures for the Reaction of $Cx^{Me}Ge_2$ and PhCCH.

3.8 Thermodynamics for Ammonia and Pyridine Affinities

Table S 3-10. Computed energies for the calculation of the thermodynamics for adduct formation of **$Cx^{Et}Ge_2$/Ge_9H_{12}** and different Lewis bases.

	r²SCAN-3c/def2-TZVPP			DSD-PBEP86(D3 BJ) /def2-QZVPP (SMD: DCM)	Donor Affinity (ΔH(Donor Adduct) – (ΔH(Lewis Acid) + ΔH(donor))
Compound	**E [a. u.]**	**G [a. u.]**	**H [a. u.]**	**E [a. u.]**	**ΔH [kJ mol^{-1}]**
Ammonia (NH_3)	-56.541	-56.5254	-56.5036	-56.5012	/
Pyridine (py)	-248.218	-248.1580	-248.1253	-247.9628	/
$Cx^{Et}Ge_2$	-5773.379	-5772.6789	-5772.5682	-5770.3885	/
$Cx^{Et}Ge_2(NH_3)$	-5829.989	-5829.2482	-5829.1362	-5826.956	- 152.4296
$Cx^{Et}Ge_2$(py)	-6021.6608	-6020.8707	-6020.7534	-6018.4124	- 156.566
Ge_9H_{12}	-18700.293	-18700.243	-18700.173	-18694.429	/
$Ge_9H_{12}(NH_3)$	-18756.875	-18756.789	-18756.714	-18750.984	- 146.252
Ge_9H_{12}(py)	-18948.562	-18948.428	-18948.346	-18942.45	- 146.445

3.8.1 Cartesian Coordinates for Ammonia and Pyridine Affinities of $Cx^{Et}Ge_2$ and Ge_9H_{12}

$Cx^{Et}Ge_2(NH_3)$

Ge	4.85036858873800	8.59309512191723	12.53127071966266
Ge	3.47500527670093	10.53450872874740	13.24438585770624
N	4.71302768691446	11.75197874918786	14.32555997617718
N	5.34093704768306	8.71732990566473	14.50632433289823
N	2.79542716913930	11.84328841198761	12.11912458676180
N	6.06462521323348	10.15322845147351	12.04134561287245
N	2.09095865835256	10.47569988453071	14.47803424893063
C	6.58131694655842	9.21578571962661	14.85162141414128
C	2.07472631495786	9.62314887587320	15.58031896569525
C	1.13391968052855	11.46940245575115	14.63488146201564
C	1.78192173503414	12.72764555151626	12.46350949132242
C	7.67754245211534	9.36323771770860	13.81013369392342
C	3.44450262655022	12.29063823336572	10.97035235342863
C	3.01648971687116	8.42791709253684	15.68998397617397
C	7.57593543978446	11.71076224834792	12.63119872848710
C	6.52881804290916	9.68023001681951	16.15468345868620
C	6.67202243408149	12.28977143439877	11.70627599231181
C	7.17624126153646	10.39928960735607	12.81981766745735
C	2.66666451921306	7.38190328605239	14.59655273445312
C	5.20970054481944	9.45987160083037	16.62234540415048
C	4.48299060445743	8.87154177553790	15.59966626239500
C	4.60025078588393	11.51805015788165	10.34354666378189
C	0.49220652999965	11.22454144790705	15.82971107889660
C	4.08480735569260	10.15981760245252	9.79420759558849
C	7.95604840268963	8.01053605893192	13.10421686951822
C	5.74243599485494	11.32611738212782	11.35074918537395
C	1.28094035285932	6.75470119215351	14.73226319439958
C	2.81526707233121	13.45105397686068	10.57975640412088
C	8.99285711454418	8.08961088547343	11.98761059207387
C	8.80016470080358	12.54106783281163	13.60949897881086
C	2.80375152863447	7.78254770664906	17.08608528708000
C	1.08127312739691	10.07286444438913	16.42061201502547
C	1.77570154461331	13.72341027140459	11.51091994267750
C	6.28653239557007	11.70415998753490	8.38767251012056
C	8.96915541046504	9.88855287404948	14.47146559560395
C	3.06516441256421	10.27380637196425	8.66339052241173
C	0.66325337812666	13.89704608001533	14.35446047989956
C	-0.58857414810650	12.18826560728277	12.98933454837593
C	5.14748662711515	12.36154294967892	9.16147494194796
C	1.95110819007475	14.38945870059452	15.02075606646689
C	3.64408403056338	6.53484349474188	17.34077669251807
C	-0.59299709964638	10.87403158403625	12.21826980759766
C	9.68593517938059	8.89221596953525	15.38284883677430
H	8.43296417534792	12.19501015576318	13.07733556792994
H	7.34456637331528	10.10334983223334	16.72379053781056
H	6.72055498881545	13.29733190409559	11.31656093800761
H	2.70797385965498	7.86338468680066	13.61166056787905
H	3.44020261151991	6.60460959777612	14.58726280080396
H	4.84411384662314	9.67507959467101	17.61726191732253
H	-0.32907576383567	11.79631093894456	16.24004702424427
H	4.94263510663160	9.55458613437405	9.47648175177574
H	3.60454342831843	9.60237348537392	10.60798631816273
H	8.24812294813642	7.27740504422364	13.86494154918594
H	7.02239423661484	7.61424179405261	12.67640943500594
H	0.51154423268423	7.52754485269011	14.83692274875266
H	1.21297411692639	6.08838772069949	15.59738982660500
H	1.04926815952528	6.16148396285853	13.84233720416841
H	3.05950727807425	14.05170812435072	9.71555417601551
H	9.98748147874160	8.34128785546088	12.36933273362263
H	8.71218834180583	8.85203022402622	11.25306783111455
H	9.07175424978629	7.12907560446221	11.46909577350177
H	1.74117671348120	7.53953389366169	17.19502681992477
H	3.01885280333742	8.53474976188809	17.85198369836114
H	0.79343760601436	9.62963599765692	17.36286144428351
H	1.08870418946411	14.55752035352816	11.46481269234956
H	6.68622508338013	12.39887301998061	7.64207150709345
H	5.95582943515945	10.80730796422370	7.85411529818551
H	7.10467197784354	11.41889554292755	9.05687081376929
H	8.72083670381479	10.79517794394031	15.03513584479714
H	9.65240784764651	10.20654768374902	13.67568923882964
H	3.51718822532269	10.63936577985120	7.73643169665444
H	2.25312332874627	10.95614178689025	8.93745901511508
H	2.62924043748671	9.29277418221042	8.45096583564547
H	-0.12914355861655	13.80094138547237	15.10620125595864
H	0.31936937871383	14.65159751485883	13.63745004273387
H	-1.32192416962153	12.14742504294409	13.80500526537179
H	-0.87997168621640	13.01152005040230	12.32428117424939
H	4.31780541012380	12.57815142594132	8.47966863361448
H	5.47551357596714	13.33077889920462	9.55060540027213
H	2.28725744791829	13.64011904925920	15.76792942387756
H	1.80115684737142	15.32405594700542	15.53510815926904
H	2.73907772668333	14.51862247903220	14.27228046601284
H	3.35490343127241	5.70484818244923	16.68824422129696
H	3.51516976918407	6.19815784061963	18.37438702909017
H	4.70801659089499	6.73703870541430	17.18102231583280
H	-0.32109164750565	10.03671028420108	12.87085871078379
H	0.11952053851810	10.90742556143928	11.38644662993200
H	-1.58534862446093	10.66964276504581	11.80420095024944
H	9.00211566503318	8.43515649936438	16.10448839850331
H	10.47999267167802	9.39735023409022	15.94228194229515
H	10.15484067401671	8.08521323474394	14.81126145309298
H	5.52802632294643	12.04196318301924	13.76886695124580
H	5.04707434689749	11.25847751271618	15.16478171046404
H	4.19133642222852	12.57934133170382	14.61027451022012

$Cx^{Et}Ge_2(pyridine)$

Ge	4.83621351333692	8.70177673796710	12.57602326383309
Ge	3.50033004403977	10.61431650344174	13.34088306876805
N	4.48685933395751	11.94637921452351	14.55660925740197
N	5.34304899567871	8.78204393126237	14.52214450876050
N	2.82966612132240	11.86164606606513	12.14516272796534
N	6.06156298194735	10.22768107507941	12.10131017688681
N	2.04295586492829	10.43997911340649	14.47090355642116
C	6.58424753025307	9.28251279414483	14.85891416705491
C	2.06319225375317	9.61175306567170	15.59219718926960
C	1.11562670953769	11.45832400326512	14.64389160000170
C	1.90658618135123	12.80791016254338	12.58071607129894
C	7.69613963698093	9.37426183380479	13.82275805914285
C	3.61616919693839	12.39915744369476	11.11988066647134
C	3.02962686492300	8.42887265983907	15.71228161234360
C	7.94217658793274	11.44349626549333	12.19529724086244
C	4.10983331856287	12.10331723720056	15.84095506760723
C	6.55406054923700	9.67351425805152	16.18579855923857
C	7.08752333258666	12.01188121208205	11.22285962722176
C	7.28246870874782	10.35043197863804	12.73040979233767
C	2.69188432084343	7.38342073999866	14.61484670955802
C	5.25281662556486	9.40817500547129	16.67006305942182
C	4.50220997474969	8.87452775817358	15.63451094595505
C	4.66016056608941	11.57470037676180	10.34973422204663
C	0.49903251955764	11.23675493871503	15.85724632596684
C	3.98785928444936	10.27485796046991	9.82768865698565
C	7.95065042488024	7.96748748102705	13.20552835779999
C	5.91863583013298	11.26288610281400	11.17750446018663
C	1.30585393208804	6.75365667828538	14.73576089637946
C	5.50518468077856	12.67408769373390	14.06223963975906
C	3.15217896276464	13.67684656601648	10.89724470009000
C	9.03294815928680	7.93437298902818	12.13122418881436
C	0.79758943724181	12.50222341527375	13.58183170074346
C	2.80388809261737	7.78656624629462	17.10680835925856
C	1.09288548094928	10.08599973796837	16.45068369108713
C	2.08614338804448	13.93203941431772	11.80618541112286
C	4.74572062495574	13.01223053357699	16.66852054466376
C	6.02015792583849	11.72117910645511	8.13718911318108
C	5.80089692199617	13.76450566122780	16.17024965333400
C	8.98747355642729	9.89765170121075	14.48860040037505
C	2.82454287909777	10.50035083603776	8.86366991467794
C	6.18223078283213	13.59174221318567	14.84645119917165
C	0.38616223123569	13.82125797207910	14.28297388937982
C	-0.45318798040730	12.00370017078501	12.78135333545841
C	5.09643517380623	12.42712188788000	9.12796157272420
C	1.46955420948929	14.46877014756829	15.13993157642704
C	3.63036599914682	6.53137931714805	17.37066904434610
C	-0.27194710740680	10.67805113505435	12.05171767465357
C	9.67460823790086	8.92742763541129	15.45130644129484
H	8.92405516856388	11.80288006654952	12.46768653768054
H	7.37432060553238	10.08271584311160	16.75819583464103
H	7.30661676689374	12.88716814133716	10.62777605321602
H	2.74224765542099	7.86559503092731	13.63086497733976
H	3.46818299968933	6.60870730547743	14.61209620997654
H	4.91232382949979	9.56769565919401	17.68464653557654
H	-0.30034237641872	11.82585967283445	16.28569480015326
H	4.75664667645602	9.64294516091772	9.36665970972152
H	3.59938785205640	9.69880163523705	10.67571220352899
H	8.18200184836396	7.27038657217281	14.01979738140896
H	7.01601632224948	7.59072142962543	12.76274262288457
H	0.53283278377159	7.52455865050638	14.82895233668605
H	1.22776269304339	6.08941003055715	15.60172941751838
H	1.08562245116493	6.15808557895409	13.84443132208992
H	3.50698728452349	14.36406714069503	10.14290869471311
H	10.01940670201282	8.18398853316032	12.53530734475985
H	8.80979253821302	8.64885855846324	11.33173730911886
H	9.10093409415057	9.93550109716549	11.68862285907435
H	1.73857993054405	7.55186087832041	17.20870895931166
H	3.01910229318964	8.53793572548536	17.87410726788757
H	0.82441199386037	9.66232194282200	17.40778554570010
H	1.50482022260827	14.84281732581382	11.85065470752427
H	6.37089572454235	12.43236615327534	7.38205207541538
H	5.50671684995847	10.91252785482855	7.60748088110639
H	8.89608776678229	11.29564874445734	8.63480577111837
H	8.74400279710392	10.83630575531298	15.00163741767662
H	9.69730945273119	10.16040285323076	13.69716778820999
H	3.15847560533227	10.88544536732436	7.89549844193855
H	2.10533599375576	11.21451231669946	9.27956409909234
H	2.29963302854173	9.55777247267012	8.67920120579264
H	-0.49955346028385	13.61795000357793	14.89684495078643
H	0.05298514264943	14.52249766985909	13.50871791358177
H	-1.28269253788520	11.91660046559084	13.49598810719387
H	-0.71670310346367	12.79072650741851	12.06248750347502
H	4.19067880643517	12.75319816201026	8.60650732687868
H	5.57339537830439	13.34278643288907	9.49341415893600
H	1.73032506260635	13.82861881956391	15.98796287315161

H	1.12407743979932	15.42966040726632	15.53578339051803
H	2.37816788247128	14.64899427433238	14.55578253896610
H	3.33385842185542	5.70202710416481	16.72048996959690
H	3.49249028592025	6.20049575747193	18.40513457642676
H	4.69666414832545	6.72132857484125	17.21387313402401
H	-0.04226698439733	9.86789759016552	12.75227219952993
H	0.53682978916223	10.73345495852707	11.31594232638887
H	-1.19047895255411	10.40971496411394	11.51972655428611
H	8.97634893727379	8.50255982356351	16.17749892073434
H	10.46534612448145	9.44524906954991	16.00444147395426
H	10.14510977673642	8.09559722879263	14.91752931944571
H	6.99979223428414	14.15117806481859	14.40581770499348
H	5.75845255099153	12.53231987169987	13.01561660333734
H	6.31684140781806	14.47864418136304	16.80552800014877
H	4.40780510430805	13.11534541495308	17.69372586842063
H	3.28166613005723	11.49914416919423	16.19445637661170

$Ge_9H_{12}(NH_3)$

Ge	-2.15548260285135	-1.52931445048883	-2.27483709515258
Ge	-1.78994913364000	-1.34812033776548	-4.71381021907148
Ge	-1.04208073341201	-3.35555476254480	-5.89007031276613
Ge	-0.16991095972544	-0.07012216963219	-1.85224767447402
Ge	-0.37104496127626	0.47745104110688	-5.50529959151667
Ge	-0.80024277733150	-3.62983622018755	-2.21326379603881
Ge	0.62194332791371	-3.88226479873208	-4.18864302113707
Ge	1.31512305745035	0.07258817601620	-3.79203392263542
Ge	2.29807280507929	-2.11157063000716	-4.25242902238916
H	-2.14414887464370	-4.42685540363193	-5.97593016677653
H	-0.53505368515533	-3.06897548614889	-7.31186266695091
H	1.27890211382281	-5.25151062547994	-4.45542387951072
H	3.35589428347777	-2.40426222805435	-3.17529566544026
H	3.02637436715902	-2.10341915576099	-5.60833249124864
H	-1.04171095852471	1.85363422822162	-5.34602305667816
H	0.05615244420223	0.31336407737814	-6.97203230123847
H	0.07718422214655	-3.71669656529065	-0.94927569367519
H	-1.70151519852673	-4.88434751501472	-2.19233734433456
H	-0.58848876811919	1.38379160217884	-1.54033997080511
H	0.64738681845977	-0.54516813306485	-0.63489762539630
H	2.40304142125923	1.16505677267865	-3.81176119659820
N	-3.73044527320685	-0.93295297380005	-5.49431154963959
H	-3.74118537035059	-0.76881553241469	-6.49779258470762
H	-4.10285508994060	-0.11122947359020	-5.02366990302600
H	-4.34820047426648	-1.71370943597097	-5.28479924879231

$Ge_9H_{12}(pyridine)$

Ge	-2.10634931689939	-1.54990898204502	-2.16230587668608
Ge	-1.85935850496449	-1.35032742318805	-4.62493637803654
Ge	-1.09179310001673	-3.34189618838319	-5.82058873411187
Ge	-0.12346758515532	-0.07503199883524	-1.80937834516485
Ge	-0.42688090824648	0.45326472319813	-5.44960550946424
Ge	-0.73878742465860	-3.64064919608123	-2.16055952654522
Ge	0.62321745200870	-3.87769042531577	-4.17881319039735
Ge	1.30949850327241	0.06800472260667	-3.78714155852273
Ge	2.29672691742291	-2.10767559104245	-4.27135656032628
H	-2.18314638209651	-4.42297460036157	-5.90929365856476
H	-0.61560059826982	-3.02842847947987	-7.25028490698757
H	1.27346328799961	-5.24614813673508	-4.46650676310942
H	3.37831060109575	-2.40223261353633	-3.21783878691739
H	2.99872394974208	-2.09125555025291	-5.64156968629913
H	-1.08985850321660	1.83418921094987	-5.30457858132121
H	-0.03326994131947	0.26555347465864	-6.92549708714340
H	0.17757528841892	-3.72220053824031	-0.92319919513205
H	-1.63082993307587	-4.90122643724781	-2.11207808344955
H	-0.54262371632460	1.37851732276889	-1.49460507308757
H	0.72435659560626	-0.53821856497800	-0.60754535556598
H	2.38831181024237	1.16903283388986	-3.83415165487498
N	-3.71767912968139	-0.94679333436826	-5.43341394994469
C	-4.78474564550254	-0.83392362550829	-4.62576699688023
C	-6.04587702148990	-0.56221676723302	-5.13262638788515
C	-6.20467629326360	-0.40416101897915	-6.50312151613840
C	-5.09110900875582	-0.52362455770906	-7.33046226377967
C	-3.86076398147382	-0.79573875350617	-6.76262629091256
H	-2.95605271390710	-0.90015003951115	-7.35656148996438
H	-7.18224212066116	-0.19048132830471	-6.92434491709216
H	-5.17032991165709	-0.40771413911070	-8.40581418931585
H	-4.58989205294180	-0.96955607728693	-3.56187366999883
H	-6.88588061223088	-0.47775792083177	-4.45178381637982

Ammonia NH_3

N	-3.02421023156202	0.96459867320802	0.03057537044493
H	-2.01163012002084	0.99829714408115	-0.01743327089443
H	-3.33408336386839	0.60419394780698	-0.86544303034321
H	-3.33409628454874	1.92975023490384	0.06527093079272

Pyridine

C	-5.13885444052865	3.49671074784758	0.00000000495439
C	-4.92022282855834	2.12214937909073	-0.00000000210080
C	-3.60971857625494	1.65906136705720	-0.00000001083167
C	-2.57634021340175	2.58870050939986	0.00000000901966
C	-2.90064462572156	3.94213325545921	-0.00000001249361
N	-4.15579134165940	4.40288618750793	-0.00000001342680
H	-5.75982521158570	1.43352403790486	-0.00000000119678
H	-6.15501065231653	3.89060228014124	0.00000001859023
H	-2.11276363379594	4.69509896746324	-0.00000000726463
H	-3.39772299355605	0.59351535935037	-0.00000001194141
H	-1.53714548262112	2.27373790877776	0.00000002669141

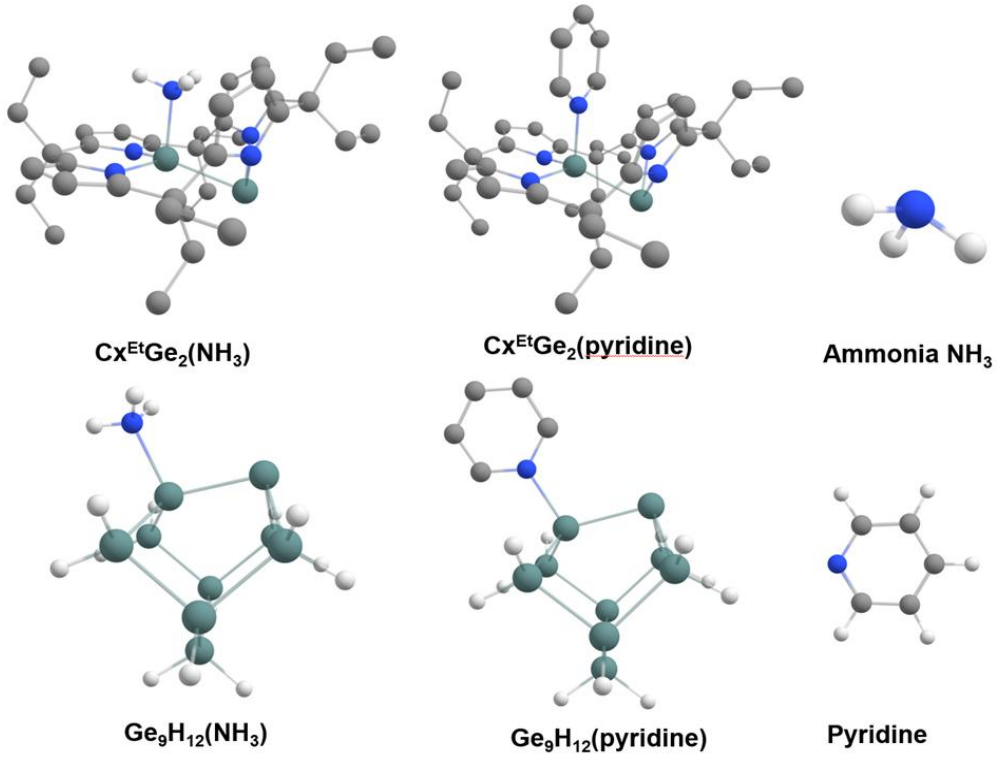

Figure S 3-11. Structures for Ammonia and Pyridine affinities of **$Cx^{Et}Ge_2$** and **Ge_9H_{12}**.

4 Determination of bent and buckling Angles

Bent und buckling angles were determined by using Chemcraft (see Fig. S4-1). By using the "custom vectors and planes" tool (toolbar under edit) a vector consisting out of the two E atoms and a plane consisting out of three atoms: ER1R2 (E = Si or Ge; R1/R2 ligand atom, bound to E) were created and the angle between the vector and the plane was determined using the "examine geometrical parameters" tool in the edit menu. XYZ files were extracted from solid-state structures accessed via the CCDC data bank or generated by geometry optimization (**$Cx^{Me}Ge_2$** and **Ge_9H_{12}**). Table S4-1 lists all relevant bent angles.

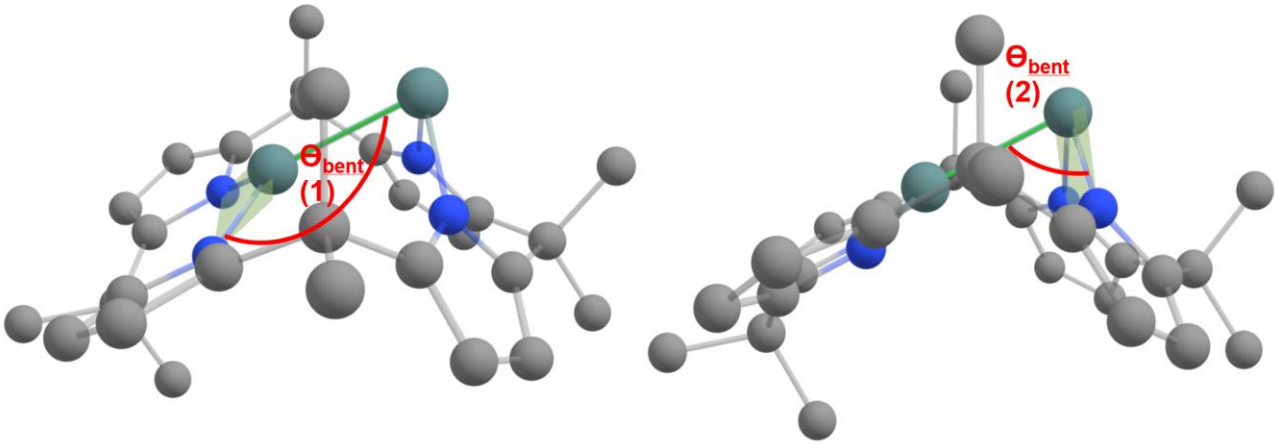

Figure S 4-1. Example for determination of bent angles Θ_{bent} of selected ditetreles between the vector of the E-E (E = Si, Ge) highlighted in green and the plane consisting of E,R1,R2.

Table S 4-1. Determined bent angles of selected ditetreles.

Compound	XYZ Source	Θ_{bent} (1) [°]	Θ_{bent} (2) [°]
$Mes_2Si{=}SiMes_2$	[44]	18.4	18.4
$Mes_2Ge{=}GeMes_2$	[45]	33.0	33.0
$Tip_2Si{=}Si(Tip)Ph$	[46]	22.3	23.6
$(SiH_2Si_2(SiMe_3)_2)Si{=}Si(SiH_2Si_2(SiMe_3)_2)$	[47]	1.6	–1.6
$(SiH_2Si_2(SiMe_3)_2)Ge{=}Ge(SiH_2Si_2(SiMe_3)_2)$	[48]	2.4	–2.4
$(^tBu_3Si)_3Ge_3Br$	[49]	34.5°	–7.2
$(^tBu_3Si)_3Ge_3I$	[49]	33.8°	–5.6
Si_6 cluster	[50]	3.8	–73.9
$Cx^{Me}Ge_2$	DFT Opt	16.5	–71.0
Ge_9H_{12}	DFT Opt	31.9	–89.1

For the determination of the buckling angle, a vector alongside the Ge-Ge bond and a plane consisting out of the four ligands were created and the angle between the two of them was measured using the same method as above (see Fig. S4-2).

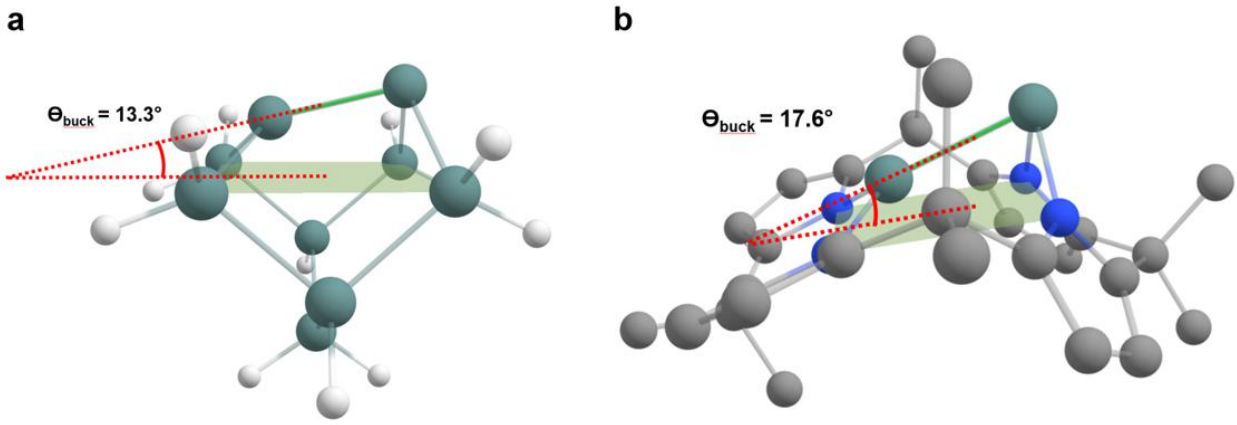

Figure S 4-2. Determination of the buckling angle Θ_{buck} for (a) **Ge_9H_{12}** and (b) **$Cx^{Me}Ge_2$**.

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