Supporting information:

Pyramidal dicationic Ge(II) complexes with homoleptic neutral pnictine coordination: a combined experimental and density functional theory study

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Table S1: X-ray crystallographic parameters[a]

Compound	[Ge(PMe$_3$)$_3$][OTf]$_2$	[Ge(tetraphos)][OTf]$_2$ · CH$_2$Cl$_2$	[Ge(AsMe$_3$)$_2$(OTf)$_2$]	[Ge(triars)][OTf]$_2$
Formula	GeP$_3$C$_{11}$H$_{27}$F$_6$O$_6$S$_2$	GeP$_4$C$_{45}$H$_{44}$Cl$_2$F$_6$O$_6$S$_2$	GeAs$_2$C$_8$H$_{18}$F$_6$O$_6$S$_2$	GeAs$_3$C$_{13}$H$_{27}$F$_6$O$_6$S$_2$
M	598.94	1126.29	610.77	754.81
Crystal system	monoclinic	Triclinic	monoclinic	monoclinic
Space group (no.)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$C2/c$ (no. 15)	$P2_1/n$ (no. 14)
a /Å	6.3351(2)	10.9685(4)	14.3439(2)	13.7970(3)
b /Å	21.9849(6)	13.8745(5)	11.6424(2)	17.9667(3)
c /Å	17.2271(6)	17.4629(5)	12.6472(2)	20.4948(5)
α /°	90	82.599(3)	90	90
β /°	90.523(3)	83.283(3)	105.623(2)	90.430(2)
γ /°	90	69.756(3)	90	90
U /Å^3	2399.23(13)	2465.12(15)	2034.02(6)	5080.24(19)
Z	4	2	4	8
μ(Mo-K$_\alpha$) /mm^{-1}	1.721	1.013	5.013	5.319
F(000)	1216	1148	1192	2960
Total no. reflns	74306	28986	27758	77036
R_{int}	0.075	0.036	0.036	0.114
Unique reflns	8642	12137	3379	12883
No. of params, restraints	271 0	618 0	117 0	610 516
GOF	1.021	1.054	1.055	1.070
R_1, wR_2 [I > 2σ(I)][b]	0.042, 0.092	0.053, 0.141	0.026, 0.056	0.063, 0.119
R_1, wR_2 (all data)	0.073, 0.092	0.074, 0.152	0.032, 0.061	0.095,0.130

[a] common items: T = 100 K; wavelength (Mo-K$_\alpha$) = 0.71073 Å; θ(max) = 27.5°;

[b] $R_1 = \Sigma ||F_o| - |F_c||/\Sigma|F_o|$; w$R_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$

Figure S1 [Ge(PMe₃)₃][OTf]₂

Figure S1.1 [Ge(PMe$_3$)$_3$][OTf]$_2$: ^{1}H NMR spectrum (CD$_3$CN, 298 K)
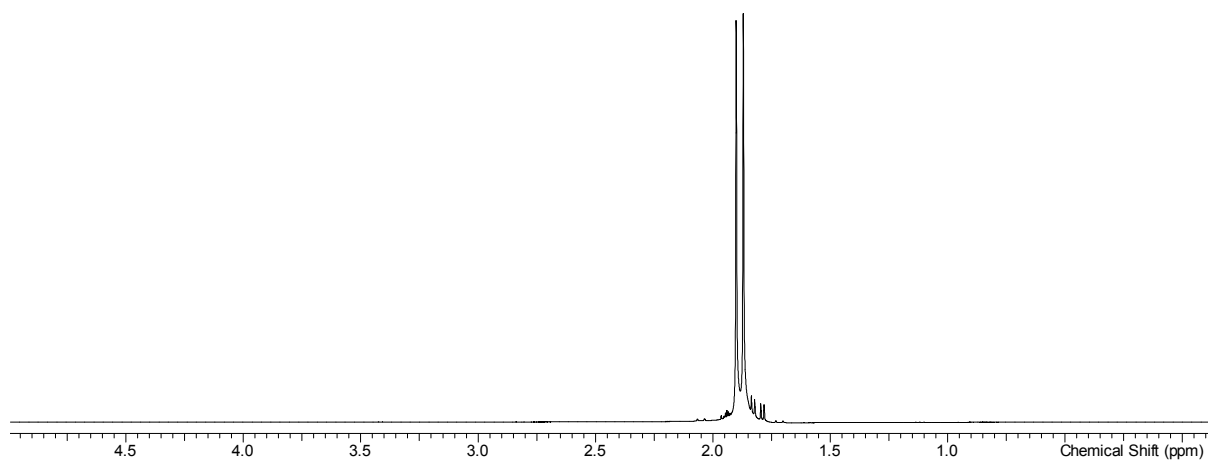
Figure S1.2 [Ge(PMe$_3$)$_3$][OTf]$_2$: ^{19}F{^{1}H} NMR spectrum (CD$_3$CN, 298 K)
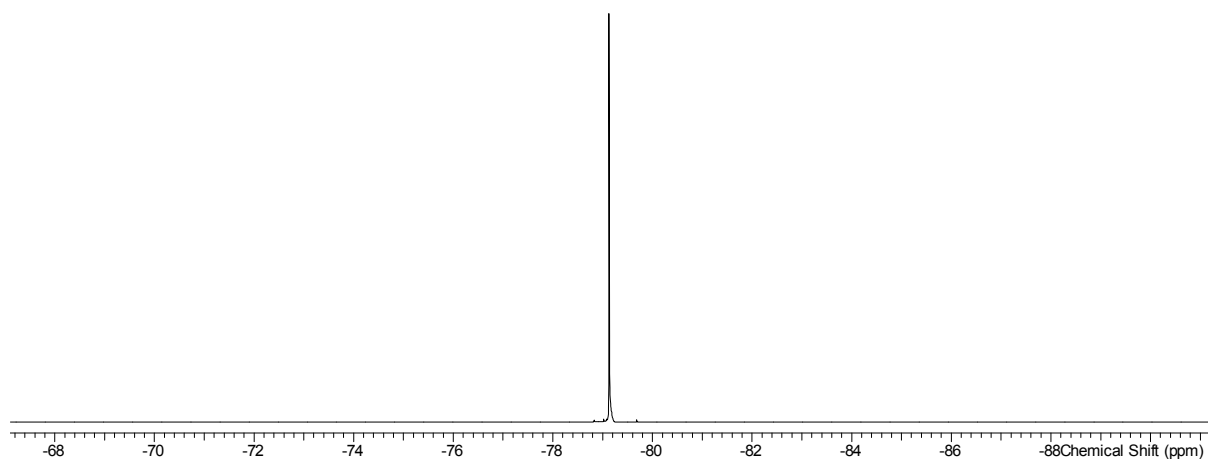
Figure S1.3 [Ge(PMe$_3$)$_3$][OTf]$_2$: ^{31}P{^{1}H} NMR spectrum (CD$_3$CN, 298 K) *minor [HPMe$_3$]$^+$ impurity*
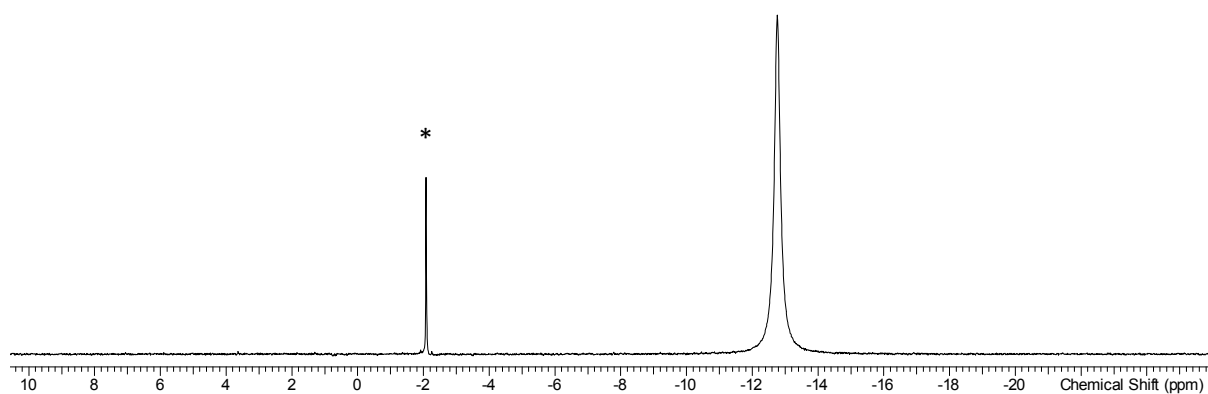
Figure S1.4 [Ge(PMe$_3$)$_3$][OTf]$_2$: IR spectrum (Nujol/cm^{-1})
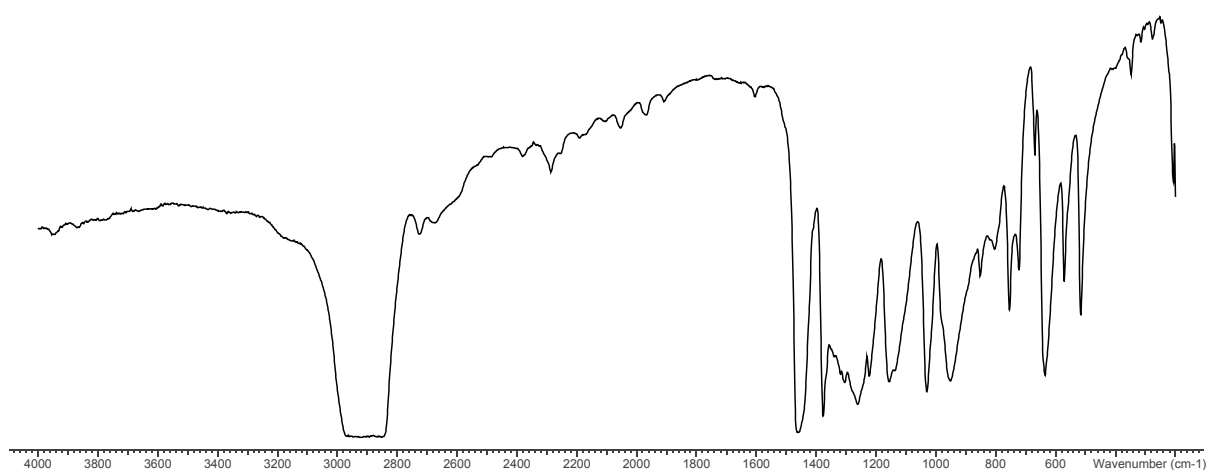
Figure S2 [Ge(AsMe$_3$)$_2$(OTf)$_2$]

Figure S2.1 [Ge(AsMe$_3$)$_2$(OTf)$_2$]: ^{1}H NMR spectrum (CD$_2$Cl$_2$, 298 K) * *minor impurity*
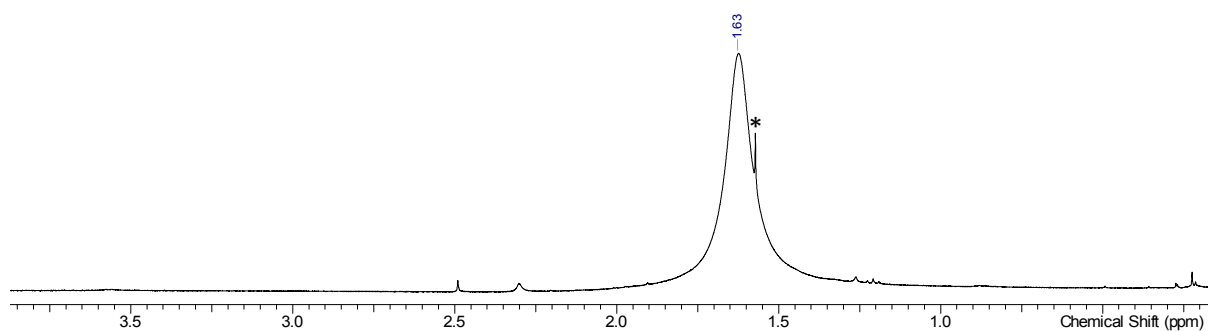
Figure S2.2 [Ge(AsMe$_3$)$_2$(OTf)$_2$]: ^{19}F{^{1}H} NMR spectrum (CD$_2$Cl$_2$, 298 K)
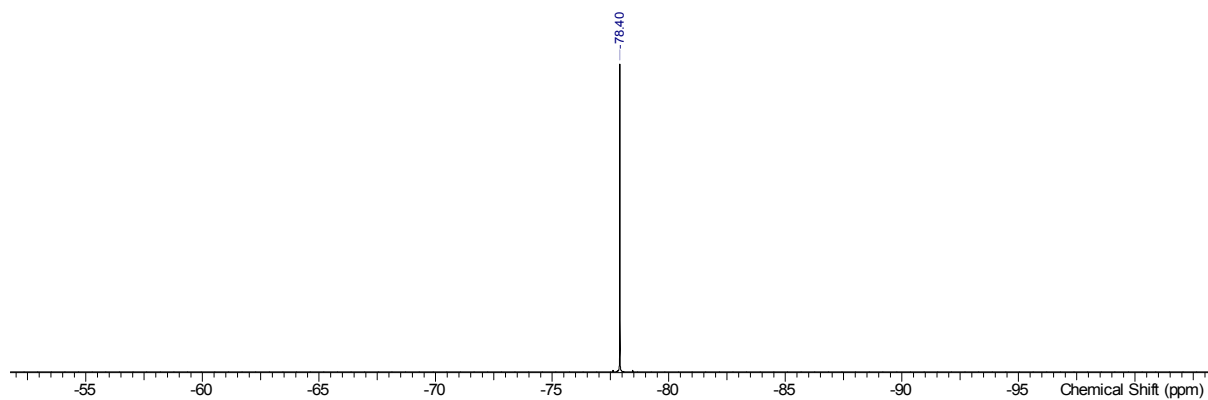
Figure S3 [Ge(triphos)][OTf]$_2$

Figure S3.1 [Ge(triphos)][OTf]$_2$: ^1H NMR spectrum (CD$_2$Cl$_2$, 298 K) * *MeCN* + *Dioxane* ° CH$_2$Cl$_2$
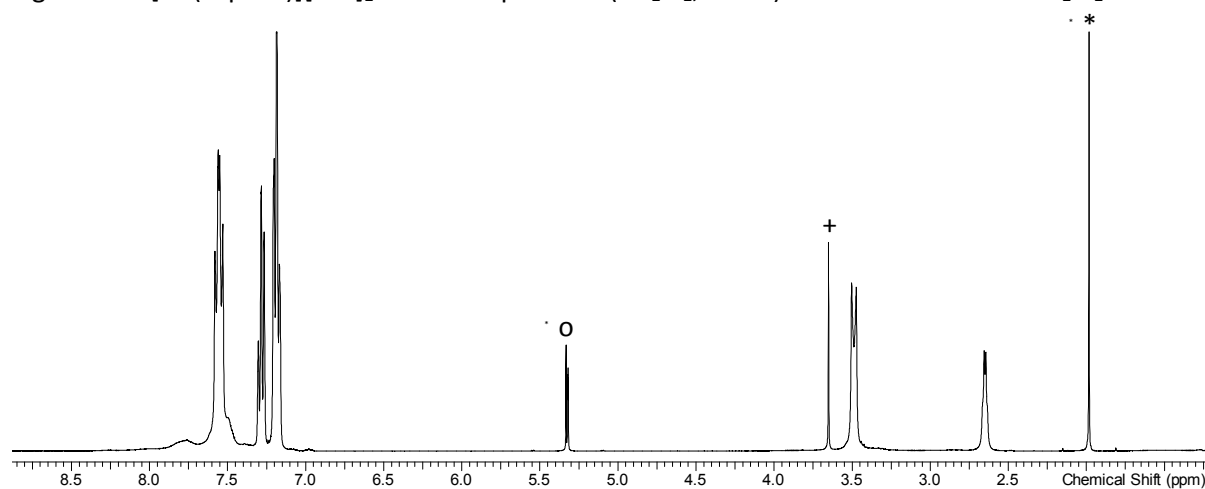
Figure S3.2 [Ge(triphos)][OTf]$_2$: $^{19}F\{^1H\}$ NMR spectrum (CD$_2$Cl$_2$, 298 K)
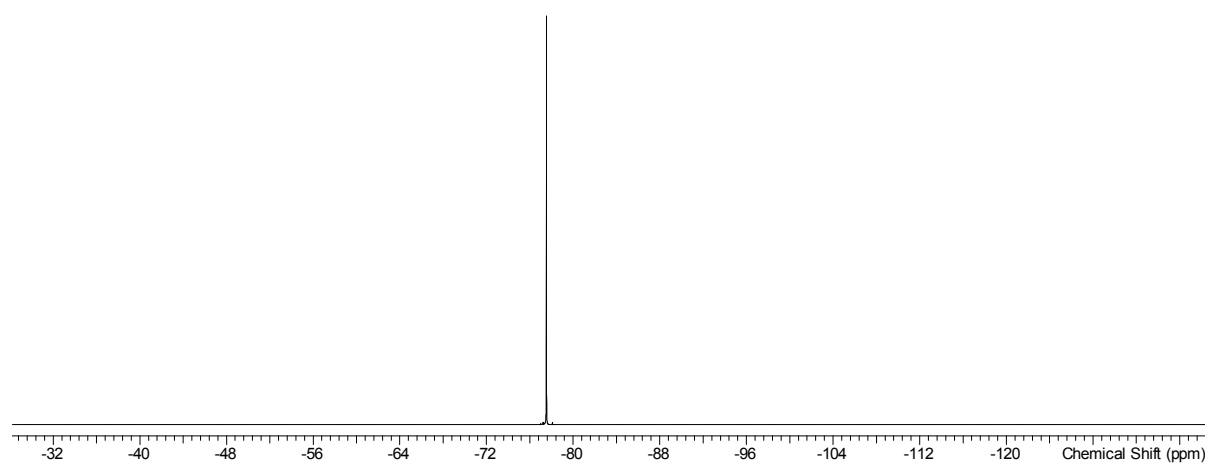
Figure S3.3 [Ge(triphos)][OTf]$_2$: $^{31}P\{^1H\}$ NMR spectrum (CD$_2$Cl$_2$, 298 K)
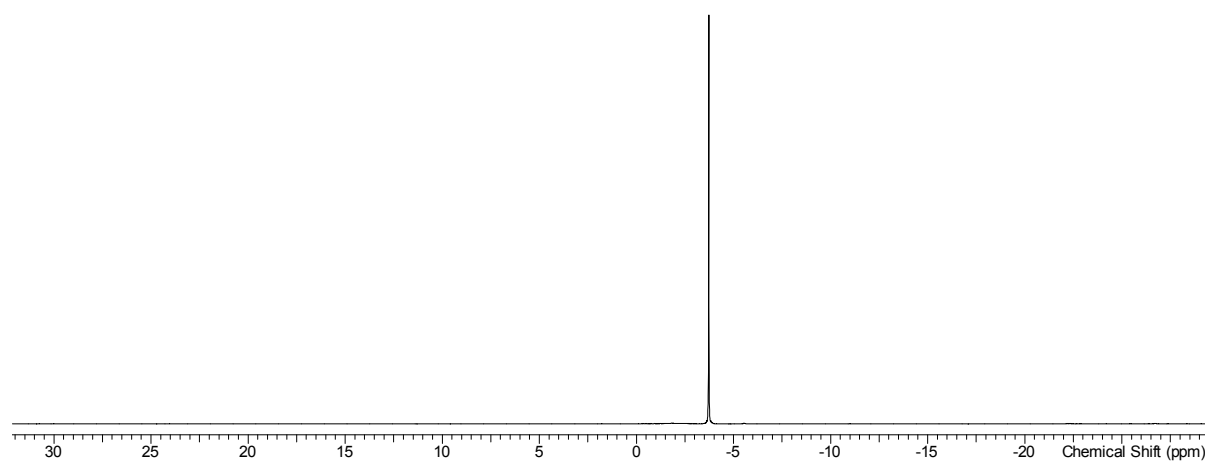
Figure S3.4 [Ge(triphos)][OTf]$_2$: IR spectrum (Nujol/cm^{-1})
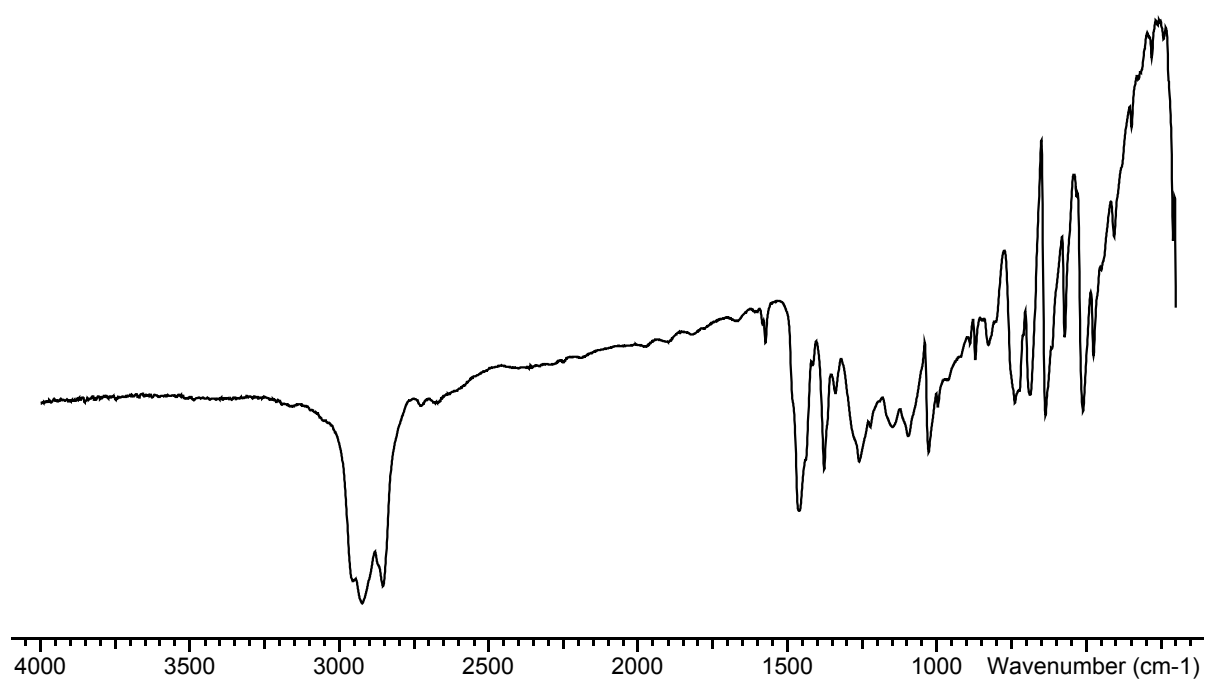
Figure S4 [Ge(triars)][OTf]$_2$

Figure S4.1 [Ge(triars)][OTf]$_2$: ^{1}H NMR spectrum (d-MeCN, 298 K) *CH$_2$Cl$_2$ $^+$MeCN*
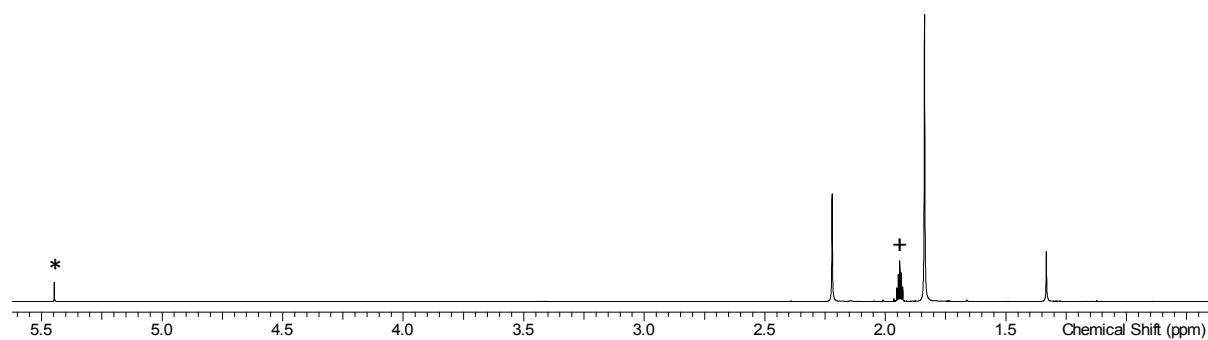
Figure S4.2 [Ge(triars)][OTf]$_2$: ^{19}F{^{1}H} NMR spectrum (d-MeCN, 298 K)
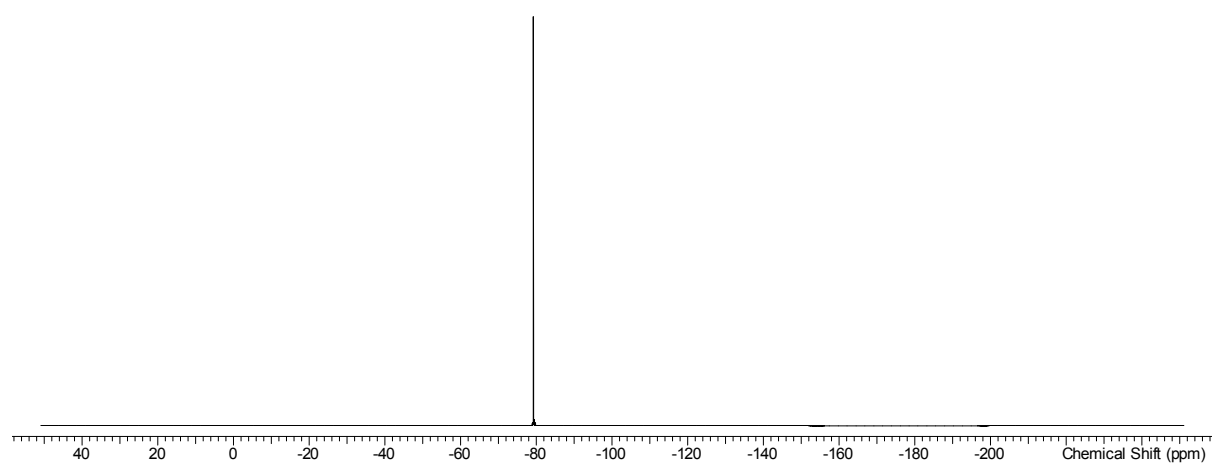
Figure S4.3 [Ge(triars)][OTf]$_2$: IR spectrum (Nujol/cm^{-1})
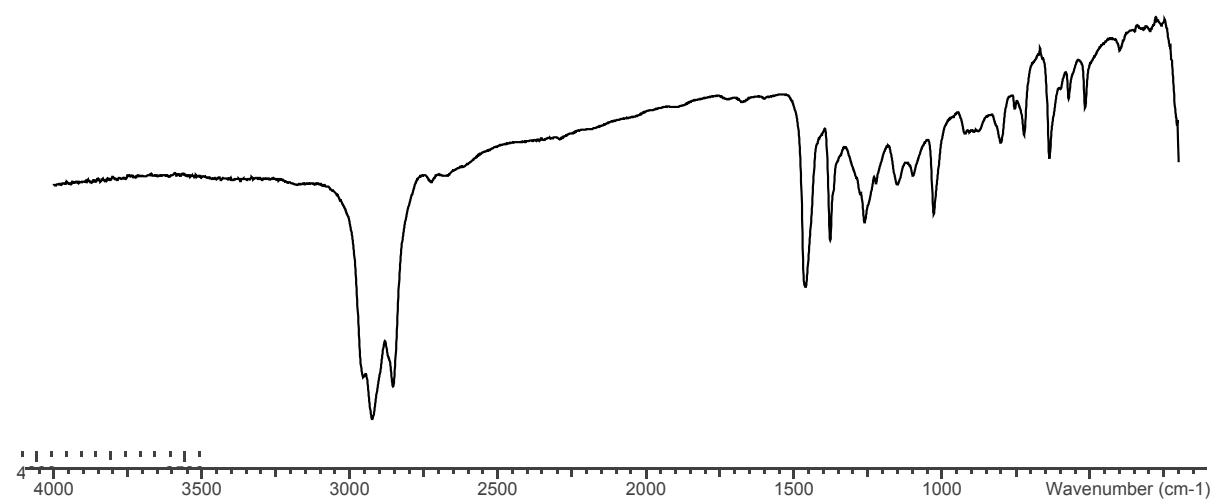
Figure S5 [Ge(tetraphos)][OTf]$_2$

Figure 5.1 [Ge(tetraphos)][OTf]$_2$: ^{1}H NMR spectrum (CD$_2$Cl$_2$, 298 K) *CH$_2$Cl$_2$ $^+$dioxane
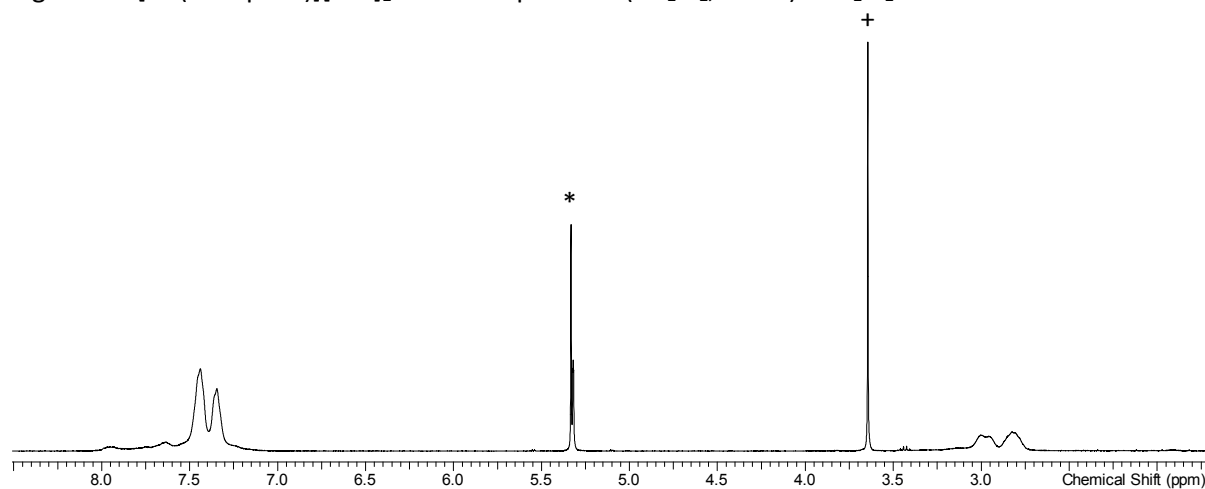
Figure S5.2 [Ge(tetraphos)][OTf]$_2$: ^{19}F{^{1}H} NMR spectrum (CD$_2$Cl$_2$, 298 K)
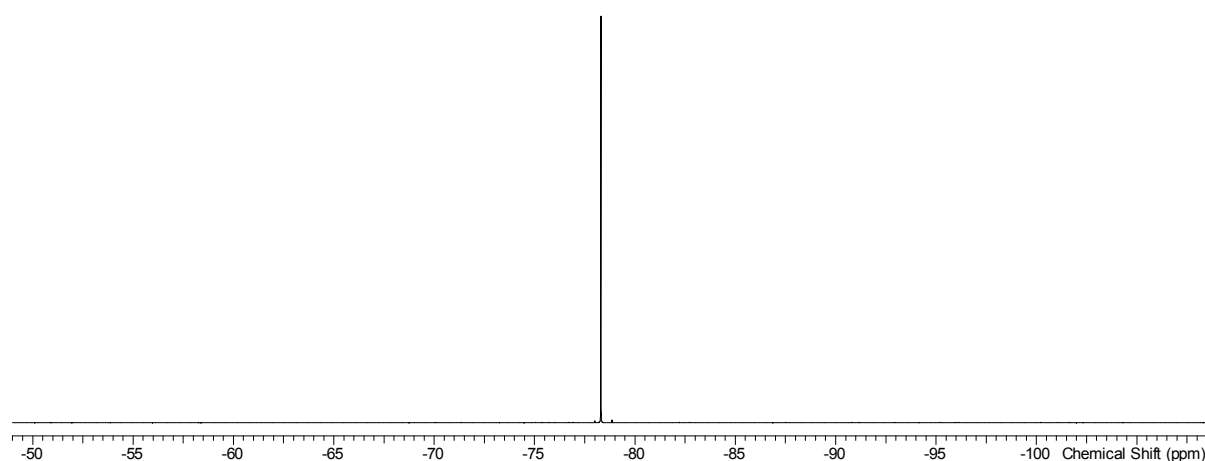
Figure S5.3 [Ge(tetraphos)][OTf]$_2$: ^{31}P{^{1}H} NMR spectrum (CD$_2$Cl$_2$, 298 K)
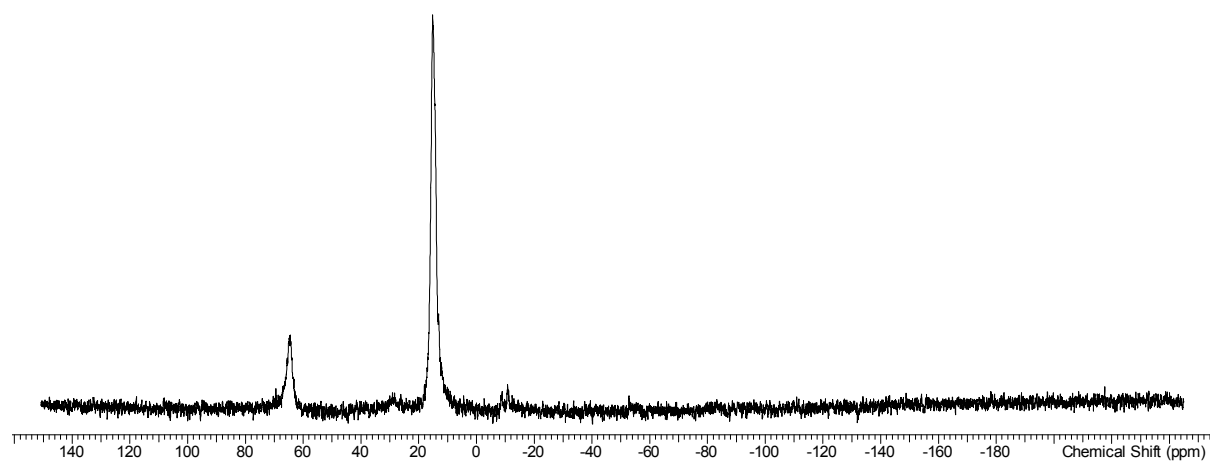
Figure S5.3 [Ge(tetraphos)][OTf]$_2$: IR spectrum (Nujol/cm^{-1})

(a)   (b)
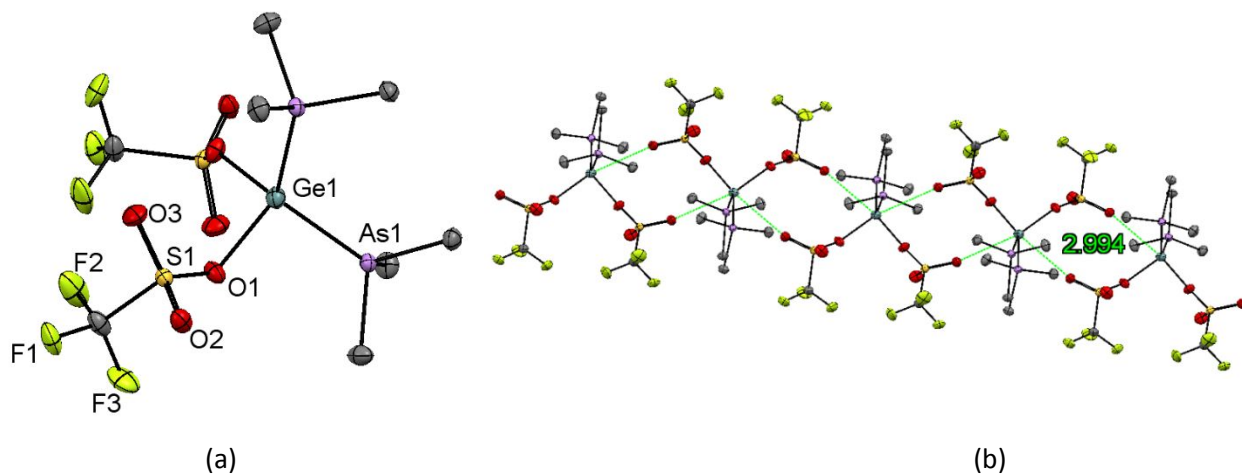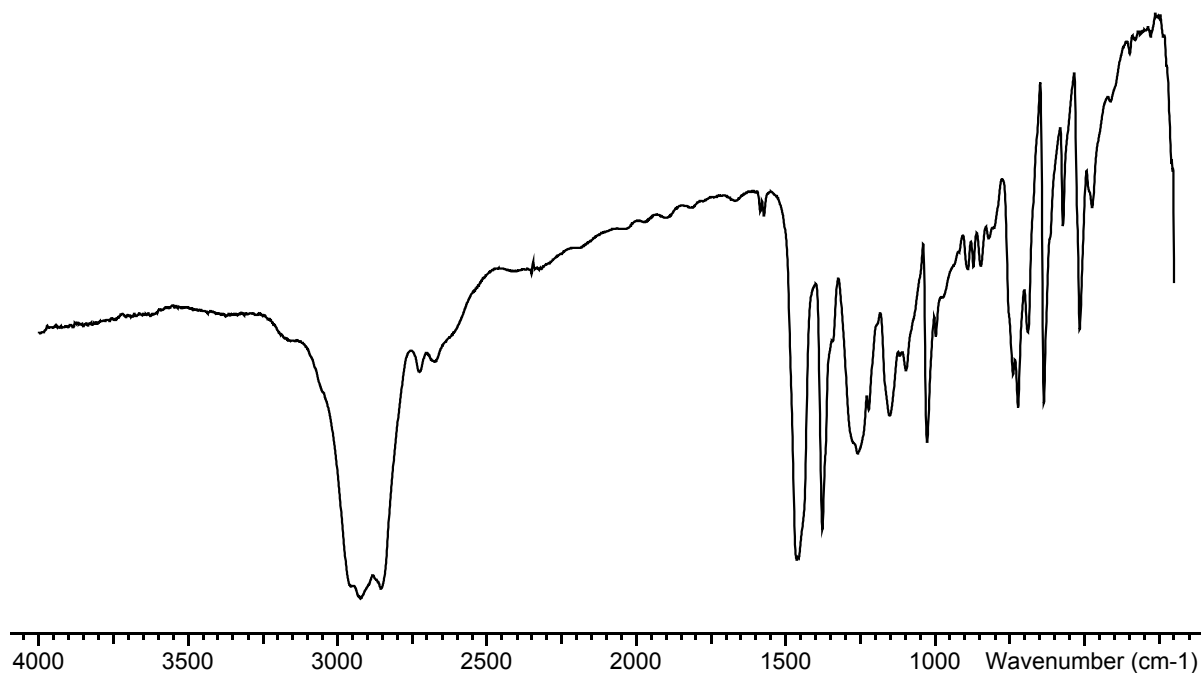
Figure S6 (a) The structure of [Ge(AsMe$_3$)$_2$(OTf)$_2$] showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (˚) are: Ge1-As1 = 2.4287(2), Ge1-O1 = 2.0170(15). As1-Ge1-As1 = 119.600(15), O1-Ge1-O1 = 98.30(9); (b) view of the weakly associated chain polymer formed along the *c*-direction.
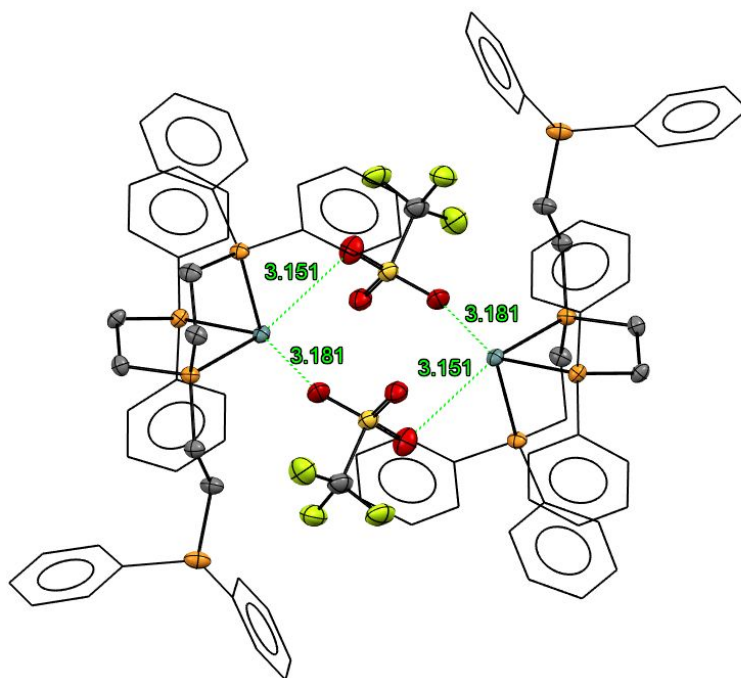
Figure S7 View of the very weakly associated dimer formed through long contacts between the Ge atoms and the O atoms from two bridging OTf⁻ anions in [Ge(tetraphos)][OTf]$_2$

DFT Calculations

Geometry optimization calculations were also undertaken on the four-coordinate complexes [Ge(AsMe$_3$)$_2$(OTf)$_2$] (X-ray crystal structure in Figure S6) and [Ge(PMe$_3$)$_2$(OTf)$_2$] (some geometrical parameters are given for this complex from an X-ray study in ref. 19). In each case, the optimized bond lengths showed reasonably good agreement with the bond lengths from the X-ray structures.

The full optimization of [Ge(PMe$_3$)$_2$(OTf)$_2$] at the B3LYP-D3 level gives a marginally lower total energy (0.037 eV), than the structure obtained from a partial optimization with fixed Ge-P bond lengths (at 2.4177 Å, the X-ray crystallographic value).[19] Although the experimental O-Ge-O angle is not reported, it appears from the calculations that the O-Ge-O angle is some 60° greater than the P-Ge-P angle (see Table S6a). The optimization of [Ge(AsMe$_3$)$_2$(OTf)$_2$] showed reasonably good agreement with the experimentally determined bond lengths, but a significant increase in the As-Ge-As bond angles from the experimentally derived values was computed (from 120° to 164°). A further calculation was performed using the B3LYP-D3 optimised structure as input, except with modifications made to the As-Ge-As and the O-Ge-O angles, making them more similar to the P-Ge-P and O-Ge-O bonds from the B3LYP-D3 optimised structure of [Ge(PMe$_3$)$_2$(OTf)$_2$]. The resulting geometry showed the As-Ge-As and O-Ge-O angles became similar to those in the B3LYP-D3 optimised structure with As-Ge-As ~ 155° and O-Ge-O ~ 92°. A further optimization calculation was performed, fixing the Ge-As bond distances at 2.429 Å as they are in the X-ray structure. The calculation showed the reverse trend with the O-Ge-O angle being significantly larger than the As-Ge-As angle (by ~ 60 deg.). The
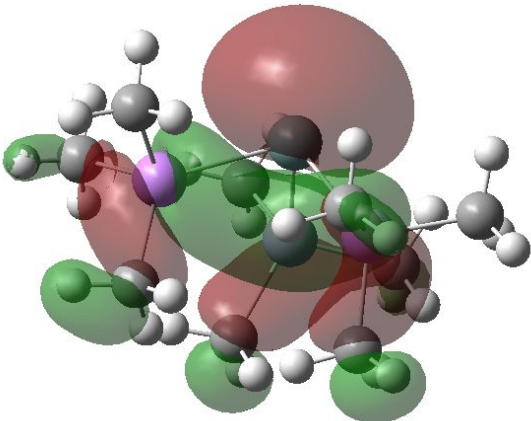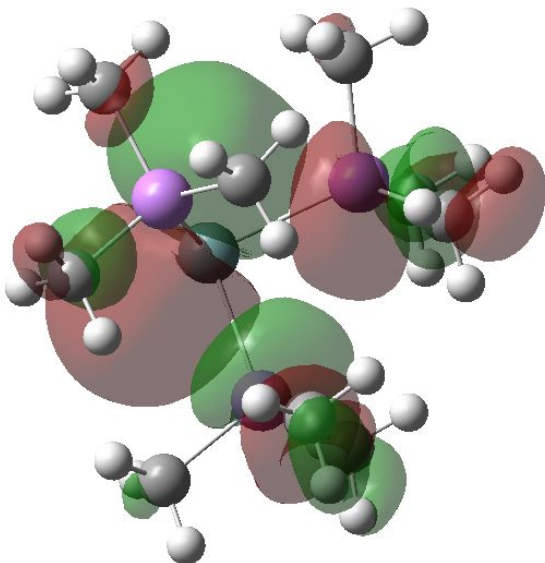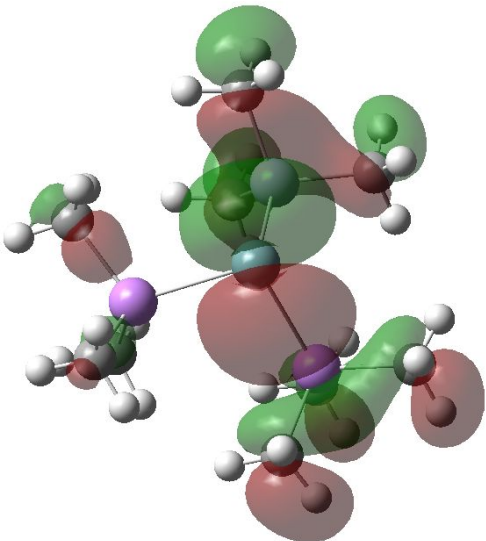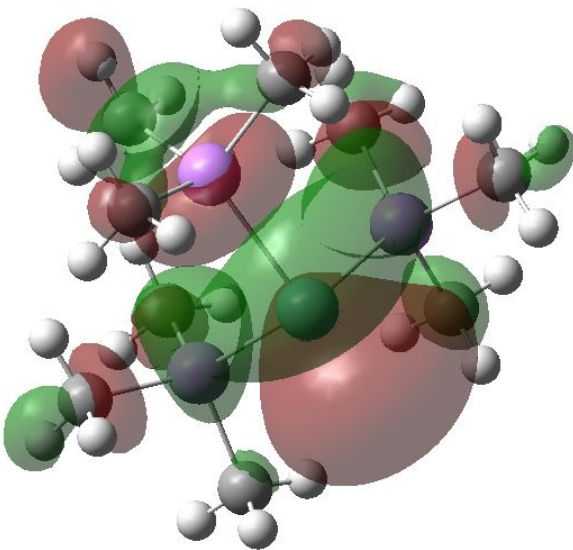
other geometric parameters are all in reasonably good agreement with the X-ray values (Table S6). For each complex, the total energies of the converged structures showed small differences, suggesting that for $[Ge(PMe_3)_2(OTf)_2]$ and $[Ge(AsMe_3)_2(OTf)_2]$, the potential energy surface is very shallow with several interconnected minima with respect to change of the P-Ge-P (As-Ge-As) and O-Ge-O angles, with the final angles in the crystal lattice being determined by short range as well as long range interactions in the complete lattice, as expected for a weakly associated chain polymer structure (Figure S6).

Table S2: Comparison of experimental (X-ray) and computed B3LYP-D3 bond distances (Å) and angles (°) of $[Ge(PMe_3)_3]^{2+}$ – with BP86-D3 values in parentheses

$[Ge(PMe_3)_3]^{2+}$	X-ray	B3LYP-D3 (BP86-D3)
Ge-P	2.3747(5)	2.455 (2.449)
	2.3828(5)	2.455 (2.448)
	2.3970(5)	2.455 (2.449)
P-C	1.804(2)	1.828 (1.831)
	1.802(2)	1.824 (1.830)
	1.7974(19)	1.826 (1.834)
P-C	1.801(2)	1.826 (1.831)
	1.793(2)	1.828 (1.834)
	1.799(2)	1.824 (1.830)
P-C	1.801(2)	1.826 (1.830)
	1.799(2)	1.828 (1.834)
	1.809(2)	1.824 (1.832)
P-Ge-P	98.085(17)	96.46 (96.17)
	100.509(18)	96.44 (96.14)
	99.276(18)	96.42 (96.11)

Table S3: Computed B3LYP-D3 bond distances (Å) and angles (°) of $[Ge(AsMe_3)_3]^{2+}$, with BP86-D3 values in parentheses.

$[Ge(AsMe_3)_3]^{2+}$	B3LYP-D3 (BP86-D3)
Ge-As	2.560 (2.553)
	2.561 (2.552)
	2.561 (2.553)
As-C	1.947 (1.955)
	1.952 (1.952)
	1.949 (1.958)
As-C	1.949 (1.955)
	1.947 (1.952)
	1.952 (1.958)
As-C	1.952 (1.952)
	1.947 (1.958)
	1.949 (1.954)
As-Ge-As	94.64 (94.27)
	94.65 (94.31)
	94.61 (94.25)

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[Ge(AsMe$_3$)$_3$]$^{2+}$ B3LYP-D3	
Energy: -9143.5496 au	HOMO-LUMO gap = 5.41 eV
HOMO (-0.49931 au = -13.59 eV)	LUMO (-0.30037 au = -8.17 eV)
HOMO-1 (-0.54526 au = -14.84 eV)	LUMO+1 (-0.30031 au = -8.17 eV)

Figure S8: Diagrams of the HOMO-1, HOMO, LUMO, and LUMO+1 of [Ge(AsMe$_3$)$_3$]$^{2+}$ determined by B3LYP-D3 calculations.

Table S4: Computed energies of dissociation products, $[Ge(PMe_3)_2]^+$, PMe_3^+, $[Ge(PMe_3)_2]^{2+}$ and PMe_3 at the B3LYP-D3 level.

Complex	Energy (au)
PMe_3	-461.16842
PMe_3^+	-460.88015
$[Ge(PMe_3)_3]^{2+}$	-3460.0822
$[Ge(PMe_3)_2]^{2+}$	-2998.7973
$[Ge(PMe_3)_2]^+$	-2999.1773

Table S5: Computed energies of dissociation products relative to $[Ge(PMe_3)_3]^{2+}$

	Energy	Relative to $[Ge(PMe_3)_3]^{2+}$ (a.u.)	Relative to $[Ge(PMe_3)_3]^{2+}$ (eV)
$[Ge(PMe_3)_3]^{2+}$	-3460.0822	0	0
$[Ge(PMe_3)_2]^{2+}$ + PMe_3	-3459.9657	+0.11648 (increase)	+3.16 (increase)
$[Ge(PMe_3)_2]^+$ + PMe_3^+	-3460.0575	+0.02475 (increase)	+0.67 (increase)

i.e. order of stability goes from the most stable "$[Ge(PMe_3)_3]^{2+}$" to least stable/highest energy "$[Ge(PMe_3)_2]^{2+}$ + PMe_3"

Table S6a: Computed geometrical parameters, bond distances (Å) and angles (°), of $[Ge(PMe_3)_2][OTf]_2$ at the B3LYP-D3 level.

	Input based on X-ray data[a]	B3LYP	input - with fixed Ge-P bond lengths	B3LYP
Ge-P	2.41770	2.49230	2.41770	2.41770
	2.41770	2.49220	2.41770	2.41770
P-C	1.93663	1.82717	1.82680	1.82665
	1.92600	1.82370	1.83084	1.82361
	1.90811	1.83082	1.82366	1.83103
	1.93652	1.82715	1.83082	1.82665
	1.92677	1.82371	1.82362	1.82361
	1.90851	1.83083	1.82678	1.83103
Ge-O	2.25300	2.29806	2.30404	2.30216
	2.23900	2.29649	2.30372	2.30223
P-Ge-P	100.270000	92.83285	94.27929	94.25360
O-Ge-O	99.21858	154.85173	155.21516	154.84386
	Energy (a.u.)	*-4922.745961*		*-4922.744600*

[a]   Values from the X-ray study[19]; no O-Ge-O values were quoted in this work, so the initial value was taken from the X-ray results of $[Ge(AsMe_3)_2(OTf)_2]$ (this work)

Table S6b: Computed geometrical parameters, bond distances (Å) and angles (°), of [Ge(AsMe$_3$)$_2$(OTf)$_2$] at the B3LYP-D3 level.

	X-ray data (this work)	B3LYP	Input with modified As-Ge-As and O-Ge-O angles	B3LYP	Input with fixed Ge-As bond lengths	B3LYP
Ge-As	2.42951	2.93125	2.93125	2.84138	2.42900	2.42900
	2.42884	2.93075	2.93075	2.93747	2.42900	2.42900
As-C	1.93663	1.97023	1.96451	1.96574	1.93663	1.95411
	1.90811	1.96451	1.97023	1.95730	1.92600	1.94368
	1.92600	1.95645	1.95645	1.96050	1.90811	1.95028
	1.93652	1.97022	1.95642	1.96377	1.93652	1.95030
	1.92677	1.96451	1.97022	1.96105	1.90851	1.94368
	1.90851	1.95642	1.96451	1.96667	1.92677	1.95412
Ge-O	2.02200	1.97208	1.97208	2.01407	2.02124	2.30606
	2.02124	1.97216	1.97216	1.97136	2.02200	2.30796
As-Ge-As	119.59585	164.46499	93.00000	155.52945	119.59585	93.79793
O-Ge-O	99.21858	97.01975	154.00000	92.19432	99.21858	155.48900
	Energy (a.u.)	*-8711.711571*		*-8711.715543*		*-8711.719243*

More Detailed Consideration of Figure 6.

The plots shown in Figure 6 are the result of constrained geometry optimizations on $[Ge(PMe_3)_3]^{2+}$ where at each point the P-Ge-P angle was held fixed and all other parameters were optimized.

As stated in the text, the B3LYP-D3 optimised geometry of $Ge(PMe_3)_3{}^{2+}$ has a P-Ge-P angle of 96.8°. This is the minimum of Figure 6(a). Using $E_{tot}=E_{elec} +E_{nn}$, plotting E_{elec} versus the P-Ge-P angle and E_{nn} versus the P-Ge-P angle gives the plots shown in Figure 6(b) and 6(c) respectively. It should be noted that the energy range on the vertical axis of Figure 6(a) is much less than that on the vertical axes of Figures 6(b) and 6(c). This means that at a given P-Ge-P angle E_{tot} is determined as the sum of two large terms, E_{elec} which is negative and E_{nn} which is positive.

This figure shows that E_{nn} dominates the E_{tot} plot at angles less than 96.8° and E_{elec} dominates at angles greater than 96.8°. With this knowledge, reasons were sought as to why E_{elec} plot exhibited the shape it does over the range 80-114 °. AIM (Atoms in Molecule) analysis indicates that this is, in part, because there are increased C···H and H···H interactions between atoms on different CH_3 groups as the P-Ge-P angle decreases (see the next section and Table S8).

In the evaluation of the E_{nn} terms all nuclear-nuclear interactions are taken into account in the calculation. $[Ge(PMe_3)_3]^{2+}$ has 40 atoms, so there will be 780 nuclear-nuclear interactions.

The results of the constrained geometry optimization calculations show that most of the bond lengths of bonded atoms go down on going from P-Ge-P angles of 80 to 120° and for the nearby H···H interactions some distances increase and some decrease (some even increase and then decrease) on going from 80 to 120° (see Table S7, Figures S9-S11).

Table S7 Table of computed bonded atom distances (Å) at different P-Ge-P angles from constrained geometry optimization calculations on $[Ge(PMe_3)_3]^{2+}$ at the B3LYP-D3 level.

P-Ge-P angle /°	80	85	90	95	100	105	110	115	119.5
Ge-P	2.57834	2.52944	2.49232	2.46294	2.44094	2.42693	2.41986	2.41137	2.30490
Ge-P	2.57826	2.52965	2.4924	2.46235	2.44106	2.42742	2.42071	2.41050	2.30466
Ge-P	2.57823	2.53034	2.49232	2.46223	2.43924	2.42755	2.41979	2.41018	2.30537
P-C	1.83306	1.83036	1.82816	1.82611	1.82466	1.82421	1.82265	1.82356	1.82153
P-C	1.83347	1.82997	1.82961	1.82453	1.82744	1.82251	1.82653	1.82678	1.82603
P-C	1.83455	1.83149	1.82691	1.82830	1.82305	1.82666	1.82408	1.82252	1.82025
P-C	1.83309	1.83164	1.82955	1.82838	1.82723	1.82428	1.82409	1.82373	1.82160
P-C	1.83353	1.83005	1.82692	1.82444	1.82287	1.82665	1.82633	1.82681	1.82648
P-C	1.83449	1.83045	1.82811	1.82622	1.82510	1.82251	1.82284	1.82247	1.82000
P-C	1.83307	1.83052	1.82814	1.82617	1.82738	1.82669	1.82264	1.82365	1.82168
P-C	1.83356	1.83008	1.82693	1.82825	1.82287	1.82251	1.82649	1.82671	1.82586
P-C	1.83454	1.8317	1.8296	1.82444	1.82476	1.82429	1.82403	1.82272	1.82027

Figure S9. Diagram and table of some nearby H···H distances (Å) at different P-Ge-P angles (°) from constrained geometry optimization calculations on [Ge(PMe$_3$)$_3$]$^{2+}$ at the B3LYP-D3 level. The positions of nearby atoms H6, H10, H14 are displayed (circled red) on graphic (a). These distances (Å) are tabulated in b) and displayed as a graph in c).
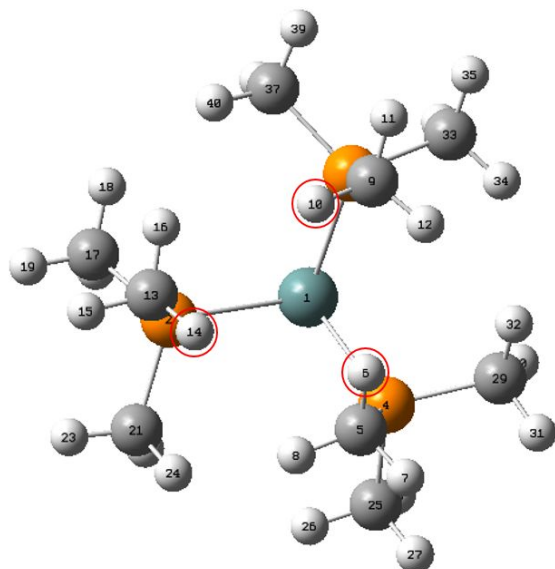
a)

	Between H6 and H14	Between H14 and H10	Between H10 and H6	H6-H10-H14 (°)
90	2.46312	2.46452	2.46057	60.01518
96.8	2.75850	2.75971	2.75572	60.01884
100	3.02905	3.02924	3.0246	60.04648
110	4.19255	4.20226	4.2051	59.82485
119.5	5.01404	5.00034	4.99996	60.18397

b)
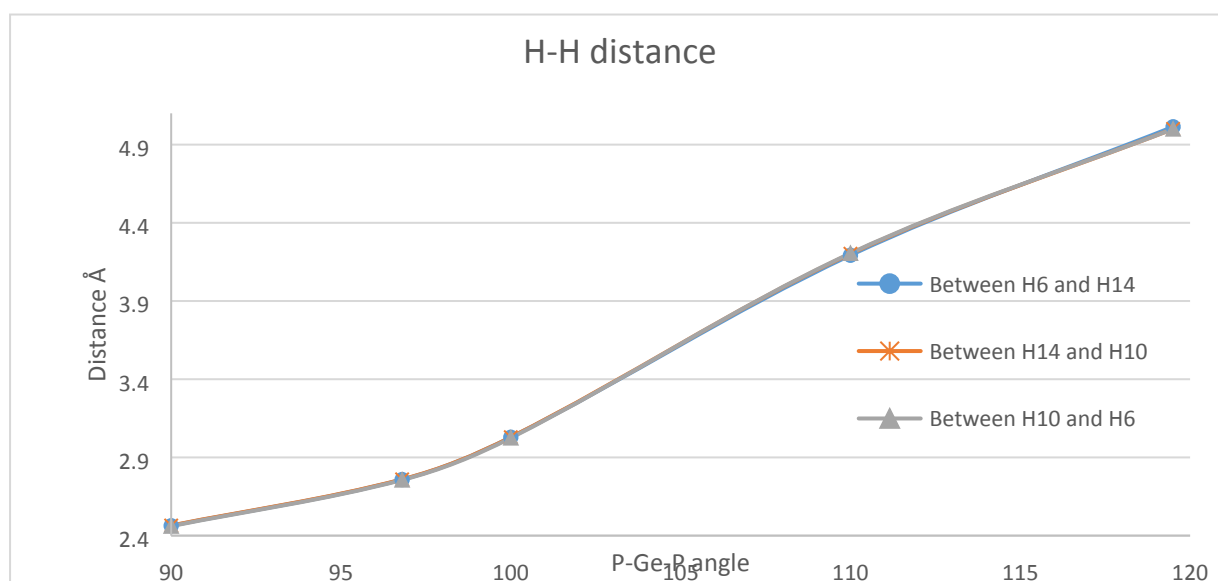
Note the orange and blue lines are hidden beneath the grey line.

c)

Figure S10. Diagram and table of some nearby Ge-C and H--H atom distances (Å) at different P-Ge-P angles (°) from constrained geometry optimization calculations on [Ge(PMe$_3$)$_3$]$^{2+}$ at the B3LYP-D3 level. The positions of nearby atoms H30, H32, H34, C29 and C33 are displayed on a graphic (a). These distances (Å) are tabulated in b) and displayed as a graph in c).

a)

|	Between H34 and H32	Between H34 and H30	Ge-C33	Ge-C29
90	2.50523	2.90328	3.45829	3.53867
96.8	2.55227	2.89664	3.43298	3.49588
100	2.56999	2.88168	3.41441	3.47513
110	2.53999	2.8206	3.35928	3.40203
119.5	2.47585	2.55677	3.34052	3.31497

b)
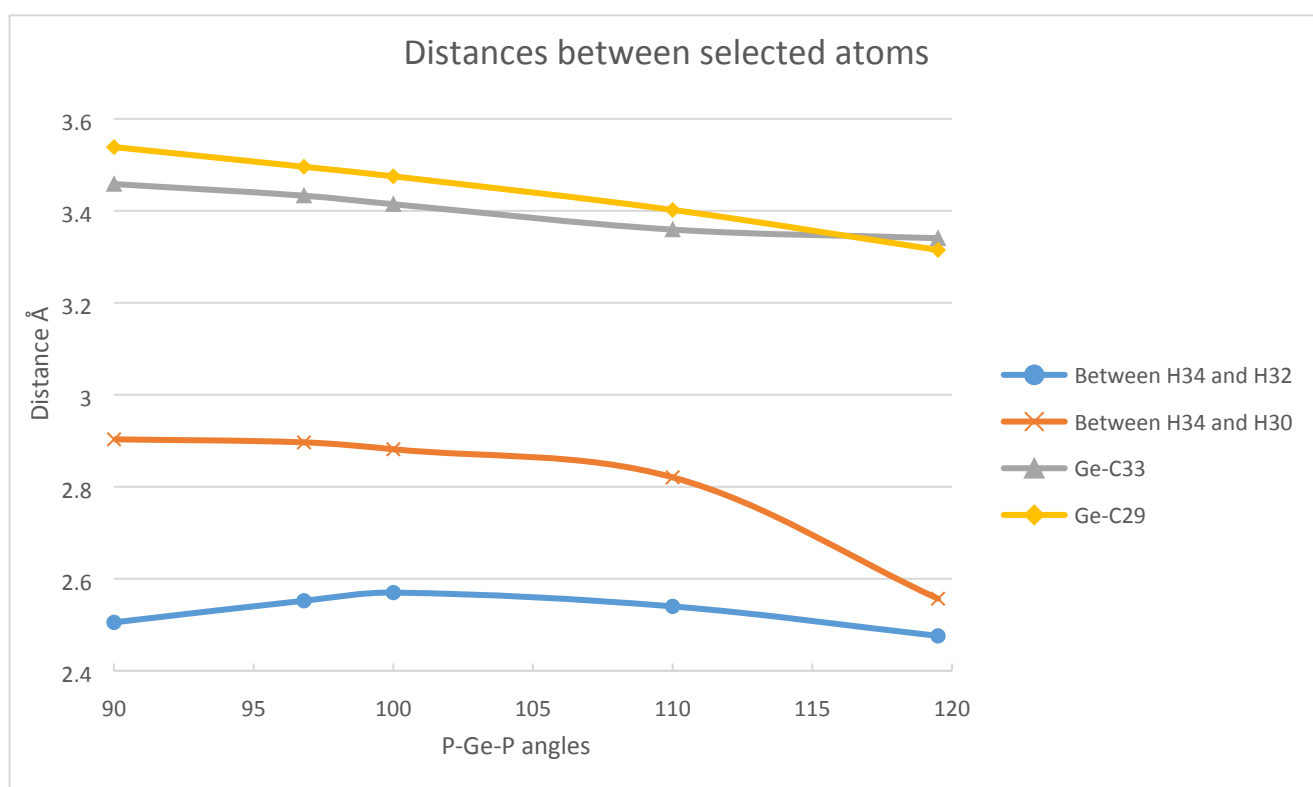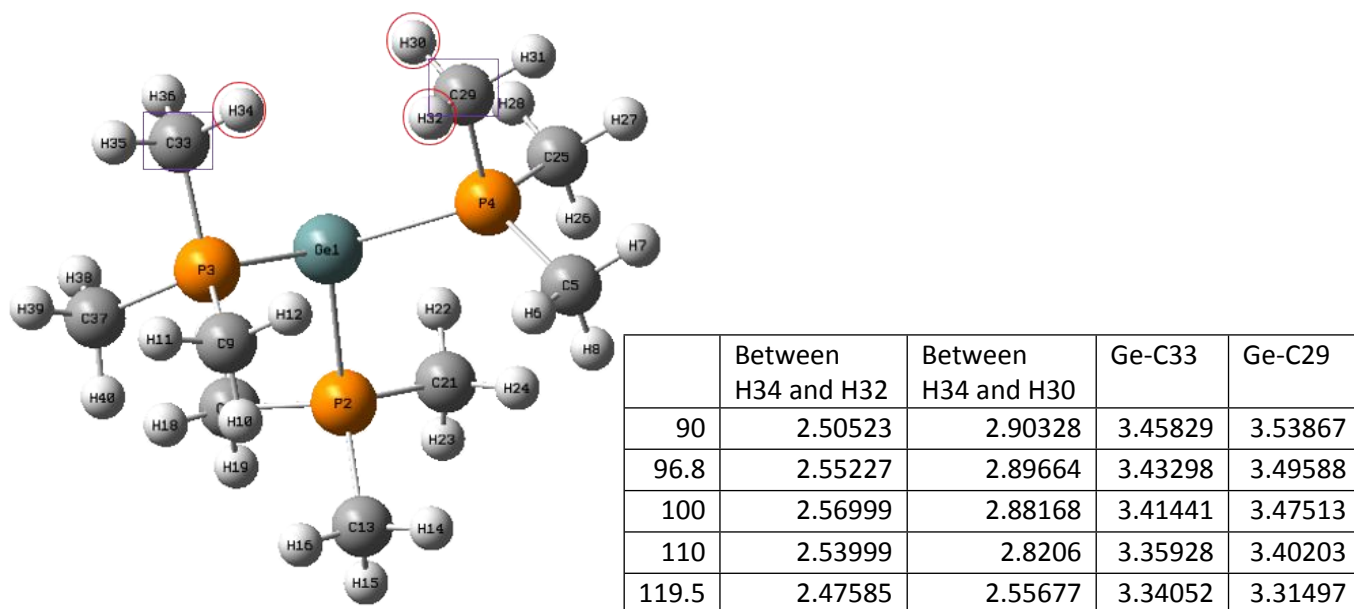
c)

Figure S11. Diagram and table of some nearby H···H distances (Å) at different P-Ge-P angles (°) from constrained geometry optimization calculations on $[Ge(PMe_3)_3]^{2+}$ at the B3LYP-D3 level. The positions of nearby atoms H8, H22, H24, H26 & H40 are displayed on a graphic (a). These distances (Å) are tabulated in b) and displayed as a graph in c).
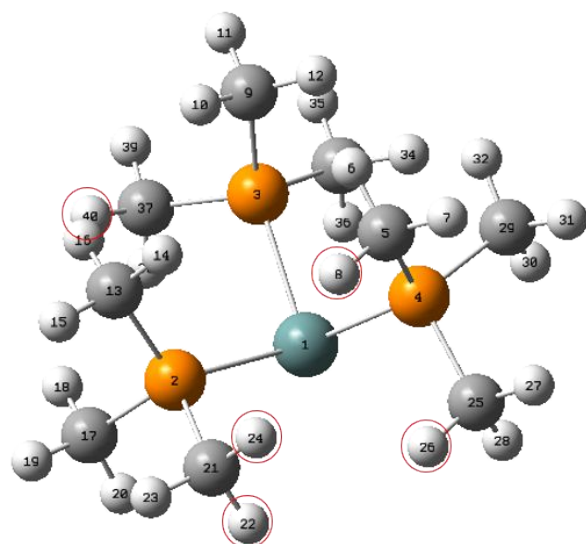
a)

	Between H26 and H24	Between H26 and H22	Between H26 and H8	Between H26 and H40
90	2.50703	2.90084	2.97694	6.84343
96.8	2.55217	2.89621	2.9829	6.91711
100	2.57396	2.88807	2.98722	6.96357
110	2.54156	2.82468	2.98771	7.08643
119.5	2.48541	2.55652	2.97324	6.9916

b)
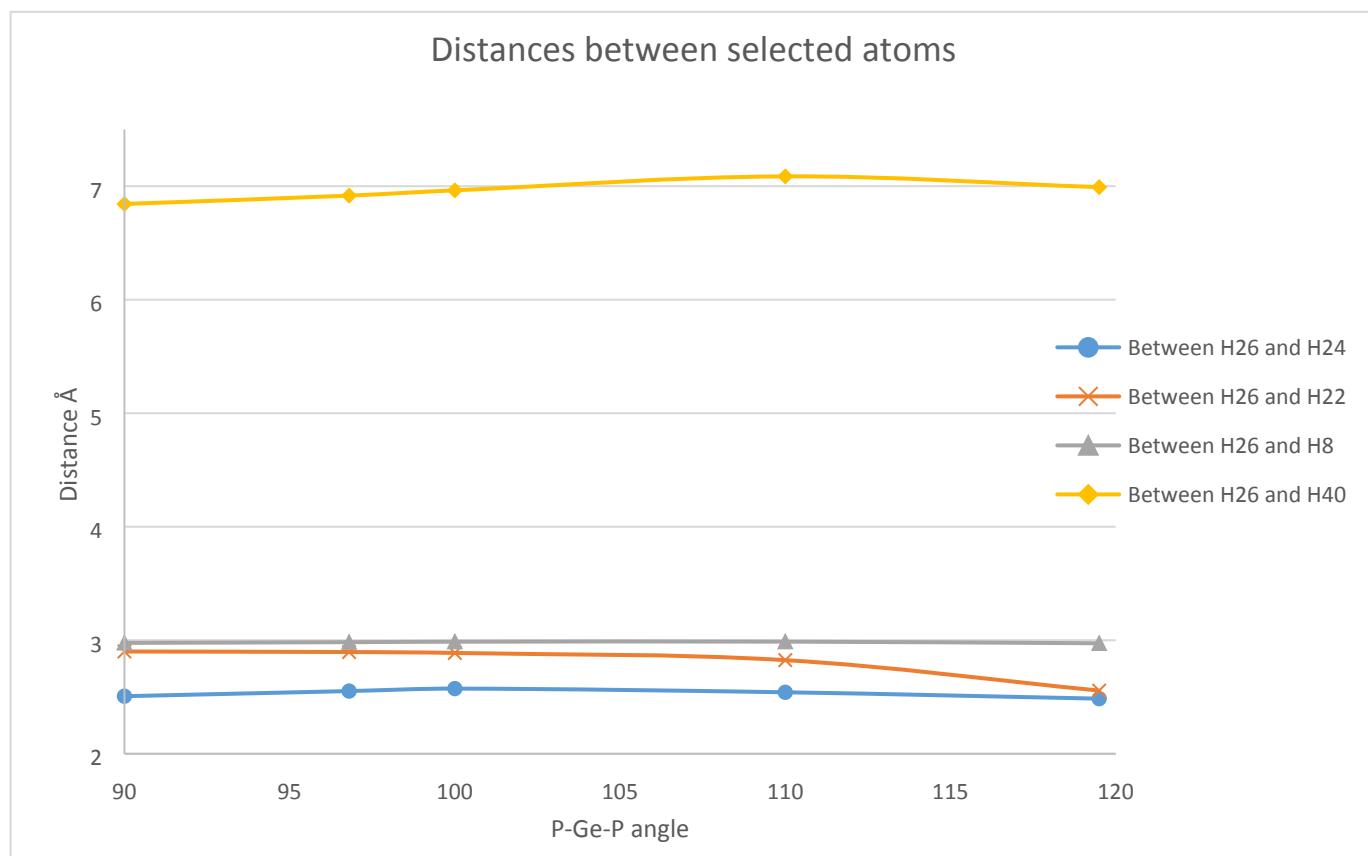
SUMMARY OF AIM CALCULATIONS ON [Ge(PMe$_3$)$_3$]$^{2+}$

Introduction

The outputs from the constrained geometry optimization calculations (at a fixed P-Ge-P angle) were used in AIM (Atoms in Molecules) calculations (using GAUSSIAN16 (30) and MULTIWFN (33)). The results obtained at four P-Ge-P angles are shown in Table S8 (a)-(d). The P-Ge-P angles selected are 80.0, 90.0, 105.0, and 119.5° (the minimum energy at the B3LYP-D3 level is at a P-Ge-P angle of 96.8°).

These tables show:-

(a) Extra "lines of interaction" obtained with the AIM analysis, apart from the 39 formal bonds in [Ge(PMe$_3$)$_3$]$^{2+}$ e.g. for a P-Ge-P angle of 80°, 39 bonds were identified as well as 9 extra "lines" (3 C--H and 6 H--H interactions) between atoms, which are not formally bonded, on different CH$_3$ groups. In each table, some other interactions are also included for comparison e.g. Ge-P, C-P, and C-H (as well as P···P, not identified as a "line" in the calculations)

(b) In column 2 of each table, the atom pairs responsible for each "extra" interaction are listed.

(c) Column 4 lists the computed Atom-Atom distance.

(d) Column 5 lists the sum of the Atom-Atom van der Waals radii taken from ref. 35.

(e) Column 6 lists the computed value of the electron density (ρ) at the BCD (bond critical point) and column 3 lists $\nabla^2\rho$.

(f) Column 7 lists the value of the computed Mayer bond order (34).

Observations from Tables S8(a)-(d)

1.As the PGeP angle decreases from 119.5 to 80.0°, the number of extra interactions identified in the calculations increase from 3 to 9

e.g. at 119.5° there are 3 C--H interaction and at 80.0° there are 3 C--H and 6 H--H interactions between atoms on different CH$_3$ groups.

2. Inspection of the ∇^2 (ρ) values for these extra interactions show that they are all positive consistent with van der Waals (C--H) and hydrogen bonded (H--H) interactions.

The atom-atom distances for these interactions are all close to but slightly higher than the sum of the van der Waals radii for the atoms involved, apart from the C--H interaction at 80.0° where the atom-atom distance is slightly lower than the sum of the van der Waals radii.

3. For the "formal" bonds C-P and C-H, the ∇^2 (ρ) values are negative at all angles, as expected for a covalent bond. However, for the Ge-P bond, ∇^2 (ρ) is negative at 119.5° but it is positive at the other three angles. This is consistent with the Ge-P bond becoming more polar as the angle decreases. The computed bond distances for the bonds C-P, C-H and Ge-P are all less than the sum of the van der Waals radii for these bonds at all four angles, as expected.

Conclusion

As shown in Figure 6, at the B3LYP-D3 level the computed minimum energy structure occurs at a P-Ge-P angle of 96.8° (the minimum of the plot of E_{TOT} vs P-Ge-P angle). E_{nn} increases for P-Ge-P angles decreasing from 115 to 80.0° whereas E_{elec} decreases for P-Ge-P angles changing from 115.0 to 80.0°. The AIM calculations indicate that one reason for this decrease in E_{elec} is that there are increased C--H (van der Waals) and H--H (hydrogen bonding) interactions between atoms on different CH_3 groups as the P-Ge-P angle decreases.

Table S8

(a) Summary of Results of Calculations at P-Ge-P = 80 deg.

48 lines of interaction identified (39 formal bonds and 9 other interactions; 3(C--H-), 6(H--H))

Line Identified in Gaussian with AIM	Atom Pair	$\nabla^2 (\rho)$ / a.u.^{3} ($Å^3$)	Distance (Å)	Sum of van der Waals radii (Å) from ref. 35	Bond Density (ρ) / a.u.^{3} ($Å^3$)	Mayer Bond Order
C···H (3 extra)						
9	9(C)-6(H)	+0.033 (0.005)	2.628	2.80	0.009 (0.0013)	0.003
14	13(C)-10(H)	+0.033 (0.005)	2.629	2.80	0.009 (0.0013)	0.003
15	5(C)-14(H)	+0.033 (0.005)	2.629	2.80	0.009 (0.0013)	0.003
H···H (6 extra)						
26	24- 8	0.0224 (0.003)	2.203	2.20	0.007 (0.001)	0.0137
29	26-24	0.0167 (0.002)	2.419	2.20	0.007 (0.001)	0.0032
36	32-12	0.0225 (0.003)	2.202	2.20	0.005 (0.0007)	0.0138
39	34-32	0.0167 (0.002)	2.420	2.20	0.005 (0.0007)	0.0032
46	40-16	0.0225 (0.003)	2.202	2.20	0.007 (0.001)	0.0138
47	40-18	0.0167 (0.004)	2.419	2.20	0.005 (0.0007)	0.0032
"Some bonded atoms"						
Ge-P						
1	1(Ge)-2(P)	+0.0155 (0.002)	2.577	3.91	0.0606 (0.089)	0.6939
2	1(Ge)-3(P)	+0.0155 (0.002)	2.577	3.91	0.0606 (0.0089)	0.6939
3	1(Ge)-4(P)	+0.0155 (0.002)	2.577	3.91	0.0606 (0.0089)	0.6939
C-P	4(P)-5(C)	-0.294 (-0.0435)	1.834	3.50	0.1637 (0.024)	0.907

C-H	5(C)-H(6)	-0.8979 (-0.132)	1.084	2.80	0.2748 (0.041)	0.883
P⋯P (not "bonded")	2-3	not found	3.314	3.60	not relevant	0.004
	2-4	not found	3.314	3.60	not relevant	0.004
	3-4	not found	3.314	3.60	not relevant	0.004

(b) Summary of Results of Calculations at P-Ge-P = 90 deg.

48 lines of interaction identified (39 formal bonds and 9 other interactions; 3(C--H), 6(H--H))

Line Identified in Gaussian with AIM	Atom Pair	$\nabla^2(\rho)$ / a.u.^{3} (Å^3)	Distance (Å)	Sum of van der Waals radii (Å) from ref. 35	Bond Density (ρ) / a.u.^{3} (Å^3)	Mayer Bond Order
C⋯H (3 extra)						
	9(C) -6(H)	+0.022 (0.003)	2.812	2.80	0.006 (0.0008)	0.002
	13(C)-10(H)	+0.022 (0.003)	2.814	2.80	0.006 (0.0008)	0.002
	5(C)-14(H)	+0.022 (0.003)	2.815	2.80	0.006 (0.0008)	0.002
H⋯H (6 extra)						
	24-8	0.0158 (0.0023)	2.357	2.20	0.005 (0.0007)	0.011
	26-24	0.0139 (0.0020)	2.507	2.20	0.004 (0.0005)	0.003
	32-12	0.0158 (0.0023)	2.358	2.20	0.005 (0.0007)	0.011
	34-32	0.0139 (0.0020)	2.505	2.20	0.004 (0.0005)	0.003
	40-16	0.0158 (0.0023)	2.357	2.20	0.005 (0.0007)	0.011
	40-18	0.0139 (0.0020)	2.507	2.20	0.004 (0.0005)	0.003
"Some Bonded Atoms"						
Ge-P						
1	1(Ge)-2(P)	0.0105 (0.0015)	2.492	3.91	0.070 (0.010)	0.732
2	1(Ge)-3(P)	0.0105 (0.0015)	2.492	3.91	0.070 (0.010)	0.732
3	1(Ge)-4(P)	0.0105 (0.0015)	2.492	3.91	0.070 (0.010)	0.732
C-P	4(P)-5(C))	-0.278 (-0.041)	1.829	3.50	0.163 (0.024)	0.914
C-H	5(C)-H(6)	-0.883	1.087	2.80	0.272	0.886

Line Identified in Gaussian with AIM	Atom Pair	$\nabla^2 (\rho)$ / a.u.^{3} (Å^3)	Distance (Å)	Sum of van der Waals radii (Å) from ref. 35	Bond Density (ρ) / a.u.^{3} (Å^3)	Mayer Bond Order
		(-0.131)			(0.040)	
P···P (not "bonded")	2-3	not found	3.524	3.60	not relevant	0.014
	2-4	not found	3.524	3.60	not relevant	0.014
	3-4	not found	3.524	3.60	not relevant	0.014

(c) Summary of Results of Calculations at P-Ge-P = 105 deg.

42 lines of interaction identified (39 formal bonds and 3 other interactions; 1(C--H), 2(H--H))

Line Identified in Gaussian with AIM	Atom Pair	$\nabla^2 (\rho)$ / a.u.^{3} (Å^3)	Distance (Å)	Sum of van der Waals radii (Å) from ref. 35	Bond Density (ρ) / a.u.^{3} (Å^3)	Mayer Bond Order
C···H (1 extra)						
	37(C)-18(H)	0.0124 (0.0018)	3.132	2.80	0.004 (0.0006)	0.0005
H···H (2 extra)						
	12-6	0.005 (0.0007)	2.995	2.20	0.0015 (0.0002)	0.0017
	14-8	0.005 (0.0007)	3.006	2.20	0.0015 (0.0002)	0.0017
"Some Bonded Atoms"						
Ge-P						
1	1(Ge)-2(P)	0.002 (0.0003)	2.427	3.91	0.077 (0.011)	0.756
2	1(Ge)-3(P)	0.002 (0.0003)	2.427	3.91	0.077 (0.011)	0.756
3	1(Ge)-4(P)	0.002 (0.0003)	2.427	3.91	0.077 (0.011)	0.756
C-P	4(P)-5(C))	-0.284 (-0.035)	1.826	3.50	0.167 (0.025)	0.925
C-H	5(C)-H(6)	-0.872 (-0.129)	1.090	2.80	0.272 (0.040)	0.897
P···P (not "bonded")	2-3	not found	3.851	3.60	not relevant	0.034
	2-4	not found	3.851	3.60	not relevant	0.034
	3-4	not found	3.851	3.60	not relevant	0.034

(d) Summary of Results of Calculations at P-Ge-P = 119.5 deg.

42 lines of interaction identified (39 formal bonds and 3 other interactions; 3(C--H))

Line Identified in Gaussian with AIM	Atom Pair	$\nabla^2 (\rho)$ / a.u.^{3} (Å^3)	Distance (Å)	Sum of van der Waals radii (Å) from ref. 35	Bond Density (ρ) / a.u.^{3} (Å^3)	Mayer Bond Order
C···H (3 extra)						
	26(H)-1(C)	+0.0184 (0.003)	2.943	2.80	0.0055 (0.0008)	0.0008
	34(H)-9(C)	+0.0186 (0.003)	2.938	2.80	0.0055 (0.0008)	0.0008
	37(C)-8(H)	+0.0184 (0.003)	2.943	2.80	0.0055 (0.0008)	0.0008
H···H (0 extra) (some "close" H···H considered)						
	11-35	not relevant	2.829	2.20	not relevant	0.00001
	11-39	not relevant	2.840	2.20	not relevant	0.0001
	12-34	not relevant	2.974	2.20	not relevant	0.0007
"Some bonded atoms"						
Ge-P						
1	1(Ge)-2(P)	-0.014 (-0.002)	2.304	3.91	0.0924 (0.014)	0.904
2	1(Ge)-3(P)	-0.014 (-0.002)	2.304	3.91	0.0924 (0.014)	0.904
3	1(Ge)-4(P)	-0.014 (-0.002)	2.304	3.91	0.0924 (0.014)	0.904
C-P	4(P)-5(C))	-0.318 (-0.047)	1.826	3.50	0.1693 (0.025)	0.936
C-H	5(C)-H(6)	-0.877 (-0.130)	1.090	2.80	0.2707 (0.040)	0.896
P···P (not "bonded")	2-3	not found	3.982	3.60	not relevant	0.079

	2-4	not found	3.982	3.60	not relevant	0.079