Supplementary Material (ESI) for Chemical Communications

Supplementary Information

1,3-Digermacyclobutanes with exocyclic C=P and C=P=S double bonds

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S1

Mes*P=C(Cl)Ge(F)*t*Bu$_2$ 1.

NMR data for **1** (solvent $CDCl_3$)δ^1H (300 MHz) 1.23 (d, $^4J_{HF}$ = 1.2 Hz, *t*BuGe), 1.29 (s, *p*-*t*Bu), 1.47 (s, *o*-*t*Bu), 7.38 (d, $^4J_{PH}$ = 1.4 Hz, arom. H);

δ^{13}C (75.5 MHz) 28.10 (*Me*$_3$C of *t*BuGe), 31.33 (*p*-*Me*$_3$C of Mes*P), 32.94 (d, $^4J_{CP}$ = 6.7 Hz, o-*Me*$_3$C of Mes*P), 33.00 (dd, $^2J_{C\text{-}F}$ and $^3J_{C\text{-}P}$ = 3.3 and 8.3 Hz, Me$_3$*C* of tBu), 35.03, (s, *p*-Me$_3$*C* of Mes*P), 37.85 (*o*-Me$_3$*C* of Mes*P), 122.00 (*m*-*C* of Mes*), 134.19 (dd, *ipso*-C, $^1J_{CP}$ = 67.15, $^4J_{CF}$ = 2.3 Hz), 150.60 (*p*-C of Mes*), 153.54 (d, *o*-C of Mes*, $^2J_{CP}$ = 2.3 Hz), 165.27 (dd, $^1J_{CP}$ = 91.0 Hz, $^2J_{CF}$ = 4.5 Hz, C=P);

δ^{19}F (188.3 MHz, CF_3COOH) -135.4;

δ^{31}P (121.5 MHz) 293.5 (d, $^3J_{PF}$ = 45.8 Hz);

MS (EI, m/z): 515 (M^+ – Me), 1), 473 (M – *t*Bu, 3), 417 (M – 2*t*Bu + 1, 10), 323 (Mes*P=CCl, 8), 289 (Mes*P=CH, 60), 57 (*t*Bu, 100);

Found : C 61.02; H, 9.04, $C_{27}H_{47}ClFGeP$ requires C 61.22; H, 8.94%.

2,4-Diphosphinylidene-1,3-digermacyclobutane 3

mp = 309 °C (**3a**), mp = 301 °C (**3b**);

NMR data for **3** (solvent $CDCl_3$); **3a** δ^1H (300 MHz) 0.56 (s, *t*BuGe), 1.23 and 1.32 (2s, *p*-*t*Bu and *t*BuGe), 1.47 (s, *o*-*t*Bu), 7.07 (s, arom. H);

δ^{31}P (121.5 MHz) 367.4.

3b δ^1H (300 MHz) 0.94, 1.19 and 1.50 (3s, *t*Bu), 7.13 (s, arom. H);

δ^{31}P (121.5 MHz) 367.7.

δ^{13}C (75.5 MHz) mixture of **3a/3b**: 31.32, 31.39, 31.47, 31.62, 31.68 and 35.11 (*Me*$_3$*C*C), 34.22, 34.51, 34.57, 34.74 and 39.04 (Me$_3$C*C*), 119.51, 121.47 and 121.64 (*m*-C of Mes*),

148.42, 149.96, 153.12 and 153.19 (arom C), 204.0 (dd, $^{1}J_{CP}$ = 96.6 Hz, $^{3}J_{CP}$ = 25.7 Hz, C=P) (**3a**), 204.3 (dd, $^{1}J_{CP}$ = 92.0 Hz, $^{3}J_{CP}$ = 24.9 Hz, C=P) (**3b**);

MS (EI, m/z): 893 (M^{+} - *t*Bu, 8), 721 (M – *4t*Bu – 1, 5), 705 (M – Mes* 2), 665 (M – 5*t*Bu, 5), 649 (M – 5*t*Bu - MeH, 5), 605 (M – Mes*P=C – *t*Bu, 20), 275 (Mes*P – 1, 10), 57 (*t*Bu, 100);

Found: C 68.03 ; H, 10.04, $C_{54}H_{94}Ge_2P_2$ requires C 68.24; H, 9.97%.

2,4-Bis(thioxophosphoranylidene)-1,3-digermacyclobutane 5.

δ^{31}P (121.5 MHz) 184.4 (**5a**), 183.7 (**5b**).

5a/**5b** δ^{1}H (300 MHz) 0.61, 1.13, 1.25, 1.26, 1.53 and 1.67 (6s, 90H, *Me*$_3$C), 7.24 – 7.46 (m, 4H, arom H).

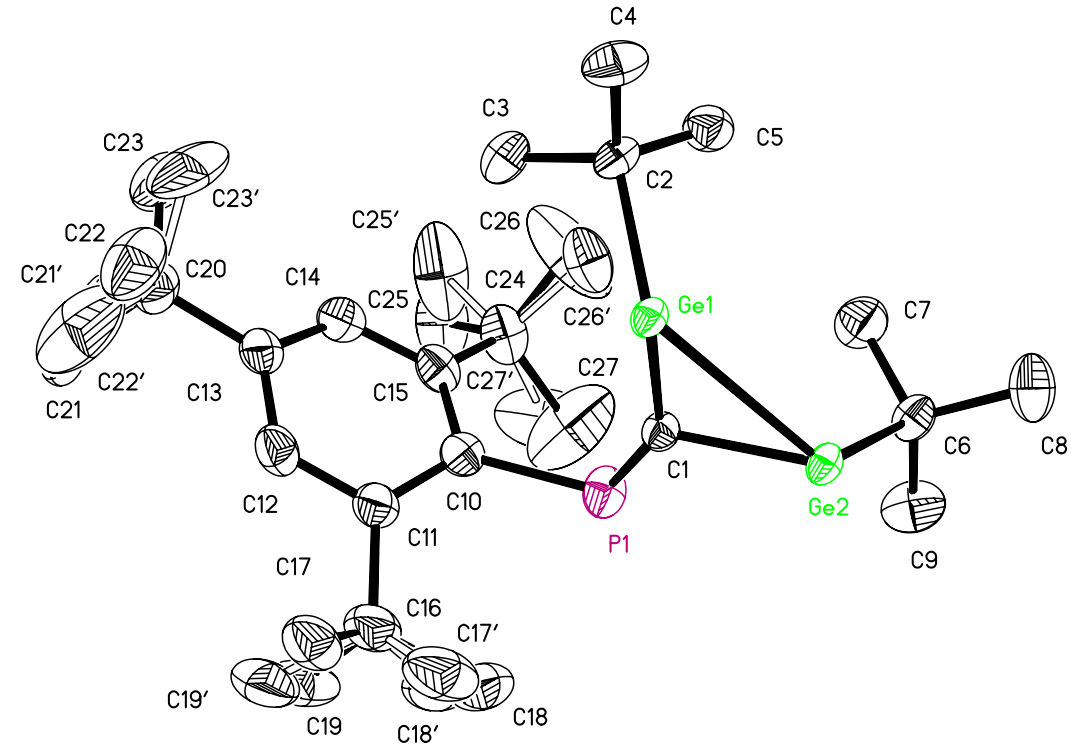
δ^{13}C (75.5 MHz) 31.03, 31.55, 31.65, 32.47, 33.31, 33.93 and 34.17 (*Me*$_3$C), 32.72, 34.81, 34.95, 35.02 and 35.93 (Me$_3$*C*), 119.49, 120.998 and 122.60 (*m*-C of Mes*), 149.92, 150.82, 152.83, 153.25 and 156.75 (arom C), 159.3 – 164.2 (m, C=P);

δ^{31}P (121.5 MHz) 184.4 (**5a**), 183.7 (**5b**);

MS (EI, m/z): 957 (M^{+} – *t*Bu, 10), 941 (M – *t*Bu – MeH, 5), 737 (M – Mes* – S), 509 (M/2 + 1, 10), 275 (Mes*P – 1, 20), 57 (*t*Bu, 100);

Found: C 64.05; H, 9.14, $C_{54}H_{94}Ge_2P_2S_2$ requires C 63.93; H, 9.34%.

Derivative **3a**



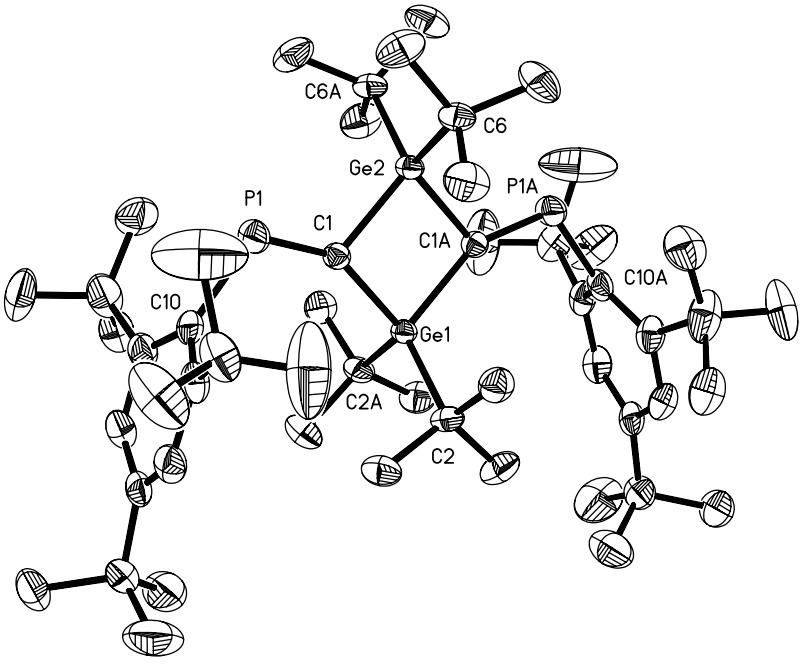
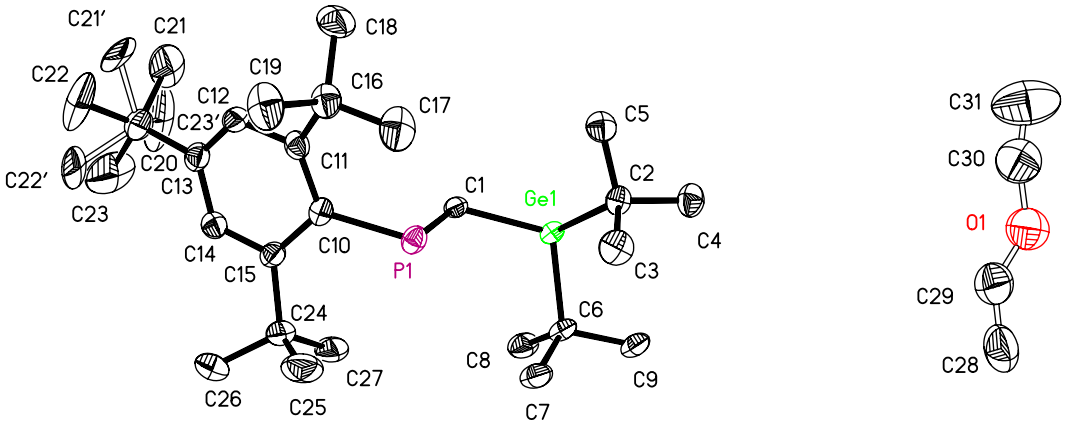


Table 1. Crystal data and structure refinement for **3a.**

Identification code	**3a**	
Empirical formula	C54 H94 Ge2 P2	
Formula weight	950.41	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 33.039(3) Å	α= 90°.
	b = 10.8738(11) Å	β= 115.321(2)°.
	c = 17.1736(17) Å	γ = 90°.
Volume	5577.0(10) Å^3	
Z	4	
Density (calculated)	1.132 Mg/m^3	
Absorption coefficient	1.166 mm^{-1}	
F(000)	2048	
Crystal size	0.1 x 0.2 x 0.5 mm^3	
Theta range for data collection	2.22 to 26.43°.	
Index ranges	-40<=h<=41, -12<=k<=13, -21<=l<=17	
Reflections collected	16226	
Independent reflections	5722 [R(int) = 0.0595]	
Completeness to theta = 26.43°	99.6 %	
Absorption correction	Semi-empirical	
Max. and min. transmission	1.000000 and 0.749303	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5722 / 90 / 354	
Goodness-of-fit on F^2	1.036	
Final R indices [I>2sigma(I)]	R1 = 0.0343, wR2 = 0.0945	
R indices (all data)	R1 = 0.0435, wR2 = 0.0997	
Largest diff. peak and hole	1.584 and -0.336 e.Å^{-3}	

Derivative **3b**



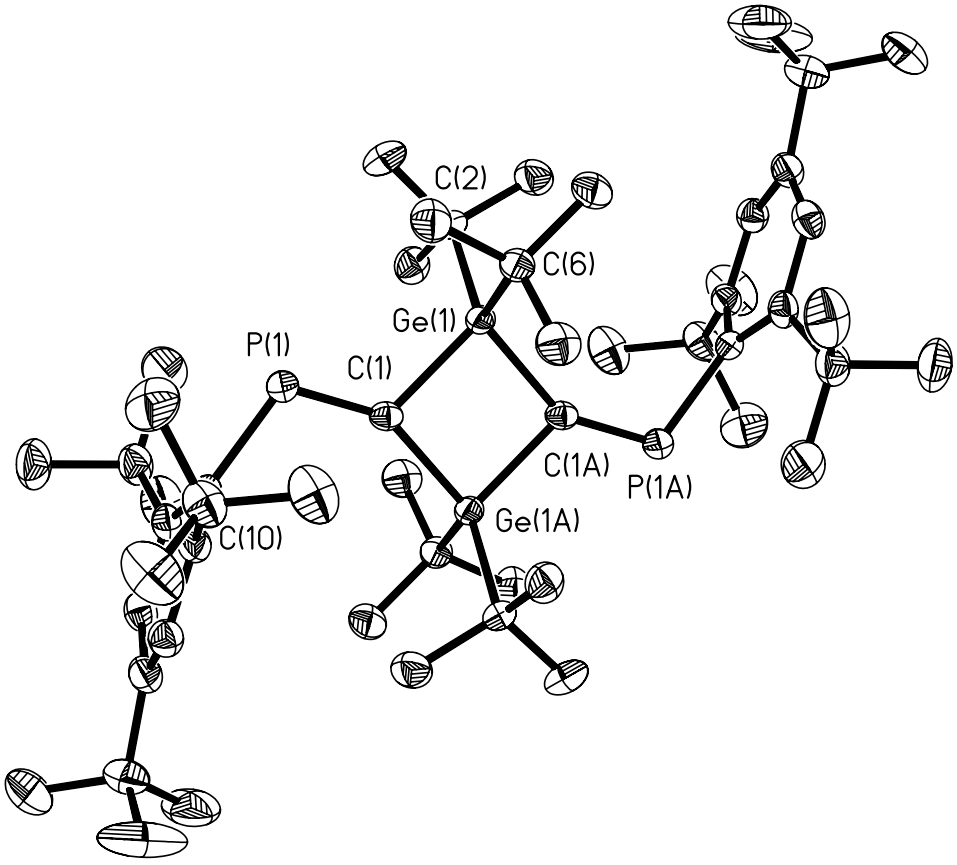


Table 1. Crystal data and structure refinement for **3b**.

Identification code	**3b**	
Empirical formula	C58 H104 Ge2 O1 P2	
Formula weight	1024.54	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 35.416(2) Å	α= 90°.
	b = 10.6099(7) Å	β= 101.1090(10)°.
	c = 16.2868(11) Å	γ = 90°.
Volume	6005.3(7) $Å^3$	
Z	4	
Density (calculated)	1.133 Mg/m^3	
Absorption coefficient	1.089 mm^{-1}	
F(000)	2216	
Crystal size	0.05 x 0.3 x 0.3 mm^3	
Theta range for data collection	5.10 to 24.71°.	
Index ranges	-41<=h<=41, -12<=k<=11, -19<=l<=13	
Reflections collected	14909	
Independent reflections	5077 [R(int) = 0.0577]	
Completeness to theta = 24.71°	99.0 %	
Absorption correction	Semi-empirical	
Max. and min. transmission	1.000000 and 0.730951	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5077 / 88 / 345	
Goodness-of-fit on F^2	0.997	
Final R indices [I>2sigma(I)]	R1 = 0.0386, wR2 = 0.0748	
R indices (all data)	R1 = 0.0726, wR2 = 0.0847	
Largest diff. peak and hole	0.386 and -0.290 $e.Å^{-3}$	

Derivative **5a**

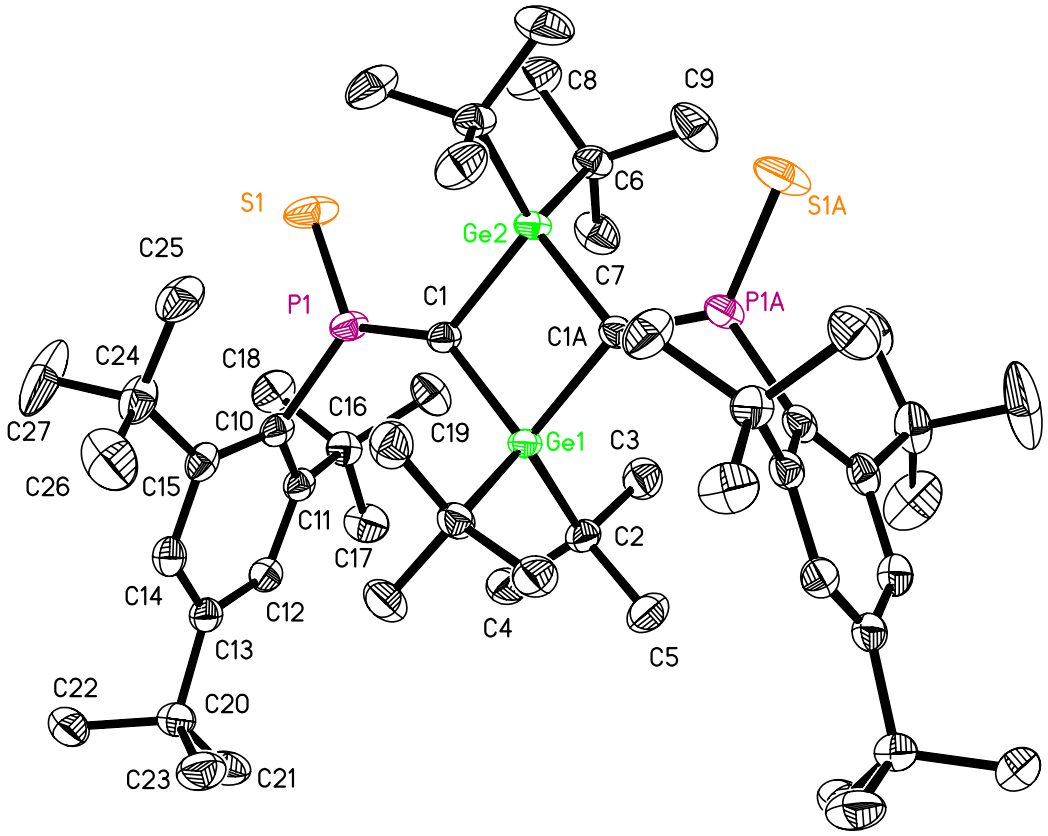
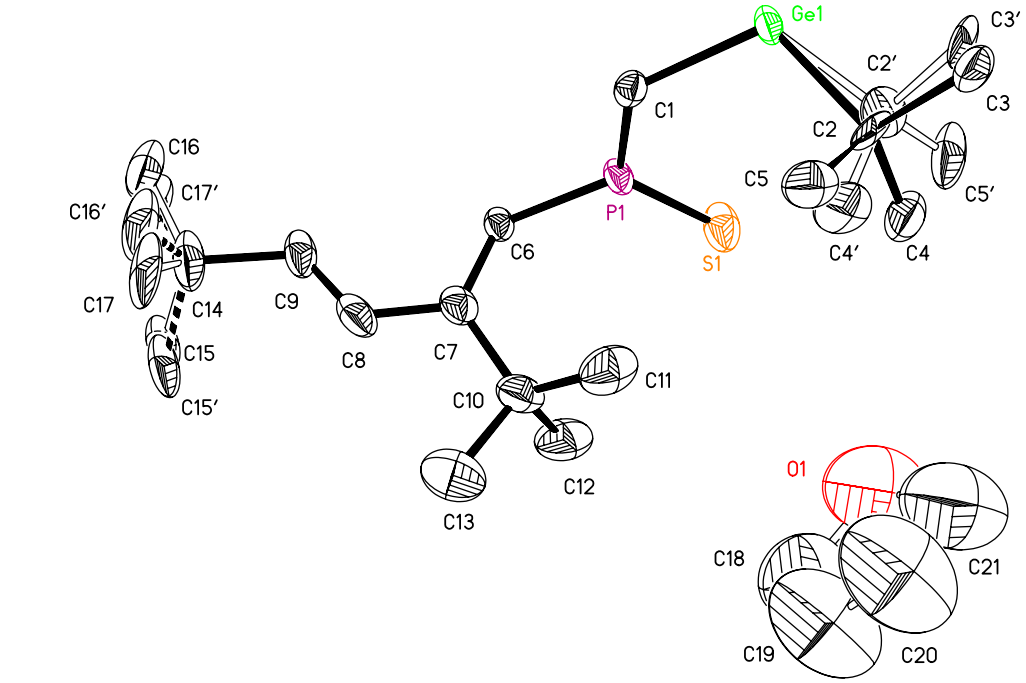


Table 1. Crystal data and structure refinement for **5a**.

Identification code	**5a**	
Empirical formula	C54 H94 Ge2 P2 S2	
Formula weight	1014.53	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 33.160(3) Å	α= 90°.
	b = 11.3364(10) Å	β= 118.224(2)°.
	c = 17.1891(15) Å	γ = 90°.
Volume	5693.4(9) $Å^3$	
Z	4	
Density (calculated)	1.184 Mg/m^3	
Absorption coefficient	1.217 mm^{-1}	
F(000)	2176	
Crystal size	0.1 x 0.2 x 0.2 mm^3	
Theta range for data collection	2.15 to 26.40°.	
Index ranges	-39<=h<=38, -14<=k<=7, -17<=l<=21	
Reflections collected	13514	
Independent reflections	5717 [R(int) = 0.0227]	
Completeness to theta = 26.40°	97.8 %	
Absorption correction	Semi-empirical	
Max. and min. transmission	1.000000 and 0.731643	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5717 / 0 / 287	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2sigma(I)]	R1 = 0.0290, wR2 = 0.0715	
R indices (all data)	R1 = 0.0394, wR2 = 0.0768	
Largest diff. peak and hole	0.636 and -0.269 $e.Å^{-3}$	

Derivative **5b**



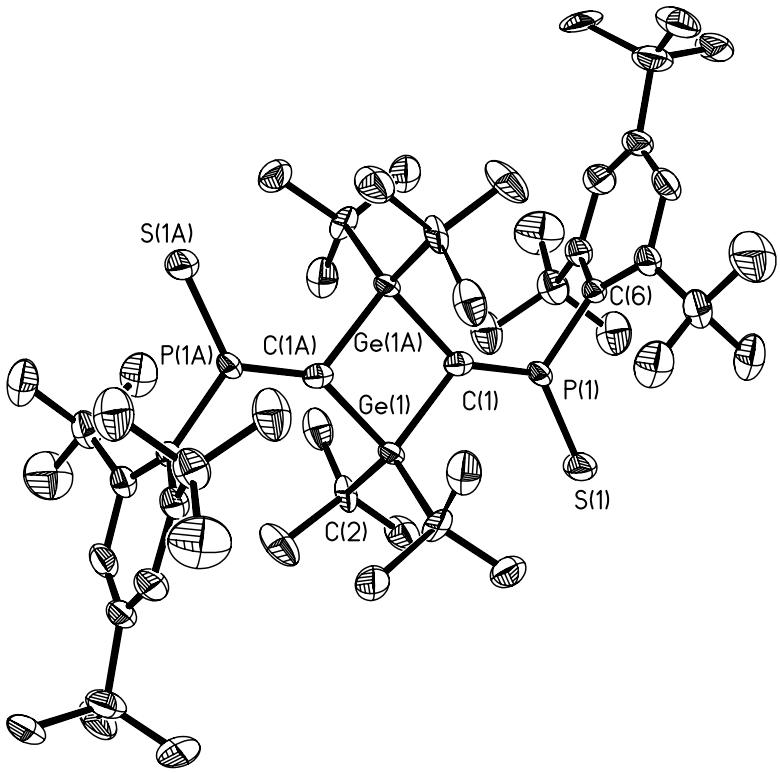
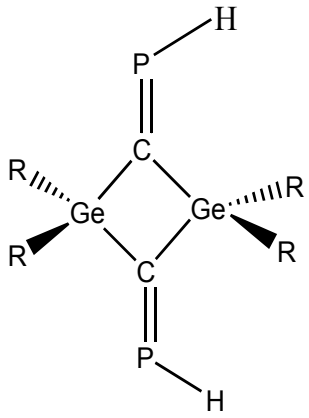


Table 1. Crystal data and structure refinement for **5b**.

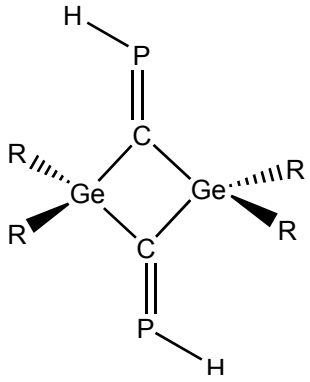
Identification code	**5b**	
Empirical formula	C62 H110 Ge2 O2 P2 S2	
Formula weight	1158.74	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Ibam	
Unit cell dimensions	a = 20.440(3) Å	α= 90°.
	b = 16.670(2) Å	β= 90°.
	c = 19.133(3) Å	γ = 90°.
Volume	6519.2(15) $Å^3$	
Z	4	
Density (calculated)	1.181 Mg/m^3	
Absorption coefficient	1.073 mm^{-1}	
F(000)	2496	
Crystal size	0.1 x 0.1 x 0.5 mm^3	
Theta range for data collection	5.11 to 23.53°.	
Index ranges	-22<=h<=22, -18<=k<=18, -14<=l<=21	
Reflections collected	14548	
Independent reflections	2491 [R(int) = 0.1131]	
Completeness to theta = 23.53°	98.8 %	
Absorption correction	Semi-empirical	
Max. and min. transmission	1.000000 and 0.617438	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2491 / 260 / 273	
Goodness-of-fit on F^2	1.049	
Final R indices [I>2sigma(I)]	R1 = 0.0504, wR2 = 0.1037	
R indices (all data)	R1 = 0.0940, wR2 = 0.1217	
Largest diff. peak and hole	0.492 and -0.710 $e.Å^{-3}$	

S2

Table S2-1
B3LYP/6-31G(d) calculated* energies of model **3** systems.



3a



3b

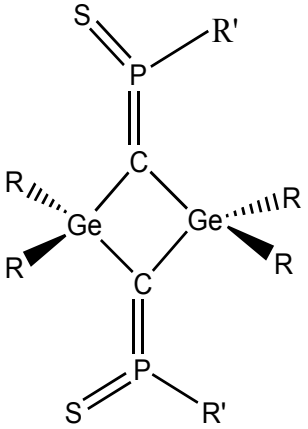
R	E **3a** (a.u.)	ZPE (kcal. mol^{-1})	E **3a** (a.u.) (corrected)	E **3b** (a.u.)	ZPE (kcal. mol^{-1})	E **3b** (a.u.) (corrected)	Relative energy of **3a** (kcal. mol^{-1})
H	-4915.9629454	44.13	-4915.8926198	-4915.9629869	44.15	-4915.8926294	+0.01
Me	-5073.2640401	122.79	-5073.0683618	-5073.2643163	122.87	-5073.0685105	+0.09
t-Bu*	-5544. 9853568			-5544. 989180			+2.40

[a)]Since the ZPE corrections are very similar for the two isomers, they cancel out in the relative energy values.
*Calculations have been carried out by using Spartan 04 [1]

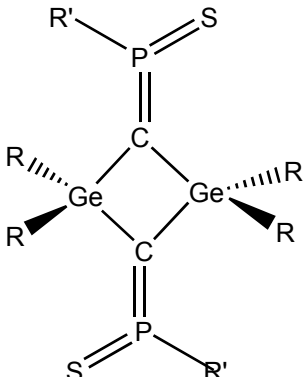
1) Wavefunction Inc. 18401 Von Karman Avenue, Suite 370 Irvine, CA 92612.

Table S2-2

B3LYP/6-31G(d) calculated energies of model **5** systems



5a



5b

R,R'	E **5a** cis (a.u.)	E **5b** trans (a.u.)	Relative energy of **5a** (kcal.mol^{-1})
H, H	-5712.3755840	-5712.3760836	+0.31
Me, H	-5869.6809540	-5869.6816550	+0.43
t-Bu, H	-6341.4016265	-6341.4026985	+0.67
Me, Ph	-6331.8034295	-6331.8050588	+1.02
Me, Mes	-6567.7062809	-6567.7070221	+0.47
t-Bu, Mes	-7039.4089528	-7039.4104373	+0.93