

Synthesis and solid state structures of tri-*t*-butyl-cyclopropenyl derivatives of main group elements: Cyp**M*Ph₃ (M = Si, Ge, Sn)

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Abstract

The reaction of Ph₃MLi (M = Si, Ge, and Sn) with tri-*t*-butylcyclopropenium tetrafluoroborate (Cyp*BF₄⁻) gives the cyclopropenyl compounds Cyp**M*Ph₃ as air and moisture stable solids in 11%, 74%, and 77% yields, respectively. Attempts to prepare Cyp*PbPh₃ by this method were unsuccessful. The X-ray crystal structures of all three of these compounds were obtained. The M–C(Cyp*) bond distances increase with the order: Sn–C (2.19 Å) > Ge–C (2.00 Å) > Si–C (1.91 Å). A high degree of steric strain is evidenced for the silicon derivative which forms an exocyclic bond angle (Si–C(Cyp*)–C(*t*Bu)) of 121.6°. The high degree of steric strain for the silicon analog is believed to be responsible for the low yields for its synthesis.

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Keywords: Cyclopropene; Silane; Germane; Stannane; Synthesis; Crystal structure

1. Introduction

3-Cyclopropenyl derivatives of silicon are fruitful sources for a variety of organic and organosilicon reactive intermediates. Fluorodesilylation of cyclopropenylsilanes have proven to be efficient sources of elusive antiaromatic cyclopropenyl anions in both gas phase [1] and solution [2]. Some 3-cyclopropenyl polysilanes are photochemical precursors to novel organosilicon reactive intermediates including both cyclopropenylsilylenes [3] and their isomeric silacyclobutadienes [4]. Recently, the tri-*t*-butyl cyclopropenyl group has been utilized for the synthesis of lattice-framework disilenes [5].

Cyclopropenyl derivatives of main group metals and metalloids, however, are relatively rare. Of the Group 14 elements, only a handful of 3-cyclopropenylsilanes and germanes have been prepared and characterized. One synthetic route involves the addition of α -silyl and α -germyl carbenes to alkynes [6]. An alternative approach is the

addition of polysilyllithium reagents to stable cyclopropenium cations. Several polysilyl-3-cyclopropenes have been previously prepared in our laboratories by the reaction of tri-*t*-butylcyclopropenium cation (Cyp*) with polysilyl lithium reagents [7].

The extension of this synthetic method to other group 14 elements is of interest. In this study, the reactions of tri-*t*-butyl cyclopropenium cation with the organometallic anions, Ph₃MLi (M = Si, Ge, Sn, and Pb) was examined [8]. Except for the case of Pb, good yields of the cyclopropenyl compounds Cyp**M*Ph₃ were obtained. The new compounds were spectroscopically and crystallographically characterized. The X-ray structures are the first reported for cyclopropenyl germanes and stannanes.

2. Results and discussion

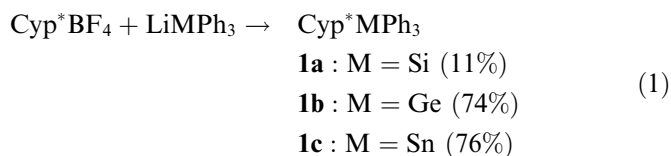
2.1. Preparation of Cyp**M*Ph₃ (M = Si, Ge, and Sn)

The compounds, Cyp**M*Ph₃ (M = Si (**1a**), Ge (**1b**), Sn(**1c**)), were synthesized by the reaction of tri-*t*-butylcyclopropenyl tetrafluoroborate with the corresponding

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lithium reagents LiMPh_3 ($M = \text{Si, Ge, and Sn}$), Eq. (1). The lithium reagents were prepared by the reaction of lithium wire in THF with chlorotriphenylsilane, bromotriphenylgermane, and chlorotriphenylstannane, respectively.



The highly colored lithium reagents were added to hexane suspensions of the cyclopropenium salt at 0°C , and then allowed to stir at room temperature for 8 h. The intense colors of the reaction mixtures faded over the course of the reaction and lithium tetrafluoroborate precipitated from solution. Removal of the solvent, followed by extraction with dry hexane, gave a crude product which was purified by column chromatography. Compounds **1a–c** are white crystalline solids stable to air and moisture and were easily recrystallized in hexane solutions. The very low yield of the silicon derivative (**1a**) compared to the germanium and tin analogs is attributed to steric congestion about the relatively short Si–C bond of this compound.

2.2. Attempted preparation of $\text{Cyp}^*\text{PbPh}_3$

Triphenylplumbyllithium was prepared by three different routes: from the reaction of hexaphenyldiplumbane with lithium metal [9], from the reaction of phenyl lithium with lead (II) chloride [10], and from the reaction of hexaphenyldiplumbane with phenyl lithium [11]. In each case, the darkly colored plumbyl lithium was not discharged upon addition to tri-*t*-butylcyclopropenium ion. No evidence for the expected plumbylcyclopropene was found.

2.3. Spectroscopic properties of Cyp^*MPh_3

The ^1H and ^{13}C NMR spectra of **1a–c** are similar and totally consistent with a classical σ bonded cyclopropene ring system with two distinct *t*-butyl groups in 2:1 ratio. The olefinic cyclopropene ring resonances in the ^{13}C spectrum appear at approximately 128 ppm for all three compounds. The chemical shift of the allylic ring carbon is somewhat sensitive to the attached metal atom, moving downfield as one proceeds from silicon to tin: Si (37.8 ppm), Ge (42.3 ppm), and Sn (47.8 ppm). The chemical shift of the *ipso* carbon of the phenyl group also moves noticeably downfield, from Si (138.0 ppm) to Ge (140.7 ppm) to Sn (143.2 ppm). A similar trend has been found for the ^{13}C NMR chemical shifts of MPh_4 ($M = \text{Si, Ge, Sn}$) derivatives [12].

No discernable parent ions were observed for **1a–c** in the EI (70 eV) mass spectra of these compounds. The highest observed masses were either M^+-CH_3 or $\text{M}^+-t\text{-Bu}$ and even these masses had relatively weak intensities. The strong base peak in all these spectra was at 207 amu which

corresponds to the aromatic tri-*t*-butyl cyclopropenium cation. Other prominent mass peaks correspond to Ph_3M^+ and *t*-Bu (57 amu). The IR spectrum shows a characteristic weak C=C stretching vibration for the cyclopropene ring between 1816 and 1824 cm^{-1} [13].

2.4. X-ray crystal structures

Compounds **1a–c** crystallize as two independent molecules occupying general positions in the monoclinic space groups $P2_1/n$ (Si and Ge) and $P2_1/c$ (Sn). Figs. 1–3 show the ORTEP diagrams of one independent molecule for each compound. Relevant structural parameters are given in Table 1.

In comparing all three structures, the most dramatic differences in metrical parameters occur about the central metal(loid). The cyclopropenyl-metal(loid) distances increase from 1.91 Å (Si), 2.00 Å (Ge) to 2.19 Å (Sn). Similarly, phenyl-metal(loid) distances increase progressively from 1.90 Å (Si), 1.98 Å (Ge) to 2.15 Å (Sn). The observed trends reflect the increasing covalent radius in going from silicon to tin.

The bond distances and angles of the cyclopropene rings are very similar for all compounds. The silicon derivative **1a** shows a very slightly elongated cyclopropenyl C–C bond and a slightly contracted cyclopropenyl C=C bond relative to the germanium and tin analogs. This effect may be due to an increased steric compression of the SiPh_3 group with the Cyp^* ring. A more pronounced measure of this steric congestion is the exocyclic bond angle, M–C(1)–C(4), which reflects the geminal interaction of the MPh_3 group and the allylic *t*-butyl substituent. This angle is greatest for $M = \text{Si}$ (121.6(2), avg.), followed progressively by $M = \text{Ge}$ (119.1(3), avg.) and $M = \text{Sn}$ (115.9(2), avg.). The steric strain along the Si–C bond in **1a** as manifested by these solid state structural

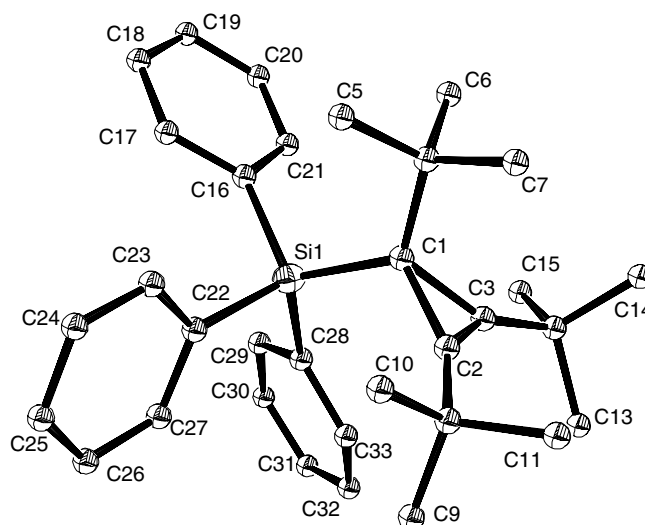


Fig. 1. ORTEP drawing of one independent molecule of **1a**. Thermal ellipsoids are at the 50% probability level.

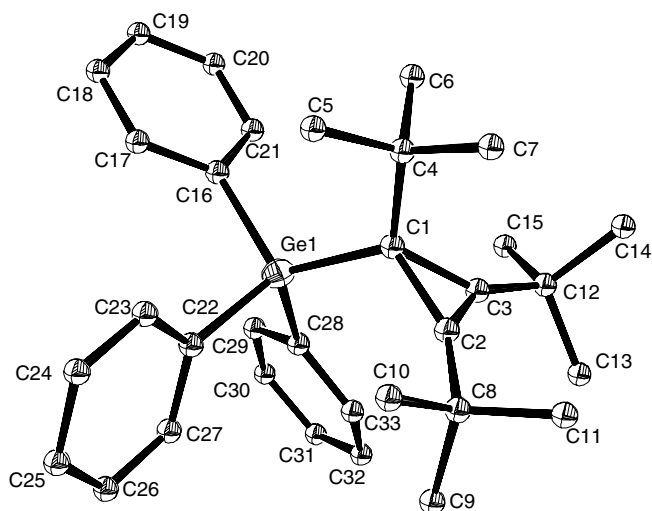


Fig. 2. ORTEP drawing of one independent molecule of **1b**. Thermal ellipsoids are at the 50% probability level.

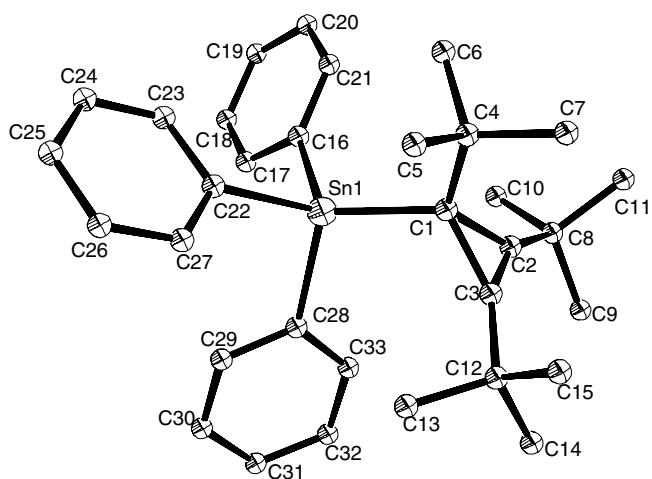


Fig. 3. ORTEP drawing of one independent molecule of **1c**. Thermal ellipsoids are at the 50% probability level.

parameters is most likely responsible for the low yields for the synthesis of **1a** as compared to the less strained germanium and tin analogs.

3. Conclusion

Highly hindered tri-*t*-butylcyclopropenyl derivatives of silicon, germanium, and tin have been prepared by the reaction of the tri-*t*-butylcyclopropenium ion directly with the corresponding triphenylmetal lithium derivatives. The lower yield of the silicon derivative is attributed to a high degree of strain along the Si-Cyp* bond relative to the germanium and tin derivatives. The strain is evident in structural distortions of the cyclopropenyl ring system. The failure of the reaction to yield the corresponding lead derivative may result from the weakness of the lead carbon bond. The generality of this technique to other main

group cyclopropenyl derivatives is currently being investigated.

4. Experimental details

All operations involving synthesis were performed under a blanket of argon and Schlenk techniques were used as required. All glassware was oven dried at 150 °C before use. Reagents were purchased from either Aldrich or Ventron and used without further purification. Tetrahydrofuran was distilled over sodium-benzophenone prior to use. Hexane and benzene were distilled over CaH₂ prior to use. The synthesis of tri-*t*-butylcyclopropenium tetrafluoroborate has been previously described [14].

All NMR spectra were recorded on a GE Omega 400 MHz spectrometer. Chemical shifts are given in ppm on the scale relative to tetramethylsilane as a reference. Carbon multiplicities and assignments in the ¹³C NMR spectra were determined using standard DEPT and HETCOR techniques. Mass spectra were obtained on a HP 5890 series GC-MS instrument in EI mode (70 eV). Infrared spectra were recorded on a Perkin-Elmer FT-IR spectrometer. Elemental analysis was performed by Galbraith Lab. Inc., Knoxville, TN. Melting points are uncorrected.

4.1. Synthesis of 3-triphenylsilyl-1,2,3-tri-*t*-butylcyclopropene (**1a**)

Chlorotriphenylsilane (2.3 g, 7.5 mmol) and finely cut lithium wire (0.21 g, 30. mmol) were placed into an argon-filled 50 mL two-neck round bottom flask. Dry THF (20 mL) was then transferred to the flask and the contents stirred with a magnetic stirrer at room temperature. After 10–30 min, a white precipitate formed and, after 40 min, the solution color changed to dark brown. The reaction was continued for another 4 h at room temperature and the resultant solution cannulated to an argon-filled 100 mL flask containing tri-*t*-butylcyclopropenium tetrafluoroborate (1.47 g, 5.00 mmol) in 50 mL of dry hexane at 0 °C. After 30 min, the color changed from black to pale brown. The reaction was continued overnight at room temperature, during which the solution color changed to pale yellow. The solvent was then removed by rotary evaporation and the residue extracted with dry hexane. After removal of the hexane by rotary evaporation, the resulting white solid was purified on a silica gel column using pure hexane as an eluent. The product was obtained as a white crystalline solid (0.25 g, 11% yield) and recrystallized in hexane. M.p. 153–155 °C. ¹H NMR (δ, CDCl₃): 0.98 (s, 9H), 1.13 (s, 18H), 7.69 (m, 6H), 7.34 (m, 9H). ¹³C NMR (δ, CDCl₃): 30.90 (CH₃, *t*-Bu), 31.58 (CH₃, *t*-Bu), 32.02 (q, *t*-Bu), 34.42 (q, *t*-Bu), 37.78 (q, allylic, Cyp*), 124.75 (CH, Ph), 127.11 (CH, Ph), 128.75 (q, C=C, Cyp*), 137.86 (CH, Ph), 137.99 (q, Ph). MS (m/e, rel intensity): 409 (M⁺ *t*-Bu, 32.5), 259 (Ph₃Si⁺, 67.6), 207 (Cyp*, 100%), 181(34.2%), 154(17.8%), 105(PhSi⁺, 24.2%), 77 (Ph⁺, 11.3), 57 (*t*-Bu, 85%). IR (KBr, cm⁻¹): 3054(m),

Table 1
Comparison of relevant structural parameters for **1a–c**

	Si (1a)	Ge (1b)	Sn (1c)
<i>Bond lengths</i>			
M–C(1)	1.909 (3)	1.995 (4)	2.193 (3)
	1.908 (3)	2.001 (5)	2.196 (3)
M–Ph	1.901 (3)	1.978 (5)	2.157 (3)
	1.900 (3)	1.977 (5)	2.154 (3)
C(1)–C(4)	1.566 (3)	1.563 (6)	1.562 (5)
	1.571 (4)	1.558 (6)	1.543 (4)
C(1)–C(2)	1.555 (3)	1.529 (6)	1.521 (4)
	1.550 (4)	1.526 (6)	1.526 (4)
C(1)–C(3)	1.554 (4)	1.540 (6)	1.523 (4)
	1.548 (4)	1.536 (6)	1.527 (4)
C(2)–C(3)	1.291 (4)	1.295 (6)	1.295 (5)
	1.291 (4)	1.285 (6)	1.298 (5)
<i>Bond angles</i>			
M–C(1)–C(4)	121.2 (2)	118.6 (3)	115.4 (2)
	122.0 (2)	119.5 (3)	116.4 (2)
M–C(1)–C(2)	115.0 (2)	115.7 (3)	115.7 (2)
	113.5 (2)	114.3 (3)	114.8 (2)
M–C(1)–C(3)	116.7 (2)	117.5 (3)	116.5 (2)
	116.3 (2)	116.6 (3)	116.3 (2)
C(2)–C(1)–C(3)	49.1 (2)	49.9 (3)	50.3 (2)
	49.2 (2)	49.6 (3)	50.3 (2)
C(1)–C(2)–C(3)	65.4 (2)	65.5 (3)	64.9 (2)
	65.3 (2)	65.6 (3)	64.8 (2)
C(1)–C(3)–C(2)	65.5 (2)	64.6 (3)	64.7 (2)
	65.4 (2)	64.8 (3)	64.9 (2)

Bond lengths are in angstroms; bond angles are in degrees. Metrical parameters are given for both independent molecules in the unit cell.

2961(vs), 1824(w), 1472(s), 1425(m), 1384(m), 1358(m), 1094(s), 737(m), 696(vs), 515(vs). Exact mass for (M^+ – CH_3 , $C_{32}H_{39}Si$). Calcd. 451.2821050 Found. 451.282410 Anal. Calc. for $C_{33}H_{42}Si$: C, 84.89; H, 9.09. Found: C, 84.31; H, 9.25%.

4.2. Synthesis of 3-triphenylgermyl-1,2,3-tri-*t*-butylcyclopropene (**1b**)

In a similar procedure to the preparation of **1a**, 0.245 g (35.3 mmol) of finely cut lithium wire was reacted with 2.9 g (7.5 mmol) of bromotriphenylgermane in dry THF at room temperature. After 3 h, a white precipitate formed and the solution changed to a deep yellow color. After 6 h, the triphenylgermanium lithium reagent was added to 1.47 g (5.00 mmol) of tri-*t*-butylcyclopropenium tetrafluoroborate in 50 mL dry hexane at 0 °C. Over a period of 30 min, the color changed from yellow to pale yellow. The solution was then stirred overnight at room temperature, after which, the solution became a lighter yellow. Column chromatography over silica gel, using hexane as an eluent, yielded 1.9 g (74% yield) of the product as a white solid. M.p. 102–103 °C. 1H NMR (δ , $CDCl_3$): 1.07 (s, 9H), 1.18 ppm (s, 18H), 7.68 (m, 6H), 7.37 (m, 9H). ^{13}C NMR (δ , $CDCl_3$) 30.77 (CH_3 , *t*-Bu), 31.50 (CH_3 , *t*-Bu), 31.64 (q, *t*-Bu), 38.69 (q, *t*-Bu), 42.33 (q, allylic, Cyp*), 127.62 (CH, Ph), 127.33 (CH, Ph), 128.15 (q, C=C, Cyp*),

136.78 (CH, Ph), 140.66 (q, Ph). MS (m/e, rel intensity): 455 (M^+ –*t*-Bu, 2.3%) 305 (Ph_3Ge^+ , 20%), 207 (Cyp*, 100%), 154 (11.7%), 150 (17.8%), 148 (13.9%), 146 (10.1%), 77 (Ph^+ , 13.4%), 57 (*t*-Bu, 83.2%) Exact mass for (M^+ – CH_3 , $C_{32}H_{39}Ge$). Calcd. 497.2263554 Found. 497.226471 IR (KBr, cm^{-1}): 3043(s), 2961(vs), 2868(s), 1818(w), 1472(s), 1425(s), 1384(s), 1218(s), 1192(s), 1078(s), 1022(m), 732(vs), 696(vs), 665(vs). Anal. Calc. for $C_{33}H_{42}Ge$: C, 77.50; H, 8.30. Found: C, 76.99; H, 8.50%.

4.3. Synthesis of 3-triphenylstannyl-1,2,3-tri-*t*-butylcyclopropene (**1c**)

In a similar procedure to the preparation of **1a**, 0.052 g (75 mmol) of finely cut lithium wire was reacted with 5.78 g (15.0 mmol) of chlorotriphenylstannane in dry THF at room temperature. After 3 h, a white precipitate formed and the solution changed to a deep olive green color. After 6 h, the triphenyltin lithium reagent was added to 2.94 g (10 mmol) of tri-*t*-butylcyclopropenium tetrafluoroborate in 50 mL dry hexane at 0 °C. After 1 h, the solution changed from green to light green. The solution was stirred overnight at room temperature which resulted in a pale yellow solution. Column chromatography over silica gel, using hexane as an eluent, yielded 4.27 g (76.6% yield) of the product as a white solid. M.p. 114–115 °C. 1H NMR (δ , $CDCl_3$): 1.05 (s, 9H), 1.25 (s, 18H), 7.63 (m, 6H), 7.37 (m, 9H). ^{13}C NMR (δ , $CDCl_3$) 30.42 (CH_3 , *t*-Bu), 31.02 (CH_3 , *t*-Bu), 31.48 (q, *t*-Bu), 39.09 (q, *t*-Bu), 47.75 (q, allylic, Cyp*), 127.90 (q, C=C, Cyp*), 130.28 (CH, Ph), 137.62 (CH, Ph), 137.78 (CH, Ph), 143.21 (q, Ph). MS (m/e, rel inten): 501 (M^+ –*t*-Bu), 351(Ph_3Sn^+ , 11.1%), 207 (Cyp*, 100%), 196 ($PhSn^+$, 19.3%), 194(14.2%), 119(Sn^+ , 11.8), 77 (Ph, 13.9), 57 (*t*-Bu, 85.7%) CI–MS (CH_4): Exact Mass for (M^+ –1, $C_{33}H_{41}^{120}Sn$). Calcd. 557.2230256 Found. 557.222900 IR (KBr, cm^{-1}) 3060(m), 2096(s), 1816(m), 1466(s), 1425(w), 1384(m), 1358(m), 1250 (m), 1212(s), 1199(vs), 1006(s), 877(m), 727(vs), 696(vs). Anal. Calc. for $C_{33}H_{42}Sn$: C, 71.09; H, 7.61. Found: C, 70.78; H, 7.68%.

4.4. Attempted synthesis of 3-triphenylplumbyl-1,2,3-tri-*t*-butylcyclopropene

4.4.1. Method A

Lithium wire, 0.112 g (16.1 mmol), was cut into small pieces, washed in dry hexane, and wiped dry. The dry lithium was quickly placed in 30 mL of dry THF under a constant flow of N_2 . A solution containing 1.78 g (2.03 mmol) of hexaphenyldiplumbane in 20 mL dry THF was added dropwise to the lithium suspension at 0 °C over a 1 h period. Sonication of the mixture with an ultrasonic bath for 2 h resulted in the formation of a dark green solution of Ph_3PbLi . This solution was cannulated to a nitrogen filled 100 mL round bottom flask containing 1.23 g (4.20 mmol) of tri-*t*-butylcyclopropenium tetrafluoroborate in 30 mL of

dry hexane at 0 °C. After 1 h, the mixture was allowed to warm to room temperature. Solvent was removed and the solid was extracted with dry hexane. No significant soluble materials were obtained.

4.4.2. Method B

A fine powder of PbCl₂, 1.39 g (5.00 mmol), was suspended in 10 mL dry ether in a 100 mL round bottom flask and chilled to –10 °C. A solution of PhLi (8.3 mL, 15.0 mmol) in 15 mL of dry ether was added via an addition funnel over an 80 min period. This solution was cannulated to a nitrogen-filled 100 mL round bottom flask containing 1.47 g (5 mmol) of tri-*t*-butylcyclopropenium tetrafluoroborate in 30 mL of dry hexane. The solution was chilled by a salt-ice bath and, after 1 h, the mixture was allowed to warm to room temperature. Solvent was removed and the solid was extracted with dry hexane. No significant soluble materials were obtained.

4.4.3. Method C

A solution of PhLi (0.45 mL, 0.80 mmol) was added to a 50 mL round bottom flask containing 0.911 g (1.04 mmol) of Ph₃PbPbPh₃ in 30 mL of dry THF. The solution was stirred at room temperature for 2 h in which time the color of the solution changed to yellow and a precipitate, identified as Ph₄Pb, had formed. This solution was cannulated to a nitrogen-filled 100 mL round bottom flask containing 0.235 g (0.800 mmol) of tri-*t*-butylcyclopropenium tetrafluoroborate in 10 mL of dry hexane at 0 °C. After 1 h, the mixture was allowed to warm to room temperature. Solvent was removed and the solid was extracted with dry hexane. No significant soluble materials were obtained.

4.5. X-ray structure determinations: general data

Diffraction crystals of **1a–c** were obtained by slow evaporation of hexane solutions at room temperature. Data collection and refinement parameters are summarized in Table 2. General procedures for crystal alignment, unit cell determination and refinement and collection of intensity data have been published [15].

4.6. X-ray crystal structure determination of **1a**

A large crystal mass, obtained by slow evaporation of a hexane solution of the compound at –30 °C was cleaved to give a suitably sized fragment which was mounted on a thin glass fiber with epoxy cement.

4.7. X-ray crystal structure determination of **1b**

A large, well-formed crystal, obtained by the slow evaporation of a hexane solution of the compound at –30 °C, was cut to size and mounted on a thin glass fiber with epoxy cement.

Table 2
Experimental crystallographic data for Cyp*MPH₃

	Si (1a)	Ge (1b)	Sn (1c)
Formula	C ₃₃ H ₄₂ Si	C ₃₃ H ₄₂ Ge	C ₃₃ H ₄₂ Sn
Molecular weight	466.76	511.26	557.36
Crystal dimensions (mm)	0.59 × 0.40 × 0.40	0.36 × 0.33 × 0.26	0.40 × 0.33 × 0.26
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>Cell dimensions</i>			
<i>a</i> (Å)	17.7823(14)	17.801(2)	32.497(2)
<i>b</i> (Å)	18.663(2)	18.7034(11)	9.6831(8)
<i>c</i> (Å)	18.4905(13)	18.616(2)	19.6470(13)
α (°)	90	90	90
β (°)	109.549(6)	109.271(9)	107.234(6)
γ (°)	90	90	90
<i>V</i> (Å ³)	5782.7(9)	5850.6(8)	5904.8(7)
<i>Z</i>	8	8	8
ρ (calcd) (g cm ³)	1.072	1.161	1.254
Radiation	($\lambda = 0.71073$)	($\lambda = 0.71073$)	($\lambda = 0.71073$)
Mo K α (Å)			
θ Range (°)	1.60–25.11	1.59–25.12	1.97–25.09
Scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
Total data collected	10,655	10,771	10,835
Unique data	10,301	10,417	10,488
Observed data with $I_0 > 2\sigma I$	5193	4882	5976
μ (cm ^{–1})	0.099	1.065	0.883
Transmission coefficient	na	0.5221–0.6364	0.5500–0.6963
<i>F</i> (000)	2032	2176	2320
<i>R</i>	0.0464	0.0465	0.0296
<i>R</i> _w	0.1062	0.0909	0.0778

na – Not applicable, no empirical absorption corrections were made.

4.8. X-ray crystal structure determination of **1c**

A large crystal mass, obtained by slow evaporation of a hexane solution of the compound at –30 °C was cleaved to give a suitably sized fragment which was mounted on a thin glass fiber with epoxy cement.

5. Supplementary materials

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 289235, 289236, and 289237 for compounds **1b**, **1a**, and **1c**, respectively. Copies of this information may be obtained free of charge The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; email: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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