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Preferential carbene insertion into Ge–H vs. other heavier group 14 hydrides via samarium carbenoids[†]

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The relative reactivities of Zn, Al, and Sm carbenoids in the chemoselective carbene insertion reaction of heavier group 14 hydrides were studied. By variation of the reaction protocols using Sm carbenoids, insertion reaction can favour the Ge–H bonds to give Ge-alkylated derivatives in good to high yield.

Metal carbenoid insertion into heteroatom-hydrogen bonds is a well-established process that surprisingly has not yet found widespread application in organic synthesis.¹ Although excellent yields can be obtained from carbenoid insertion into Si-H bonds,² chemoselective carbene insertions into group 14 hydrides have not been reported. This lack of attention is surprising because many protocols and reagents have been developed for catalytic enantioselective metal carbene insertion into Si-H bonds.³ Samarium carbenoids are generated from Sm or SmI₂ and gem-dihaloalkanes under mild conditions.⁴ Among the various metal carbenoids, samarium carbenoids exhibit unique reactive properties. Their notable uses include the chemoselective Simmons–Smith cyclopropanation,⁵ methylene insertions into B-H or C-H bonds,6,7 and several rearrangement reactions.⁸ However, the reactivity of samarium carbenoids toward heavier group 14 hydrides has not been reported. Here, we describe chemoselective carbene insertion into heavier group 14 hydrides. We found that the samarium carbenoids undergo extremely preferential carbene insertion into hydrogermanes over hydrosilanes and hydrostannanes.

Initially, we compared the reactivities of Zn, Al, and Sm carbenoids toward methylene insertion into triphenylsilane, triphenylgermane, and triphenylstannane as model reactions.⁹ As shown in Scheme 1, an equimolar solution of the heavier group 14 hydrides was treated with 4 equiv. of Zn, Al, and Sm carbenoids prepared *in situ*. The reaction was monitored by GC-MS and quenched with H₂O once one of the starting materials had disappeared. The Zn and Al carbenoids led to poor selectivity in the methylene insertion reaction.^{10–12} In contrast, the samarium carbenoid was found to attack

Ph		Ph		Ph		
Ph−Śi−H	+	Ph-Ge-F	1 +	Ph-Sn-H		
Ρ́h		Ρ'n		Ρ́h		
1.0 mmol		1.0 mmo	I	1.0 mmol		
M (4.0 CH ₂ XI (4	mmol) 1.0 mm	→ Ph- ol)	Ph ·Śi−CH₃ Ph	Ph + Ph-Ge-CH ₃ Ph	Ph + Ph-Sn-CH₃ Ph	
			1	2	3	
M = Zn, X = I: ether, reflux: ^a				1 / 2 / 3 = 4	1 / 2 / 3 = 47 / 53 / 0	
M = Et ₂ Zn, X = I: toluene, rt: ^a				1 / 2 / 3 = 4	1 / 2 / 3 = 40 / 60 / 0	
$M = (iBu)_{3}AI, X = I: hexane-CH_{2}CI_{2}, rt:^{a}$				rt: ^a 1 / 2 / 3 =	49 / 51 / 0	
M = Sm, X = I: THF, -78 °C to rt: ^{a,b}				1 / 2 / 3 = 3	3 / 97 / 0	
M = Sm, X = Br: THF, -78 °C to rt: ^{a,b}				(2: 85% iso 1 / 2 / 3 = (2: 85% iso	blated yield) 1 / 99 / 0 blated yield)	

Scheme 1 Intermolecularly competitive methylene insertion reaction of heavier group 14 hydrides using metal carbenoids. ^{*a*}Decomposition of triphenylstannane was observed by GC-MS. ^{*b*}Almost recovery of triphenylsilane was observed by GC-MS.

triphenylgermane exclusively. Methylene insertion using the samarium carbenoid was limited to triphenylgermane with almost complete selectivity. Triphenylsilane did not react with the samarium carbenoid and was recovered quantitatively. Triphenylstannane gave a complex mixture during the transformation in the presence of the Sm carbenoid. A samarium carbenoid prepared from Sm and CH₂BrI showed a slightly better selectivity compared with that prepared from Sm and CH₂I₂, probably because the lifetime of the former samarium carbenoid was longer than that of the latter. Deuterium labeling of Sm using CD₂I₂ led to the selective incorporation of the CD₂ group into triphenylgermane (>99%D) (eqn (1)), confirming that the methylene unit inserted directly into the Ge–H bond.

$$\begin{array}{cccc} \begin{array}{c} Ph & Sm \\ (3.0 \text{ eq}) & Ph \\ Ph-Ge-H & & Ph \\ Ph & CD_2l_2 & Ph \\ (3.0 \text{ eq}) & 4 \\ & THF \\ -78 \ ^{\circ}C \text{ to rt} & 83\% \ (>99\%D) \end{array}$$

The scope and limitations of the carbene insertion methodology were examined by conducting reactions of the hydrogermanes with the samarium carbenoids.[‡] The results

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 $[\]dagger$ Electronic supplementary information (ESI) available: Compound characterization data and copies of the 1H and ^{13}C NMR spectra. See DOI: 10.1039/c1cc11256b



 Table 1
 Alkylidene insertions into the Ge–H bond via the samarium carbenoid

^{*a*} Reaction conditions: substrate (1.0 mmol), Sm (3.0 mmol), R'CHI₂ (3.0 mmol), THF (3.0 mL), -78 °C to rt. ^{*b*} GC yield. (These compounds were volatiles.) ^{*c*} Reaction conditions: substrate (1.0 mmol), Sm (3.0 mmol), R'CHI₂ (3.0 mmol), THP (3.0 mL), -40 °C to rt. ^{*d*} Reaction conditions: substrate (1.0 mmol), Sm (5.0 mmol), R'CHI₂ (5.0 mL), -78 °C to rt. ^{*e*} Reaction conditions: substrate (1.0 mmol), Sm (6.0 mmol), R'CHI₂ (6.0 mmol), THF (6.0 mL), -78 °C to rt. ^{*f*} Reaction conditions: substrate (1.0 mmol), Sm (6.0 mmol), R'CHI₂ (6.0 mmol), Sm (6.0 mmol), Sm (6.0 mmol), THF (5.0 mL), -78 °C to rt. ^{*f*} Reaction conditions: substrate (1.0 mmol), Sm (6.0 mmol), THF (6.0 mL), -78 °C to rt. ^{*f*} Reaction conditions: substrate (1.0 mmol), Sm (6.0 mmol), THF (6.0 mL), -78 °C to rt. ^{*f*} Reaction conditions: substrate (1.0 mmol), Sm (6.0 mmol), THP (6.0 mL), -40 °C to rt.

are shown in Table 1. Tri-n-butylgermane led to an alkylated product (5) in good yield. 1,1-Diiodoethane was also found to be effective and gave the ethylated product, 6, in good yield. The reaction efficiency was not hampered by the presence of a proximal phenyl moiety (7). The highly sterically hindered 2,2-dimethyl-1-propylene group was also smoothly inserted into the Ge-H bond (8). It is worth noting that the presence of amino (-NH₂) and cyano (-CN) groups on the aromatic ring of hydrogermane was tolerated under the transformation, whereas these functional groups were highly sensitive and coordinative toward organometallic reagents (9 and 10).13 The reaction of the Sm carbenoid with the secondary or primary germanes gave, respectively, doubly and triply methyleneinserted compounds (11 and 12). Neither monoalkylated (for 11 and 12) nor doubly alkylated (for 12) products were observed by GC-MS.^{14,15} In all cases, reaction of the corresponding hydrosilanes with the samarium carbenoid gave carbene-inserted products in very low yield (<5% GC yield) under the same reaction conditions.

To demonstrate the synthetic utility of this methodology, we selectively inserted a carbene into a compound containing both Si–H and Ge–H moieties in the same molecule (Fig. 1(a)).¹⁶ As expected, the Sm carbenoid exhibited complete Ge–H selectivity, and the Si–H functionality remained unaffected during the transformation (13).¹⁷ The corresponding reaction product was fully identified by the presence of hydride peaks in the ¹H NMR spectrum (Fig. 1(b)).

The relative reactivity of the samarium carbenoid with group 14 hydrides was $R_3Sn-H < R_3Si-H \ll R_3Ge-H$. This



Fig. 1 (a) Selective carbene insertion into the Ge–H bond (b) 1 H NMR (400 MHz, CDCl₃) showing the hydride region of the starting material and 13.

ordering arises from electronegativity differences among the group 14 elements (Allen values. H: 2.300, Si: 1.916, Ge: 1.994, and Sn: 1.824).¹⁸ The non-monotonic trend in electronegativity among the group 14 elements (Si–Ge–Sn) is due to incomplete screening of the 4s electrons by the 3d electron in the first transition series, which can influence the reactivity of the element. In previous work, samarium carbenoids were inserted into B–H and P–H bonds, which exhibited only weak hydride properties (electronegativity of B is 2.051, and P is 2.253).^{6,18} These results suggested that weak polarization is essential for the transformation, although the mechanistic details of this reaction remain unclear.

In summary, samarium carbenoids were shown to prefer insertion into hydrogermanes over hydrosilanes or hydrostannanes, as demonstrated in competition experiments. The synthesis is suitable for the selective alkylation of a wide range of hydrogermanes. Further investigations are in progress.

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Notes and references

‡ A typical experimental procedure for methylene insertion reaction to the Ge–H bond using a samarium carbenoid. To a mixture of Sm powder (ca. 50 mesh, 227 mg, 1.51 mmol) and triphenylgermane (154 mg, 0.504 mmol) in THF (1.5 mL) was added diiodomethane (120 μ L, 1.50 mmol) at -78 °C. After the reaction mixture was warmed to room temperature, the reaction mixture was quenched with water, extracted with CH₂Cl₂ three times, and dried over Na₂SO₄. The solvent was evaporated under a reduced pressure, and fractionated column chromatography was carried out on silica gel to afford the desired methylated product **2** as a colorless solid (139 mg, 85%).¹⁹ ¹H NMR (400 MHz, CDCl₃) δ 7.50–7.45 (m, 6H), 7.38–7.32 (m 9H), 0.90 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 138.0 (C_q), 134.5 (CH), 128.8 (CH), 128.2 (CH), -4.2 (CH₃); EI-MS *m*/z 320 (M⁺).

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