# Chromium-Mediated Stannylcyclopropanation of Alkenes with (Diiodomethyl)stannanes

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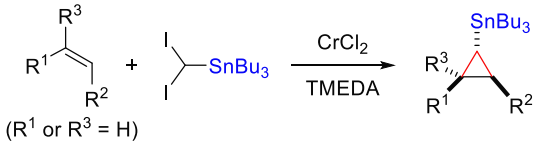
*Supporting Information*




**ABSTRACT:** A stannyl group-substituted *gem*-dichromiomethane species, generated *in-situ* from $CrCl_2$, TMEDA, and tributyl(diiodomethyl)stannane, worked as an efficient stannylcarbene equivalent to promote cyclopropanation of alkenes. The reaction provided synthetically useful stannylcyclopropanes directly from commercially available unactivated alkenes without using potentially flammable alkylzinc and diazo compounds. Structural characterization of stannyl and germyl group-substituted *gem*-dichromiomethane complexes, and effect of group 14 element containing substituents for cyclopropanation is also described.

Due to their unique electronic and steric features, cyclopropanes are key subunits in many natural products, pharmaceuticals, secondary metabolites, and functional materials.[1] The inherent ring strain also allows them to participate in various organic transformations involving ring-opening cycloadditions as indispensable synthetic building blocks.[2] However, their highly distorted structure also gives rise to many synthetic challenges for the construction and manipulation. Thus, novel and efficient approaches to suitably functionalized cyclopropyl rings using readily available chemicals is of interest for both academic studies and for the development of new pharmaceuticals.[3] Chromium-mediated cyclopropanation of olefins with functionalized diiodomethanes provides one of the most straightforward approaches toward functionalized cyclopropyl rings, and we have reported syntheses of iodo- and silylcyclopropanes in a single step from commercially available terminal alkenes.[4a-d,5] Recent our study also described the regioselective borylcyclopropanation of alkenes with (diiodomethyl)boronate ester.[4e,6] Practical factors, such as reactivity, stability, and functional group tolerance, make cyclopropylstannanes a useful synthon for the introduction of a cyclopropyl group into target molecules through stannane-lithium or stannane-halogen exchanges and Migita-Kosugi-Stille cross-coupling reaction.[7] Previous approaches to cyclopropylstannanes include Simmons-Smith cyclopropanation using alkenylstannanes or stannylcarbene species, hydrostannylation of cyclopropenes or methylenecyclopropanes, electrophilic stannylation of cyclopropylmetal reagents, Kulinkovich cyclopropanation, and cyclization of 3,3-distannylpropanols (Figure 1).[8,9] Among them, cyclopropanation of stannyl group-substituted carbenes and carbenoids with olefins is operationally simple and practical because of the availability of olefins as starting materials. However, cyclopropanation of trimethylstannylcarbene generated from (chloromethyl)trimethylstannane with LiTMP *via* α-elimination of HCl provided the corresponding stannylcyclopropanes in low yield (eq 1).[9c] Because this type of carbenoid species is generally unstable, an additional functional group is needed to stabilize the generated carbene species for practical application of the transformation (eq 2).[9a,b,d,e] We envisioned that the use of stable metalcarbenoid equivalents would overcome this limitation. The present report describes the chromium-mediated stannylcyclopropanation of olefins with tri(*n*-butyl)(diiodomethyl)stannane ($^nBu_3SnCHI_2$). Effect of stannyl substituents on the cyclopropanation was determined by comparison of reactivity of other group 14 element containing diiodomethane derivatives. Structural characterization of key intermediates, stannyl and germyl group-substituted *gem*-dichromiomethane complexes, has also provided useful insights into the reactivity of the *gem*-dichromiomethane species.[10]

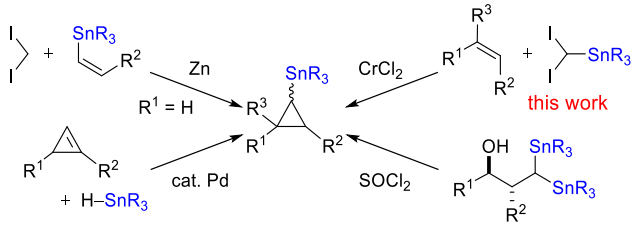
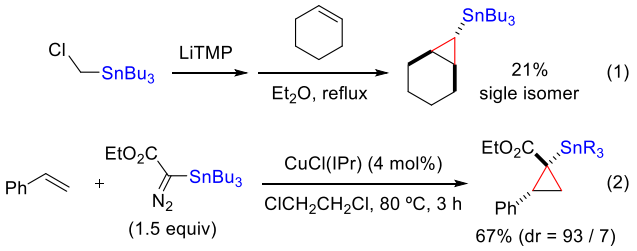



**Figure 1.** Representative approach to stannylcyclopropanes

Treatment of 1,2-dihydronaphthalene with $^nBu_3SnCHI_2$ in the presence of $CrCl_2$ and TMEDA in THF at 50 °C gave the corresponding stannylcyclopropane **1a** in 86% yield as a single diastereomer (Figure 1). A NOESY study determined that the stereochemistry of **1a** involved a stannyl group *anti* to the fused five-membered ring. This outcome was explained by the steric repulsion of the bulky tributylstannyl group and substituents on the olefins. The use of TMEDA as a ligand is crucial,




and other nitrogen- and phosphine-based mono- and bidentate ligands decreased reaction efficiency.[11] Reaction temperature was also an important factor, and the yield of **1a** was highest when the reaction was conducted at 50 °C.[12]

Scope and functional group tolerance were investigated with several di- and monosubstituted alkenes (Figure 2). In several cases, yields dropped after purification by silica gel column chromatography due to the difficulty of removing tin residues resulting from the decomposition of $^{n}Bu_3SnCHI_2$. Reaction of acenaphthylene gave the corresponding cyclopropane **1b** as a single diastereomer. Cyclopropanation of a *cis*-disubstituted olefin, (*Z*)-1-phenyl-1-propene, proceeded stereospecifically to provide **1c** in moderate yield. A strained double bond of 2-norbornene was also cyclopropanated smoothly to afford **1d** as a mixture of two stereoisomers. However, the bulkiness of the alkenes greatly decreased the reactivity, and *trans*-disubstituted olefins, such as (*E*)-1-phenyl-1-propene, gave the expected adducts in low yields (less than 10% yield). In this case, coordinating functional groups, such as an aminocarbonyl group, promoted access of the reactive chromium species, and cyclopropanation of (*E*)-*N*,*N*-diethylcinnamamide provided **1e** in 77% yield.[13] The series of monosubstituted alkenes containing alkyl and aryl groups reacted successfully to afford the corresponding stannylcyclopropanes **1f** and **1g** in good yields. Both the benzyl group in 1f as protection of the hydroxy group, and the bromo group in 1g were well-tolerated. Conjugated 1,3-dienes, including myrcene, were applicable to the reaction, and the

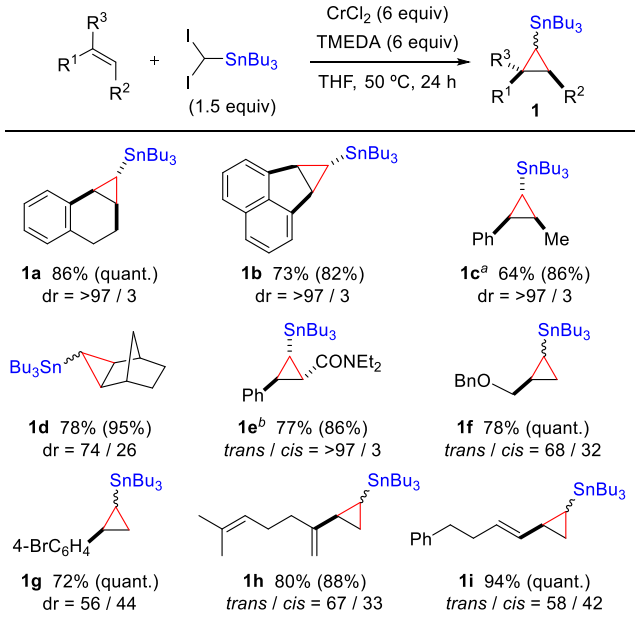
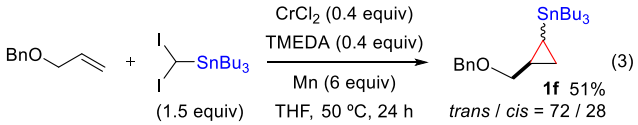


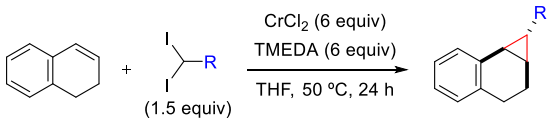

**Figure 2.** Chromium-mediated stannylcyclopropanation of olefins. Values in parentheses were yields determined by $^{1}H$ NMR of crude product. [a](*Z*)-1-Phenyl-1-propene or [b](*E*)-*N*,*N*-diethylcinnamamide were used as precursors, respectively.

terminal double bonds reacted chemoselectively to provide **1h** and **1i**. Here, the other double bond geometry of **1i** was retained during cyclopropanation. Although yield was moderate, the amount of $CrCl_2$ could be reduced to 0.4 equiv by using manganese powder to reduce $Cr(III)Cl_2I$ to regenerate $CrCl_2$ species (eq 3, see also Scheme 2).[4d,14]




To obtain insight into the effect of stannyl substituents on cyclopropanation, reactivity of $Me_3SiCHI_2$ and $Me_3GeCHI_2$containing other group 14 elements was next examined. Although previous reports indicate that the substrate scope for chromium-mediated silylcyclopropanation was limited to monosubstituted alkenes,[4b-d] 1,2-dihydronaphthalene was found to be applicable and furnished the corresponding silylcyclopropane **2a** in this study (Table 1, entry 1). The current chromium-mediated method could be also applied to germylcyclopropanation using $Me_3GeCHI_2$ (entry 2). While germylcyclopropanes are potentially important building blocks in organic synthesis, synthetic approach for them have been limited.[15] The current germylcyclopropanation provides a straightforward approach toward the synthesis of germylcyclopropanes. In contrast, the expected stannylcyclopropane was not obtained by reaction of $Me_3SnCHI_2$ (entry 3). This was unexpected because reaction of $^{n}Bu_3SnCHI_2$ gave **1a** in good yield (entry 5). Comparison of the reactivity of $^{n}Bu_3SiCHI_2$ and $^{n}Bu_3SnCHI_2$ (entry 4) along with the aforementioned results concluded that efficiency of overall cyclopropanation process increased in the order of $GeR_3 < SiR_3 << SnR_3$. *gem*-Dichromiomethane species is thought to be stabilized with the stannyl group by efficient orbital overlap.

**Table 1.** Effect of substituents on chromium-mediated cyclopropanation of 1,2-dihydronaphthalene



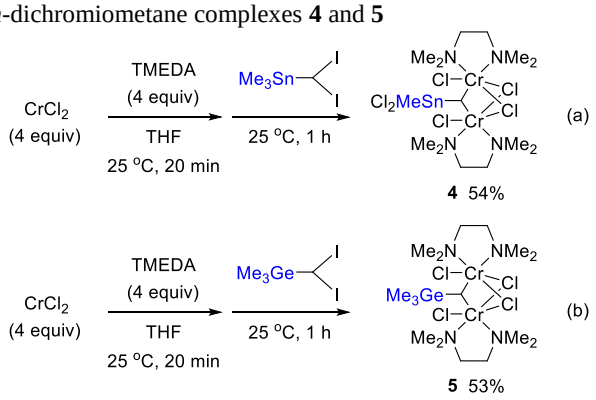

| entry | R | product | yield / % | dr |
|---|---|---|---|---|
| 1 | $SiMe_3$ | **2a** | 70 (74) | >97 / 3 |
| 2 | $GeMe_3$ | **3** | 57 (65) | >97 / 3 |
| 3 | $SnMe_3$ | — | 0 | — |
| 4 | $SiBu_3$ | **2b** | 20 (28) | >97 / 3 |
| 5 | $SnBu_3$ | **1a** | 63 (76) | >97 / 3 |

Values in parentheses were yields determined by $^{1}H$ NMR of crude mixture.

Attempted synthesis and isolation of *gem*-dichromiomethane complex by reaction of (tmeda)$CrCl_2$ with $Me_3SnCHI_2$ unexpectedly gave *gem*-dichromiomethane complex **4**, having a $SnMeCl_2$ group as a red solid (Scheme 1(a)). The structure of **4** was determined unambiguously by X-ray crystallographic analysis, and two of three Sn–Me bonds in $Me_3SnCHI_2$ reproducibly converted into Sn–Cl bonds (left of Figure 3). Because the $SnMe_3$ group remained intact in the chromium-mediated stannylalkylidenation of aldehydes without using TMEDA (eq 4),[16] conversion of a Sn–Me bond occurred in the presence of (tmeda)$CrCl_n(L)$ complex (n = 2 or 3). In contrast, the expected (tmeda)*Ge*$CH(CrCl_2)_2$ **5** (*Ge* = $GeMe_3$) was obtained from reaction with $Me_3GeCHI_2$ (Scheme

1(b), and right of Figure 3 for ORTEP drawing), and isolation of (tmeda)*Si*CH($CrCl_2$)$_2$ (*Si* = $SiMe_3$) has been also reported in our recent work.[4d] As expected by the result in Table 1, treatment of **5** with 1,2-dihydronaphthalene gave **3**, whereas the corresponding stannylcyclopropane was not obtained from reaction of **4** (eq 5).[17] These different outcomes can be explained by the higher affinity of Sn atoms for Cl atoms.[18] Coordination of a TMEDA ligand increases the electron density of a chromium center, which may promote the exchange of Sn–Me and Cr–Cl bonds to Sn–Cl and Cr–Me bond. No similar exchange reaction was observed in the reaction with $^n$Bu$_3$SnCHI$_2$, probably due to kinetic stabilization by bulky butyl groups, and cyclopropanation proceeded successfully in this case.[19]

**Scheme 1.** Synthesis of stannyl and germyl group-substituted *gem*-dichromiometane complexes **4** and **5**



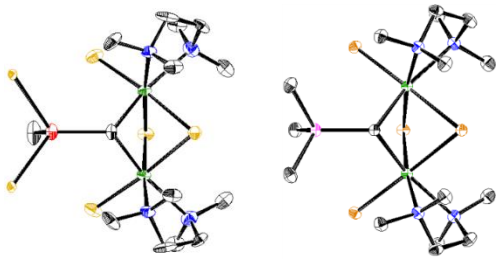
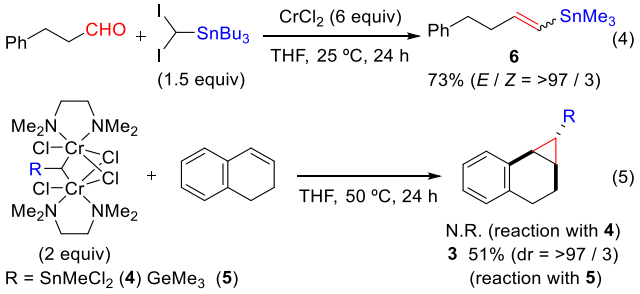
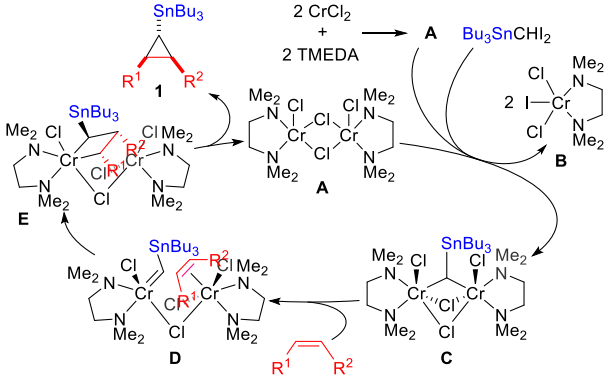



**Figure 3.** X-ray crystal structure of (tmeda)($MeCl_2Sn$)CH($CrCl_2$)$_2$ **4** (left) and (tmeda)($Me_3Ge$)CH($CrCl_2$)$_2$ **5** (right). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Green: Cr, red: Sn, pink: Ge, blue: N, yellow: Cl.




A reaction mechanism for the current stannylcyclopropanation is proposed in Scheme 2. $^n$Bu$_3$SnCHI$_2$ is initially reduced by 2 equiv of [(tmeda)$CrCl_2$]$_2$ **A**[4d] to give (tmeda)*Sn*CH($CrCl_2$)$_2$ **C** (*Sn* = Sn$^n$Bu$_3$) and (tmeda)$CrCl_2$I **B**. Coordination of olefins then induces conversion of **C** into chromocarbene intermediate **D**,[20] which then undergoes [2+2]cycloaddition to furnish chromocyclobutane **E**. Involvement of the unique structure of the chloride-bridged dinuclear chromium complex **D** was suggested by kinetic studies in the previous our related work.[4d] Subsequent reductive elimination of $Cr^{II}$ furnishes stannylcyclopropane **1** along with the regeneration of **A**. Because substitution of a relatively electron-deficient $SnMeCl_2$ group decreased the nucleophilicity of the carbene carbon in intermediate **D**, cyclopropanation with (tmeda)($MeCl_2Sn$)CH($CrCl_2$)$_2$ **4** may be suppressed in eq 5.

**Scheme 2.** Proposed reaction mechanism




In conclusion, chromium-mediated stannylcyclopropanation of olefins using readily available tributyl(diiodomethyl)stannane as a stannylcarbene equivalent was achieved. Stannylcarbene species were previously reported to be unstable, and a key for the current success might be employing it as a chromocarbene species. Importantly, heteroatom-containing coordinating functional groups, which are essential for typical Simmons-Smith cyclopropanation to promote the access of reactive carbene species, were not required, and unsaturated hydrocarbons could be directly used as substrates. A comparison of the reactivity of other group 14 element substituted diiodomethanes indicated that efficiency of overall cyclopropanation process increased in the order of Ge < Si << Sn. Structural characterization of stannyl and germyl group substituted *gem*-dichromiomethane species also provided insights into the unique reactive nature of this new family of *gem*-dimetalloalkanes.

## ASSOCIATED CONTENT

### Supporting Information

Experimental procedures, spectroscopic data for all new compounds, and copies of $^1$H and $^{13}$C NMR spectra. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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(12) **1a** was obtained in 75% yield (dr = >97 / 3) with the recovery of 19% of 1,2-dihydronaphthalene at 30 °C.

(13) For chromium-mediated cyclopropanation of α,β-unsaturated amides, see: (a) Concellón, J. M.; Rodríguez-Solla, H.; Méjica, C.; Blanco, E. G. *Org. Lett.* **2007**, *9*, 2981. (b) Concellón, J. M.; Rodríguez-Solla, H.; Méjica, C.; Blanco, E. G.; García-Granda, S.; Díaz, M. R. *Org. Lett.* **2008**, *10*, 349. Reaction with other olefins having coordinating functional groups, such as ethyl cinnamate, phenyl acrylate, *N*-allylbenzylamine, *N*-methylmaleimide, and 2-vinylpyridine did not gave the corresponding cyclopropane derivatives.

(14) For catalytic redox processes based on a $Cr^{II}$ and $Cr^{III}$ cycle by using manganese powder as a reductant, see: (a) Hu, C.-M.; Chen, J. *J. Chem. Soc., Chem. Commun.* **1993**, 72. (b) Fürstner, A.; Shi, N. *J. Am. Chem. Soc.* **1996**, *118*, 2533; (c) Fürstner, A.; Shi, N. *J. Am. Chem. Soc.* **1996**, *118*, 12349. See also refs 4d, 16f and 16g. Use of zinc, iron, and bis(trimethylsilyl)cyclohexadiene as a reductant gave inferior results. For a bis(trimethylsilyl)cyclohexadiene, see: (d) Tsurugi, H.; Mashima, K. *Acc. Chem. Res.* **2019**, *52*, 769.

(15) For synthetic methods of germylcyclopropanes, see: (a) Butkowskyj-Walkiw, T.; Szeimies, G. *Tetrahedron* **1986**, *42*, 1845. (b) Zaitseva, G. S.; Lutsenko, I. F.; Kisin, A. V.; Baukov, Y. I.; Lorberth, J. *J. Organomet. Chem.* **1988**, *345*, 253. (c) Mochida, K.; Kayamori, T.; Wakasa, M.; Hayashi, H.; Egorov, M. P. *Organometallics* **2000**, *19*, 3379. (d) Trofimov, A.; Rubina, M.; Rubin, M.; Gevorgyan, V. *J. Org. Chem.* **2007**, *72*, 8910. For our contribution on the synthesis of functionalized germanium compounds, see: (e) Murai, M.; Matsumoto, K.; Okada, R.; Takai, K. *Org. Lett.* **2014**, *16*, 6492. (f) Murai, M.; Matsumoto, K.; Takeuchi, Y.; Takai, K. *Org. Lett.* **2015**, *17*, 3102. (g) Murai, M.; Okada, R.; Asako, S.; Takai, K. *Chem. Eur. J.* **2017**, *23*, 10861.

(16) For stannylalkylidenation of aldehydes with $^n$Bu$_3$SnCHBr$_2$, see: (a) Hodgson, D. M. *Tetrahedron. Lett.* **1992**, *33*, 5603. (b) Hodgson, D. M.; Boulton, L. T.; Maw, G. N. *Tetrahedron Lett.* **1994**, *35*, 2231. For chromium-mediated alkylidenation of aldehydes, see: (c) Takai, K.; Nitta, K.; Utimoto, K. *J. Am. Chem. Soc.* **1986**, *108*, 7408. (d) Okazoe, T.; Takai, K.; Utimoto, K. *J. Am. Chem. Soc.* **1987**, *109*, 951. (e) Takai, K.; Kataoka, Y.; Okazoe, T.; Utimoto, K. *Tetrahedron Lett.* **1987**, *28*, 1443. For chromium-catalyzed alkylidenation, see: (f) Takai, K.; Ichiguchi, T.; Hikasa, S. *Synlett* **1999**, 1268. (g) Takai, K.; Kunisada, Y.; Tachibana, Y.; Yamaji, N.; Nakatani, E. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 1581.

(17) Pretreatment of $ZnCl_2$ to remove a TMEDA ligand of **4** (see ref 4d) followed by addition of aldehyde did not provide the corresponding stannylalkylidenation product.

(18) Because bond dissociation energies are $Me_3Sn$–C 65, $Me_3Sn$–Cl 101, $Me_3Si$–C 76, and $Me_3Si$–Cl 91 kcal/mol, respectively, the Sn–Me is more easily converted into Sn–Cl than Si–Me into Si–Cl.

(19) Attempted isolation and structural characterization of (tmeda)($^n$Bu$_3$Sn)CH($CrCl_2$)$_2$ did not provide a single crystal suitable for X-ray analysis.

(20) For the conversion of *gem*-dimetallomethane complexes to me-

tallocarbene species, see: (a) Straus, D. A.; Grubbs, R. H. *Organometallics* **1982**, *1*, 1658. (b) van de Heisteeg, B. J. J.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F. *J. Organomet. Chem.* **1986**, *310*, C25. (c) Meinhart, J. D.; Anslyn, E. V.; Grubbs, R. H. *Organometallics* **1989**, *8*, 583. For a review, see: (d) Beckhaus, R. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 686. See also ref 4d.