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Access to Fully Alkylated Germanes by $B(C_6F_5)_3$-Catalyzed Transfer Hydrogermylation of Alkenes

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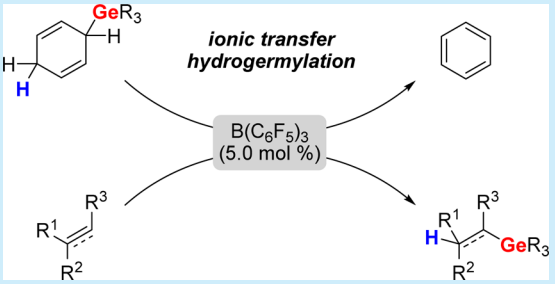
Supporting Information

ABSTRACT: Various cyclohexa-2,5-dien-1-yl-substituted germanes are shown to serve as easy-to-handle surrogates of hydrogermanes, including gaseous $MeGeH_3$ and Me_2GeH_2. The Ge−H functional group is liberated by treatment with catalytic amounts of $B(C_6F_5)_3$ and participates in situ in the $B(C_6F_5)_3$-catalyzed hydrogermylation of alkenes. The range of suitable alkenes is broad, and the overall procedure provides a convenient access to tetraalkyl-substituted germanes at room temperature. Transfer hydrogermylation of internal alkynes works equally well and selectively forms the *trans* or *cis* diastereomer depending on the electronic bias of the C≡C bond.

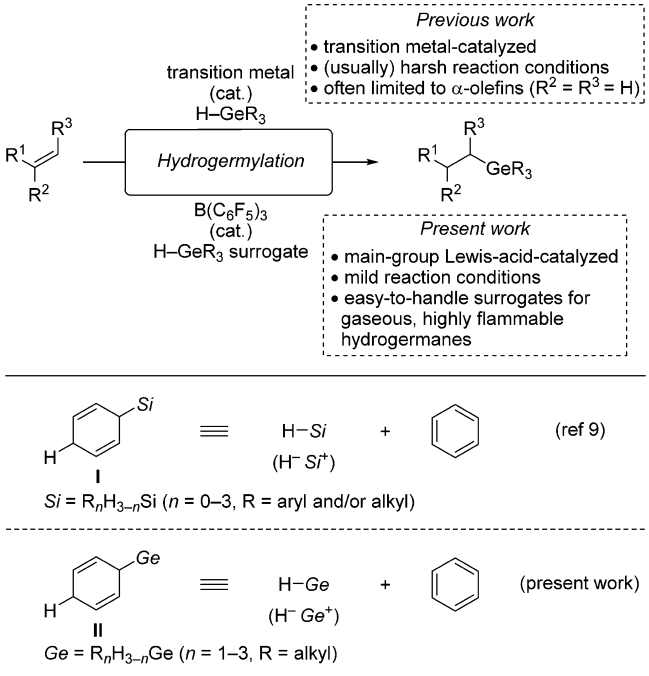


Hydrogermylation[1] of alkenes is a prevalent method for the catalytic synthesis of alkyl-substituted germanes.[2] The addition of hydrogermanes across the C=C bond typically relies on the activation of the Ge−H bond by transition-metal complexes[3] or radical initiators such as Et_3B/O_2[4] and AIBN.[5,6] Previously reported radical-based hydrogermylation protocols have been limited to triarylgermanes and are therefore not suitable for the preparation of tetraalkyl-substituted germanes.[4,5] Conversely, transition-metal catalysts such as H_2PtCl_6 have been shown to activate alkyl-substituted hydrogermanes R_nGeH_{4-n} (R = alkyl, n = 1−3) for alkene hydrogermylation.[1] However, these protocols are usually constrained by the need for elevated reaction temperatures and terminal alkenes, i.e., α-olefins (Scheme 1, top).[7] Also, applications of volatile or even gaseous hydrogermanes such as $MeGeH_3$ (bp −35 °C) or Me_2GeH_2 (bp 3 °C) in hydrogermylation reactions are rare, as handling of these flammable hydrogermanes is hazardous and inconvenient.[8]

Our group recently demonstrated the potential of adequately substituted cyclohexa-1,4-dienes to serve as easy-to-handle synthetic equivalents of H^-/Si^+ (**I**, Scheme 1, bottom),[9] H^-/H^+,[10] and H^-/tBu^+[11] when activated by the Lewis acid $B(C_6F_5)_3$.[12] As part of this research program, we anticipated that this approach could provide an entry into the mild preparation of fully alkylated germanes. The hydrogermylation of alkenes catalyzed by $B(C_6F_5)_3$ is in fact unprecedented.[13] By analogy to the ionic transfer hydrosilylation using cyclohexa-2,5-dien-1-ylsilanes **I**,[9,14] we imagined that the related bisallylic germanes **II** would be equally able to liberate the corresponding hydrogermanes by treatment with catalytic amounts of $B(C_6F_5)_3$ (Scheme 1, bottom).

We then prepared cyclohexa-2,5-dien-1-ylgermanes **1a**−**1c** as surrogates of Et_3GeH, Me_2GeH_2, and $MeGeH_3$, respectively, from lithiated cyclohexa-1,4-diene and the requisite chlorogermane (Figure 1; see the Supporting Information for details). Attempts to synthesize surrogates of the parent monogermane, GeH_4, either fully decorated with cyclohexa-2,5-dien-1-yl substituents (as in **1d**) or with three cyclohexa-1,4-diene units and one hydride (as in **1e**) were unsuccessful.

Scheme 1. Access to Alkyl-Substituted Germanes by Alkene Hydrogermylation (Top) and Surrogates for Hydrosilanes and Hydrogermanes (Bottom)



To demonstrate the feasibility of our proposal, we subjected surrogate **1a** to the typical protocol of the alkene transfer

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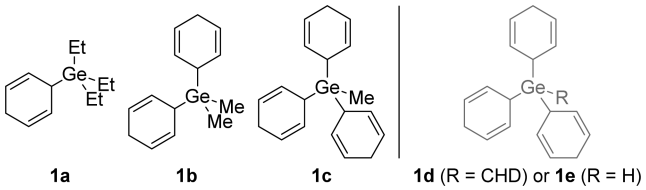
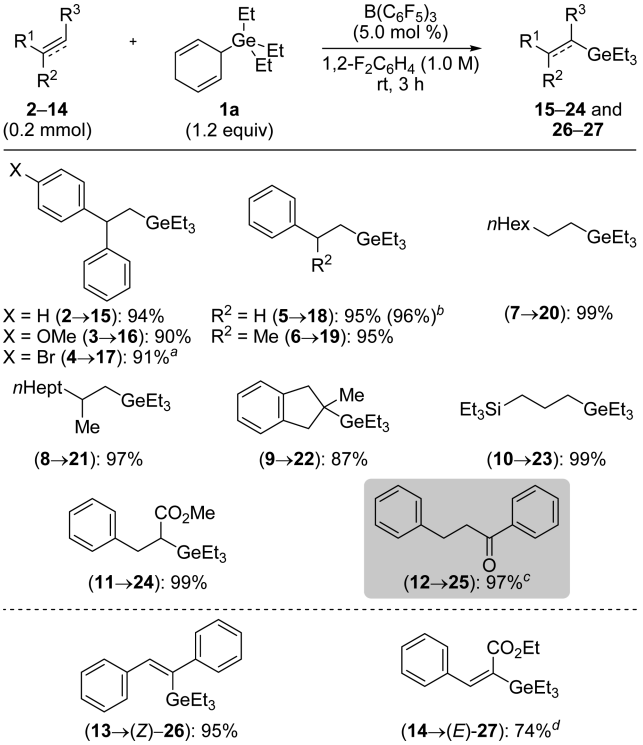


Figure 1. Cyclohexa-2,5-dien-1-ylgermanes as surrogates of hydrogermanes Et_3GeH, Me_2GeH_2, and $MeGeH_3$ (left) and GeH_4 (right). CHD = cyclohexa-2,5-dien-1-yl.

hydrosilylation[9] using 5.0 mol % of $B(C_6F_5)_3$ and 1,1-diphenylethylene (**2**) as the model substrate (Scheme 2). Quantitative conversion of **2** and 94% isolated yield of **15** were obtained in 1,2-$F_2C_6H_4$ after 5 h at a substrate concentration of 1.0 M (see the Supporting Information for a screening of solvents). A practical aspect of this protocol is the convenient removal of the byproducts benzene and unreacted Et_3GeH from the crude reaction mixture under reduced pressure. Encouraged by this result, we subjected differently substituted alkenes **3**−**12** to this protocol (Scheme 2, top). Electronically modified 1,1-diphenylethylene derivatives **3** and **4** showed the expected reactivity trend, giving full conversion for methoxy-substituted **3** in 3 h, while more electron-deficient **4** required double the amount of $B(C_6F_5)_3$ and more of the surrogate to secure quantitative conversion. Styrenes **5** and **6** participated well with an excellent 95% yield of **18** and **19**, respectively. Likewise, α-olefin **7** and 1,1-dialkyl-substituted **8** furnished **20** and **21** in near-quantitative yields. Trisubstituted 2-methylindene favored C−Ge bond formation in the sterically more

Scheme 2. Transfer Hydrogermylation of Alkenes and Alkynes Using Et_3GeH Surrogate 1a



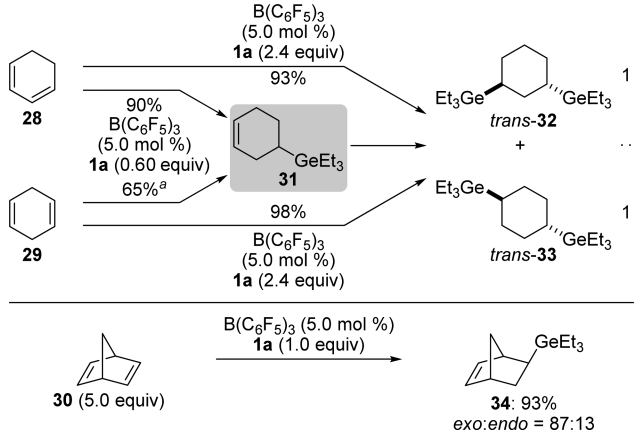
[a]10 mol % of $B(C_6F_5)_3$ and 1.6 equiv of **1a** used. 24 h. [b]Reaction run on a 1.0 mmol scale. [c]Performed at 90 °C. [d]2.0 equiv of **1a** used. Reaction run on a 0.1 mmol scale.

hindered position at C2 (**9** → **22**); this is in agreement with the regioselectivity previously found in the $B(C_6F_5)_3$-catalyzed hydrosilylation of **9**,[9b] again emphasizing that a benzylic (secondary) carbocation is favored over a tertiary. An allylic silyl group as in **10** was tolerated, and 1,3-difunctionalized **23** was formed quantitatively. α,β-Unsaturated ester **11** reacted selectively to yield **24** with incorporation of the germyl group in the α-position and no reduction of the carboxyl group.[15] In contrast, chemoselective 1,4-reduction of chalcone occurred to yield the corresponding ketone after hydrolysis (**12** → **25**).

We also probed electronically unbiased and biased C≡C bonds in the transfer hydrogermylation, as Gevorgyan and coworkers had reported the stereodivergent addition of Et_3GeH across internal alkynes (*trans*-hydrogermylation) and propiolates (*cis*-hydrogermylation) catalyzed by $B(C_6F_5)_3$.[13a] Accordingly, **13** and **14** converted diastereoselectively into (*Z*)-**26** and (*E*)-**27**, respectively, under the setup of our transfer hydrogermylation (Scheme 2, bottom).

We also investigated cyclic dienes **28**−**30** (Scheme 3). When using 0.6 equiv of surrogate **1a**, cyclohexa-1,3-diene reacted

Scheme 3. Transfer Hydrogermylation of Cyclic Dienes



[a]Isolated as a mixture with *trans*-**32** and *trans*-**33** in a ratio of **31**:(*trans*-**32**+*trans*-**33**) = 53:47.

completely regioselectively to afford the homoallylic germane (**28** → **31**). The same adduct was obtained using cyclohexa-1,4-diene (**29** → **31**) along with significant amounts of fully hydrogermylated cyclohexanes *trans*-**32** and *trans*-**33**.[16] These outcomes are particularly noteworthy, as the related H_2PtCl_6-catalyzed hydrogermylation of **28** and **29** yields the corresponding vinylic germane due to migration of the unreacted double bond.[17] Interestingly, cyclohexa-1,4-diene (**29**) was reported to engage in transfer hydrogenation of alkenes under this setup,[10b] but we did not observe any reduction. Treatment of either diene with 2.4 equiv of surrogate **1a** led to an equimolar mixture of *trans*-1,3- and *trans*-1,4-bis(triethylgermyl)cyclohexane (**28** or **29** → *trans*-**32** and *trans*-**33**).[16] Transfer hydrogermylation of norborna-2,5-diene proceeded with an *exo*/*endo* ratio of 87:13 (**30** → **34**).

We then continued with **1b** (surrogate for Me_2GeH_2) and **1c** (surrogate for $MeGeH_3$) in the transfer hydrogermylation of representative alkenes (Scheme 4). 1,1-Diphenylethylene derivatives **3** and **2** required a longer reaction time (72 h) or higher catalyst loading (10 mol %), respectively, to form diadduct **35** and triadduct **36** in good yields. Conversely, styrenes **5** and **6** gave high yields with surrogate **1b** or **1c** in the

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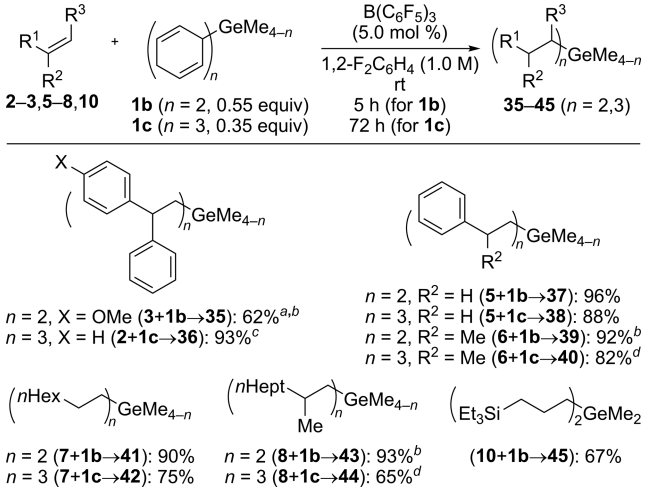
Scheme 4. Transfer Hydrogermylation of Selected Alkenes Using Me_2GeH_2 and $MeGeH_3$ Surrogates 1b and 1c

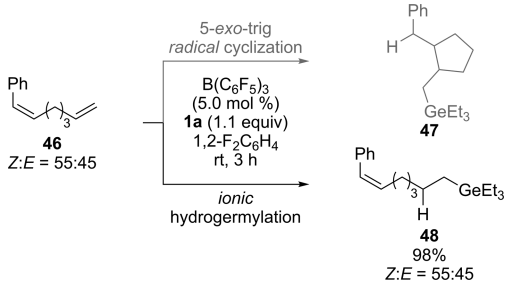


[a]72 h. 72% conversion of the substrate determined by ^{1}H NMR analysis. [b]Obtained as a 1:1 mixture of *meso* and C_2-symmetric compounds. [c]10 mol % of the catalyst used. [d]Obtained as a 3:1 mixture of C_1- and C_3-symmetric compounds.

presence of a lower catalyst loading (5.0 mol %). Likewise, terminal alkenes **7** and **8** furnished the diadducts **41** and **43** in excellent yields whereas slightly lower yields were obtained for triadducts **42** and **44**. Allylic silane **10** was prone to decomposition in combination with surrogates **1b** and **1c**, and only diadduct **45** was isolated in satisfactory yield.

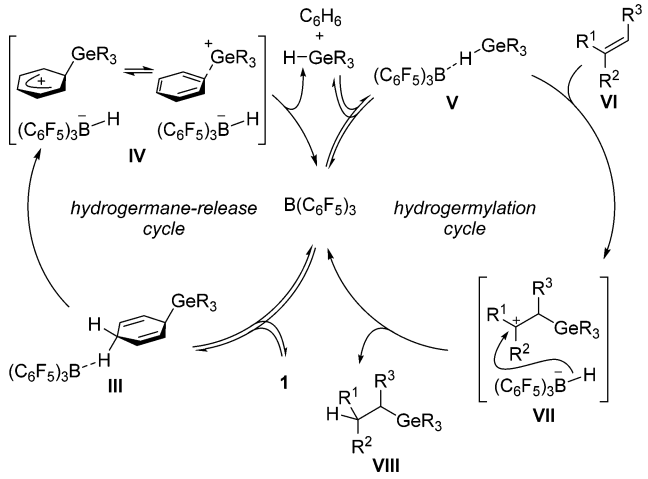
We also performed control experiments (1) to distinguish between hydrogermane release from surrogate **1** followed by Ge−H bond activation and direct transfer of the electrofuge (= germylium ion) onto the π-basic substrate as well as (2) to exclude the involvement of radical intermediates.[18] ^{1}H NMR analysis confirmed for all three surrogates **1** that treatment of **1** with catalytic amounts of $B(C_6F_5)_3$ in CD_2Cl_2 triggers the liberation of the hydrogermane together with benzene even in the absence of any alkene (see the Supporting Information for details). Further, acyclic diene **46** cleanly afforded **48** under the standard setup, and **47** was not detected (Scheme 5).[19]

Scheme 5. Mechanistic Control Experiment to Exclude Radical Intermediates



These observations support the stepwise ionic mechanism described earlier for the related transfer hydrosilylation (Scheme 6).[9,20] Liberation of the hydrogermane commences with $B(C_6F_5)_3$-triggered hydride abstraction from the bisallylic methylene group of surrogate **1**,[9e] thereby forming ion pair **IV** consisting of a germanium-stabilized Wheland complex or a benzene-stabilized germylium ion together with borohydride

Scheme 6. Proposed Catalytic Cycles for the $B(C_6F_5)_3$-Mediated Hydrogermane Release (Left) and the $B(C_6F_5)_3$-Catalyzed Alkene Hydrogermylation (Right)



$[HB(C_6F_5)_3]^-$ (**1** → **III** → **IV**). **IV** eventually collapses to release the hydrogermane along with stoichiometric benzene (left cycle). Subsequent activation of the hydrogermane by $B(C_6F_5)_3$ and transfer of the electrophilic germyl moiety to π-basic substrate **VI** forms ion pair **VII** (**V** + **VI** → **VII**)[21] that, after hydride transfer from $[HB(C_6F_5)_3]^-$, gives adduct **VIII** concomitant with regeneration of $B(C_6F_5)_3$ (right cycle).[22]

We have introduced here three cyclohexa-2,5-dien-1-yl-substituted germanes to serve as synthetic equivalents of hydrogermanes. These engage in ionic transfer hydrogermylation reactions of a broad range of differently substituted alkenes (and alkynes) by catalytic treatment with the strong boron Lewis acid $B(C_6F_5)_3$. This enables the metal-free synthesis of alkyl-substituted germanes at room temperature.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b00672.

General procedures, experimental details, a screening of solvents, time-dependent NMR experiments, characterization data, and NMR spectra for all compounds (PDF)

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Notes

The authors declare no competing financial interest.

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(4) For an overview, see: Yorimitsu, H.; Oshima, K. *Inorg. Chem. Commun.* **2005**, *8*, 131−142.

(5) For an early example, see: Satgé, J.; Rivière, P. *J. Organomet. Chem.* **1969**, *16*, 71−82.

(6) The addition of halogen-substituted hydrogermanes to alkenes often takes place even in the absence of any catalyst. However, (over) stoichiometric amounts of organometallic reagents are necessary to arrive at tetraalkylgermanes. See refs 1a and 2.

(7) In fact, only selected alkenes have been shown to participate in the hydrogermylation with trialkylgermanes at room temperature. Examples include: (a) Green, M.; Howard, J. A. K.; Proud, J.; Spencer, J. L.; Stone, F. G. A.; Tsipis, C. A. *J. Chem. Soc., Chem. Commun.* **1976**, 671−672 (hex-1-ene). (b) Traylor, T. G.; Koermer, G. S. *J. Org. Chem.* **1981**, *46*, 3651−3657 (allyltrimethylsilane). (c) Trofimov, A.; Rubina, M.; Rubin, M.; Gevorgyan, V. *J. Org. Chem.* **2007**, *72*, 8910−8920 (cyclopropenes). (d) Handzlik, J.; Kochel, A.; Szymańska-Buzar, T. *Polyhedron* **2012**, *31*, 622−631 (norborna-2,5-diene). (e) Greenhalgh, M. D.; Thomas, S. P. *Chem. Commun.* **2013**, *49*, 11230−11232 (styrene). (f) Ahrens, T.; Teltewskoi, M.; Ahrens, M.; Braun, T.; Laubenstein, R. *Dalton Trans.* **2016**, *45*, 17495−17507 (trifluoromethylethylene).

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(15) Comparable regioselectivity was observed by Gevorgyan and coworkers in the $B(C_6F_5)_3$-catalyzed hydrogermylation of propiolates. See ref 13a.

(16) The relative configuration of *trans*-**32** was verified by NMR spectroscopy, and we assume the same for *trans*-**33**, for which unambiguous assignment by NMR spectroscopic analysis was not possible.

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(19) Gevorgyan and co-workers had also proposed an ionic mechanism for their $B(C_6F_5)_3$-catalyzed hydrogermylation using hydrogermanes. See ref 13a.

(20) Conversely, transfer hydrogenation and transfer hydro-*tert*-butylation from these cyclohexa-1,4-dienes were shown to proceed by direct transfer of the electrofuge. See refs 10b and 11.

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