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cis-Selective Hydrogenation of Aryl Germanes: A Direct Approach to Access Saturated Carbo- and Heterocyclic Germanes

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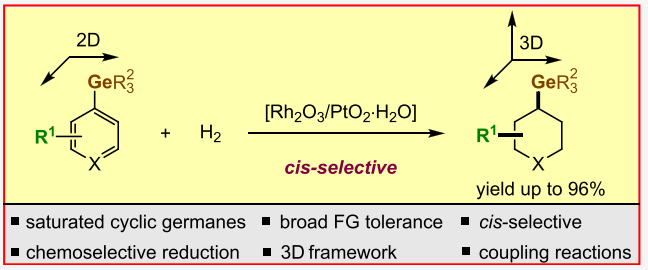
ABSTRACT: A catalytic approach of synthesizing the *cis*-selective saturated carbo- and heterocyclic germanium compounds (3D framework) is reported *via* the hydrogenation of readily accessible aromatic germanes (2D framework). Among the numerous catalysts tested, Nishimura's catalyst ($Rh_2O_3/PtO_2{\cdot}H_2O$) exhibited the best hydrogenation reactivity with an isolated yield of up to 96%. A broad range of substrates including the synthesis of unprecedented saturated heterocyclic germanes was explored. This selective hydrogenation strategy could tolerate several functional groups such as $-CF_3$, $-OR$, $-F$, $-Bpin$, and $-SiR_3$ groups. The synthesized products demonstrated the applications in coupling reactions including the newly developed strategy of aza-Giese-type addition reaction (C−N bond formation) from the saturated cyclic germane product. These versatile motifs can have a substantial value in organic synthesis and medicinal chemistry as they show orthogonal reactivity in coupling reactions while competing with other coupling partners such as boranes or silanes, acquiring a three-dimensional structure with high stability and robustness.



INTRODUCTION

The efficient and active protocols to access the novel 3D chemical space are vital within the field of applied sciences. Their installation is essential for the discovery of unprecedented organic frameworks as per their applications in the field of drug discovery,[1−4] life sciences,[5−7] and agrochemicals.[8,9] Owing to the huge potential chemical space as such, a significant interest is present in the chemical community to develop novel methodologies that allow the synthesis of diverse 3D chemical compounds *via* modular approaches from readily accessible flat building blocks. Organogermanium compounds are versatile intermediates in organic synthesis as they are non-toxic and hydrophobic with the manifestation of biological activities (Scheme 1, entry a).[10−14] These compounds are subjected to medicinal applications[15−17] revealing antitumor reactivity[18,19] and possess a vital role to understand the pharmacology of plants.[20,21] They also represent a broad application in material sciences.[22−25] In organic synthesis, they are of immense importance and treated as cross-coupling,[13,14,26−33] radical coupling,[34,35] and germanium-halogen exchange partners.[36,37] Moreover, organogermanium compounds were also added as the selective organic toolbox where the orthogonal reactivity for the cross-coupling reactions between aromatic rings can be attained over organoboranes, organosilanes, and organohalides using nanoparticle catalysis.[13,14,33]

Various methods such as trans-metalation,[38,39] strong base-promoted C−H germylation,[40,41] or coupling reactions under palladium catalysis[42−44] have been reported for the synthesis of organogermanes comprising aromatic rings.[45] While aromatic and therefore two-dimensional germanes are well developed and explored, only a handful of reports are present for the synthesis of saturated alkyl germanes[46−50] with no comprehensive study for the preparation of saturated carbo- and heterocyclic analogues (three-dimensional structures) (Scheme 1, entry a). Saturated carbocyclic and heterocyclic germanes are vital chemical motifs that can readily be installed preceding to access the 3D aliphatic chemical space and can be utilized as valuable intermediates for the stereoselective preparation of target molecules.

In a traditional approach, alkyl germanes are predominately developed by organometallic methods comprising the substitution reactions of Ge-electrophile with alkyl-Mg/Li or vice-versa (Scheme 1, entry b).[51−54] However, these procedures are mostly restricted to the synthesis of non-cyclic alkyl germanes and suffer from the incompatibility of functional groups. Considering the catalytic approach, the Xiao group developed a catalytic system where alkyl carbagermatranes were synthesized *via* the zinc-mediated decarboxylative cross-

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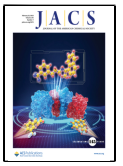

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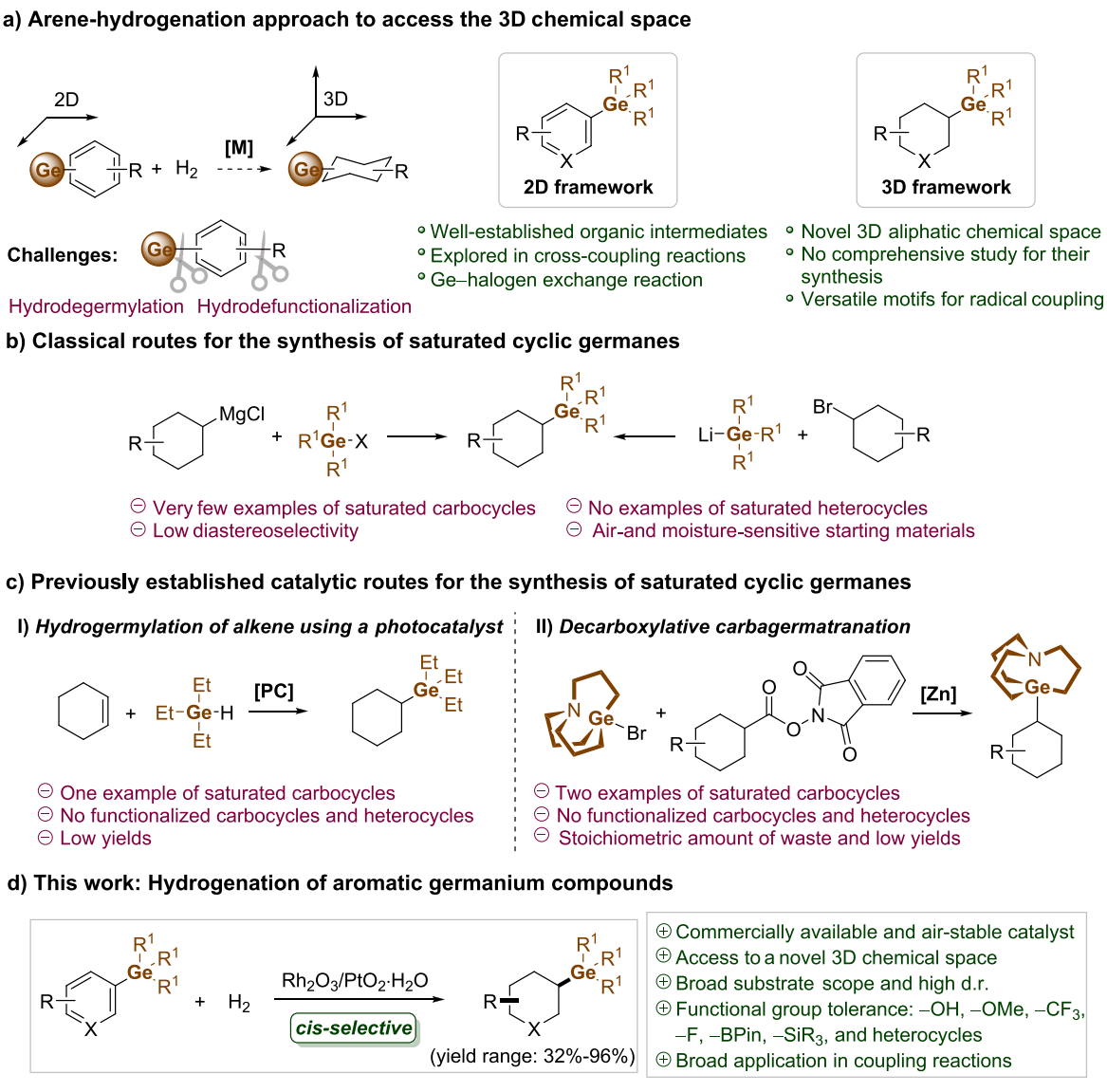
Scheme 1. (a–d) Development of the Catalytic System to Access the Functionalized Saturated Carbo- and Heterocyclic Germanes



coupling of bromocarbagermatranes and aliphatic *N*-hydroxyphthalimide (Scheme 1, entry c).[49] Very recently, the Schoenebeck group also disclosed the catalytic methodology where alkyl germanes were prepared by the hydrogermylation of alkenes using an organic photocatalyst (Scheme 1, entry c).[50] However, both methods were restricted to the synthesis of alkyl linear germanes, only a few examples of saturated carbocycles were described with no functional group tolerance, and no example of saturated heterocycles was shown. Due to the challenging synthesis of cyclic alkyl germanes, the utilization of these motifs is also frequently hindered.

Keeping all these in perspective, arene hydrogenation can be a direct and facile approach for synthesizing aliphatic germanes directly from the aromatic germanes that can link the chemical space between 2D aromatic rings with the 3D aliphatic saturated rings.[55−67] However, a major barrier to achieve this goal is the tolerance of sensitive functional groups, which are directly connected to the aromatic rings including the germane group itself. For example, organogermane can be unstable in the presence of electrophiles as well as nucleophiles.[51] Under hydrogenation conditions, these groups may promote the defunctionalization or even could lead to reaction termination. Another major challenge during hydrogenation is to control the diastereoselectivity as reduction of functionalized arenes can generate multiple stereocenters. Encouraged by the work reported by Zeng et al. and our group on chemo-selective hydrogenation of aromatic ketones,[58] *cis*-selective hydrogenation of fluoroarenes,[68−70] and silylated[71] and borylated arenes,[72] we set to explore the diastereoselective hydrogenation of aromatic germanium derivatives (Scheme 1, entry d). The crucial aspect to achieving this goal is unraveling the catalytic species that decreases the activation barrier of arene hydrogenation and displays tolerance toward the sensitive functional groups.

RESULTS AND DISCUSSION

Herein, we describe the first comprehensive study for the direct preparation of diastereoselective saturated carbo-cyclic germanes including the unprecedented preparation of valuable saturated heterocyclic germanes *via* the additive-free hydrogenation of aryl germanes. Previously, the groups of Zeng et

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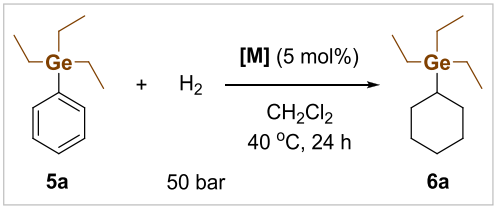
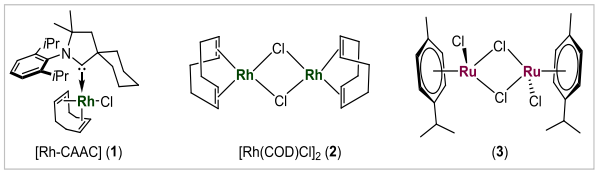
Table 1. Hydrogenation of Triethyl(phenyl)germane (5a): Influence of the Catalyst Precursor and Reaction Conditions[a]





#	catalyst [M]	conv. (%)	yield (%)
1[b]	[Rh-CAAC] (1)	87	71
2	$[Rh(COD)Cl]_2$ (2)	48	29
3	3	0	0
4	$Rh_2O_3/PtO_2{\cdot}H_2O$ (4)	80	76
5	Rh/C (5 wt %)	60	52
6	Ru/C (5 wt %)	47	41
7	Pd/C (5 wt %)	17	6
8	$Pd(OH)_2/C$ (20 wt %)	15	1
9	Pt/C (5 wt %)	16	1
10[c]	$Rh_2O_3/PtO_2{\cdot}H_2O$ (4)	>99	82

[a]Reaction conditions: **5a** (0.1 mmol), H_2 (50 bar), [M] (5 mol %), CH_2Cl_2 (1.0 mL), T = 40 °C, and reaction time = 24 h. [b]Molecular sieves (50 mg, 4 Å) were used. [c]Reaction temperature was increased to 50 °C.

al.,[58,73] Bullock et al.,[74,75] Andersson et al.,[67] our group,[7,68−72,76−81] and others[82−85] have reported novel catalytic arene hydrogenation reactions using rhodium and ruthenium metal-based catalytic systems. Intrigued by these reports, we examined the hydrogenation of aryl germanes employing various molecular complexes and heterogeneous metal species as catalysts. At the outset, triethyl(phenyl)-germane (**5a**) was chosen as a benchmark substrate to identify the rationale of catalyst assignment and for optimization (Table 1). At first, the reaction condition was set comprising a substrate (**5a**) (0.1 mmol), H_2 (50 bar), and dichloromethane as a solvent employing a series of organometallic precursors as catalysts, which were previously established to perform the arene hydrogenation. The well-proven arene hydrogenation catalyst [Rh-CAAC(COD)Cl] (CAAC = cyclic(alkyl)-(amino)carbene and COD = 1,5-cyclooctadiene)[86] (**1**) already showed good reactivity for the hydrogenation of **5a** confirming 87% conversion and 71% yield to the corresponding hydrogenation product **6a** (Table 1, entry 1). However, other organometallic precursors such as $[Rh(COD)Cl]_2$ (**2**) and $[Ru(p\text{-cymene})Cl_2]_2$ (**3**) exhibited low to no reactivity (Table 1, entries 2 and 3). As complex **1** in the presence of molecular sieves generates *in situ* heterogeneous Rh nanoparticles,[75,87] we further focused to test other commercially available heterogeneous catalysts. Among the examined Rh-heterogeneous catalysts, Nishimura's catalyst ($Rh_2O_3/PtO_2{\cdot}H_2O$) (**4**) showed the best reactivity even compared to complex **1** resulting in 80% conversion with a yield of 76% of product **6a** (Table 1, entry 4).[88] However, other heterogeneous catalysts such as Ru/C, Pd/C, $Pd(OH)_2/C$, and Pt/C showcased very low to moderate reactivity (Table 1, entries 6−9). In the case of Pd and Pt heterogeneous catalysts, the degermylated homo-coupling product was also observed by GC−MS analysis.

Surprisingly, the functionalized aryl germanes such as rings substituted with methyl and methoxy groups under the optimized reaction conditions employing **4** as a catalyst did not show any reactivity toward the hydrogenation (Section S6, Supporting Information). Based on the observations, we further focused on optimization using $Rh_2O_3/PtO_2{\cdot}H_2O$ (**4**) as a catalyst and triethyl(*p*-tolyl)germane (**5e**) as a standard substrate. Thorough investigation for the hydrogenation of **5e** led to optimized reaction conditions comprising 80 bar of H_2, 2,2,2-trifluoroethanol (TFE) as a solvent, 50 °C reaction temperature, and 40 h of reaction time, resulting in >99% conversion with an isolated yield of 84% and high diastereomeric ratio (84:16 d.r.) (Table 2, **6e**). With the optimized reaction conditions at hand, **5a** was hydrogenated quantitatively to the corresponding product **6a** (Table 2). Subsequently, the reaction condition-based sensitivity screening[89] and substrate scope for diverse aryl germanes were investigated. The sensitivity screening affirmed the adverse effect of a high-water concentration and low pressure. Modest variations in other reaction parameters such as the substrate and oxygen concentration, temperature, and high pressure were insignificant to the high product yield, thus confirming the robustness of the reaction system.

The hydrogenation of functionalized arenes was tested as the preliminary substrate scope. Hydrogenation of methoxy-substituted arene derivatives resulted in moderate to good reactivity confirming the product formation with a yield range of 57−88% and high d.r. (Table 2, **6b−d**). The presence of aliphatic substituents in arene rings such as methyl and ethyl groups were well tolerated (Table 2, **6e−h**). However, the substituent in the meta-position for methoxy and methyl groups showed poor d.r. (Table 2, **6c** and **6f**). After the initial screening with the functionalized arenes, we turned our attention to hydrogenating the bicyclic rings.

Triethyl(naphthalen-1-yl)germane (**5i**) was fully hydrogenated to decalin germane with an isolated yield of 80% (Table 2, **6i**). The full hydrogenation of triethyl(3-methoxynaphthalen-2-yl)germane (**5j**) required an extended reaction time of 60 h affording 62% yield, resulting in the selective formation of one diastereomer (Table 2, **6j**). The electron-withdrawing trifluoromethyl group was tolerated during the hydrogenation and provided the hydrogenated product **6k** (Table 2). Interestingly, fluorine-substituted aryl germane (**5l**) was hydrogenated confirming a 34% isolated yield with high diastereoselectivity (Table 2, **6l**). However, the hydrodefluorinated reduced product and the starting material were also observed in the reaction mixture. Furthermore, the hydrogenation of unprotected phenol germane derivatives was explored and successfully realized. Consequently, the hydrogenation of these motifs can lead to a free-hydroxyl group attached to saturated carbocycles that can subsequently be functionalized to a range of chemical compounds. Notably, unprotected phenol germane derivatives underwent smooth hydrogenation (Table 2, **6m−6o**). Similarly, protected alcohol such as phenyl-protected alcohol was fully hydrogenated, resulting in product **6p** (Table 2). However, in the case of benzyl protection, low product yield was observed (Table 2, **6q**). The GC analysis revealed the formation of unprotected hydrogenated alcohol as the side product. Hydrogenation of

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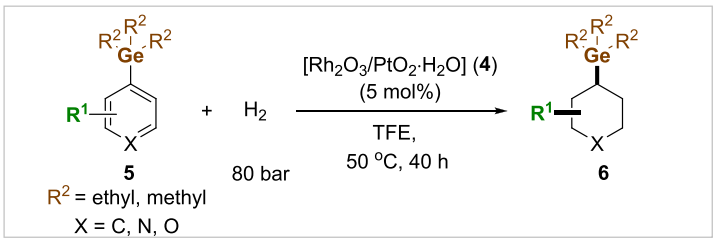
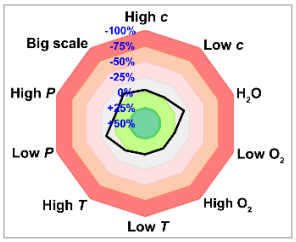
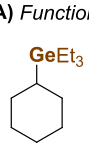
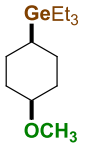
Table 2. (A–F) Substrate Scope for the Hydrogenation of Aryl Germane Derivatives Using Nishimura's Catalyst (4) under Optimized Reaction Conditions and Reaction Condition-Based Sensitivity Assessment[a]

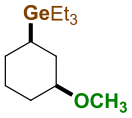


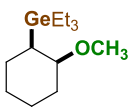


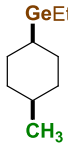
(A) *Functionalized arenes*

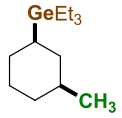

6a, 96%

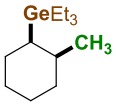

6b, 78%
83:17 d.r.

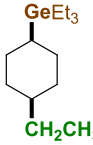

6c, 57%
66:34 d.r.

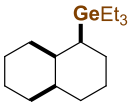

6d, 88%
>99:1 d.r.

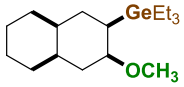

6e, 84%
84:16 d.r.

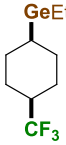

6f, 88%
59:41 d.r.

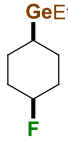

6g, 83%[b]
84:16 d.r.

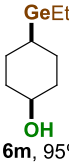

6h, 86%
89:11 d.r.

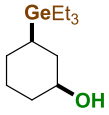

6i, 80%
51:39:10 d.r.

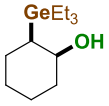

6j, 62%[c]
>99:1 d.r.

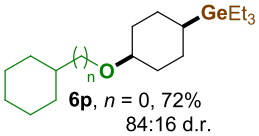

6k, 58%
86:14 d.r.

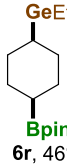

6l, 34%
85:15 d.r.

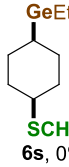

6m, 95%
62:38 d.r.


6n, 89%
71:29 d.r.

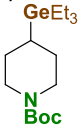

6o, 74%
>99:1 d.r.

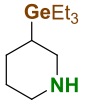

6p, *n* = 0, 72%
84:16 d.r.
6q, *n* = 1, 42%
89:11 d.r.

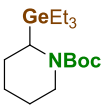

6r, 46%[f]
75:25 d.r.

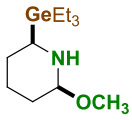

6s, 0%

(B) *Heterocycles*

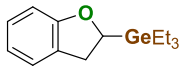

6t, 83%[c]


6u, 92%

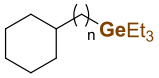

6v, 54%[c]

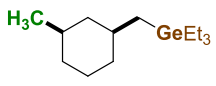

6w, 0%

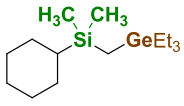

6x, 82%[c]


6y, 32%

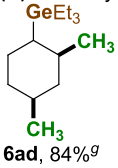
(C) *Aryl alkyl germanes*

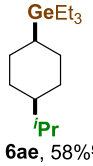

6z, *n* = 1, 96%
6aa, *n* = 2, 92%

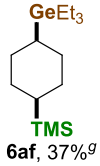

6ab, 92%
80:20 d.r.


6ac, 94%

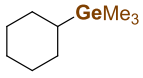
(D) *Sterically hindered aryl germanes*

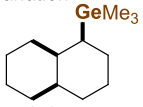

6ad, 84%[g]
62:24:14 d.r.

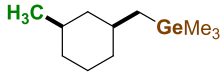

6ae, 58%[g]
80:20 d.r.

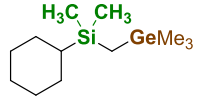

6af, 37%[g]
85:15 d.r.

(E) *Germanium group variation*

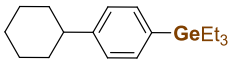

6ag, 96%

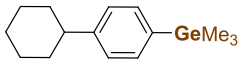

6ah, 71%
54:40:6 d.r.

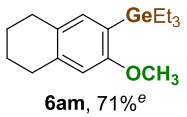

6ai, 88%[b]
75:25 d.r.

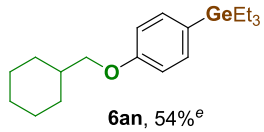

6aj, 90%

(F) *Selective one-ring hydrogenation*


6ak, 72%[d]


6al, 51%[d]


6am, 71%[e]


6an, 54%[e]

[a]Reaction conditions: **5** (0.2 mmol), H_2 (80 bar), **4** (5 mol %, based on total metal loading), T = 50 °C, TFE (1.5 mL), and reaction time (t) = 40 h; the diastereomeric ratio was determined by GC analysis. [b]GC yield was reported because of the low boiling point of the products. [c]t = 60 h. [d]t = 32 h. [e]t = 24 h. [f]NMR yield was reported because of difficult isolation. [g]$Yb(OAc)_3·4H_2O$ (10 mol %) was used.

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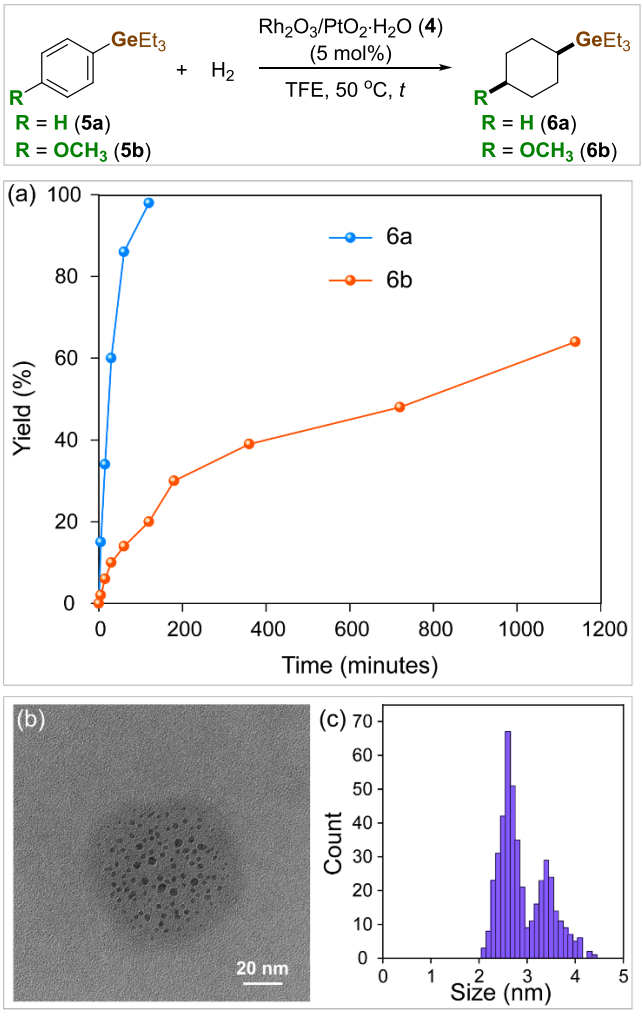

Figure 1. (a) Yield/time profile for the hydrogenation of **5a** and **5b** based on ^{1}H NMR analysis of reaction mixtures. Reaction conditions: **5a** or **5b** (0.1 mmol), H_2 (80 bar), **4** (5 mol %), T = 50 °C, TFE (1.0 mL). (b) Characterization of the grayish residue after catalysis and TEM image of the isolated nanoparticles after catalysis. (c) Histogram showing the particle size distribution of nanoparticles with the particle in the range of 2.6 ± 0.3 and 3.4 ± 0.4 nm.

boron-substituted aryl germane (**5r**) was also accomplished resulting in a 46% yield that can be further utilized for coupling reactions[90] and can exhibit orthogonal reactivity in the presence of germane functionality (Table 2, **6r**). The reduction of sulfur-substituted aryl germane did not show any reactivity, which might arise from the high chemisorption on the metal surface and therefore poisoning of the catalyst (Table 2, **6s**).[91] The *cis*-selectivity of the transformation was confirmed using NMR analysis of the major diastereomer products such as **6c**, **6d**, **6j**, **6m**, and **6o**.[78]

Saturated heterocycles are vital organic motifs and are present in numerous drug molecules, natural products, and agrochemicals.[92−94] We further investigated the unprecedented hydrogenation of heteroaryl germanes. Under the optimized reaction conditions, 3-(triethylgermyl)pyridine (**5t**) was hydrogenated with an NMR yield of 69%. Further elevation in the yield was made possible by extending the reaction time to 60 h resulting in 83% isolated yield after Boc protection (Table 2, **6t**). Similarly, other pyridine rings were hydrogenated with good to excellent yields (Table 2, **6u** and **6v**). However, no conversion was observed for the hydrogenation of 2-methoxy-6-(triethylgermyl)pyridine (Table 2, **6w**). This might be elucidated due to the strong coordination of the substrate molecules with the catalyst. The hydrogenation of furyl germane provided the saturated product with a notable yield of 82% (Table 2, **6x**). Interestingly, regarding the reduction of benzofuryl germane, selective one-ring hydrogenation was observed (Table 2, **6y**).

Next, hydrogenation of aryl alkyl germanes was carried out where various aryl alkyl germanes were screened and revealed quantitative yields toward the hydrogenated products (Table 2, **6z−6ac**). No degermylated product on alkane chains was observed under the operating reaction conditions. Interestingly, silane-substituted aryl alkane germane was also hydrogenated with a very good yield (Table 2, **6ac**).

Under the optimized reaction conditions, sterically hindered substrates such as di-methylated and *iso*-propyl functionalized aromatic rings revealed very low reactivity (less than 20% product formation). Very recently, the Kobayashi group has reported the effect of Lewis acids in arene hydrogenation where they discovered the acceleration in hydrogenation reaction rate by employing the catalytic amount of Lewis acid.[95] Following this report, various Lewis acids were screened for the hydrogenation of (2,4-dimethylphenyl)triethylgermane (**5ad**) (Section S7, Supporting Information). Lewis acids like $Zn(OTf)_2$, $In(OTf)_3$, $Sc(OTf)_3$, and $Eu(OTf)_3$ mostly showed a substantial amount of degermylation of the aromatic ring with a small amount of the hydrogenated product. Notably, employing the optimized conditions, the catalytic addition of $Yb(OAc)_3{\cdot}4H_2O$ enhanced the hydrogenation of **5ad** along with a small amount of the degermylation product yielding 84% to the desired product (Table 2, **6ad**).

Using the $Yb(OAc)_3{\cdot}4H_2O$ as a cooperative catalyst, other sterically hindered substrates such as ^{i}Pr- and TMS-substituted arene rings were tolerated with high d.r. (Table 2, **6ae** and **6af**). Notably, the TMS-substituted arene ring was hydrogenated without any desilylation as a side product and can be further utilized in Hiyama couplings,[96] Fleming−Tamao oxidations,[97] or Brook rearrangements[98] followed by functionalization *via* demasking of the C-germanium bond.[37] To check the reactivity of different germane groups, trimethyl(aryl) germanes were also employed for the hydrogenation (Table 2, **6ag−6aj**). Under optimized reaction conditions, trimethyl(phenyl)germane (**5ag**) provided the hydrogenation product with very high yield. Similarly, naphthyl and aryl alkyl rings that functionalized with trimethyl germane were hydrogenated with very good yields (Table 2, **6ah−6aj**).

Chemoselective reduction of one aromatic ring is one of the most challenging aspects in arene hydrogenation and can be a vital tool for post-functionalization. Acquiring the knowledge from the obtained experimental results and previous literature reports,[7,99,100] we envisaged that the hydrogenation of aryl germanes is difficult in comparison to other aromatic rings. Based on this hypothesis, we also investigated selective one-ring hydrogenation. Decreasing the reaction time from 40 to 32 h, chemoselective hydrogenation was observed for biphenyl germane rings (Table 2, **6ak** and **6al**). Similarly, **5j** and **5q** demonstrated selective one-ring hydrogenation affirming 71 and 54% isolated yield, respectively, after 24 h (Table 2, **6am** and **6an**).

To understand the catalytic system in detail, kinetic experiments on the reduction of substrates **5a** and **5b** were conducted (Figure 1a). Analysis of the composition of the

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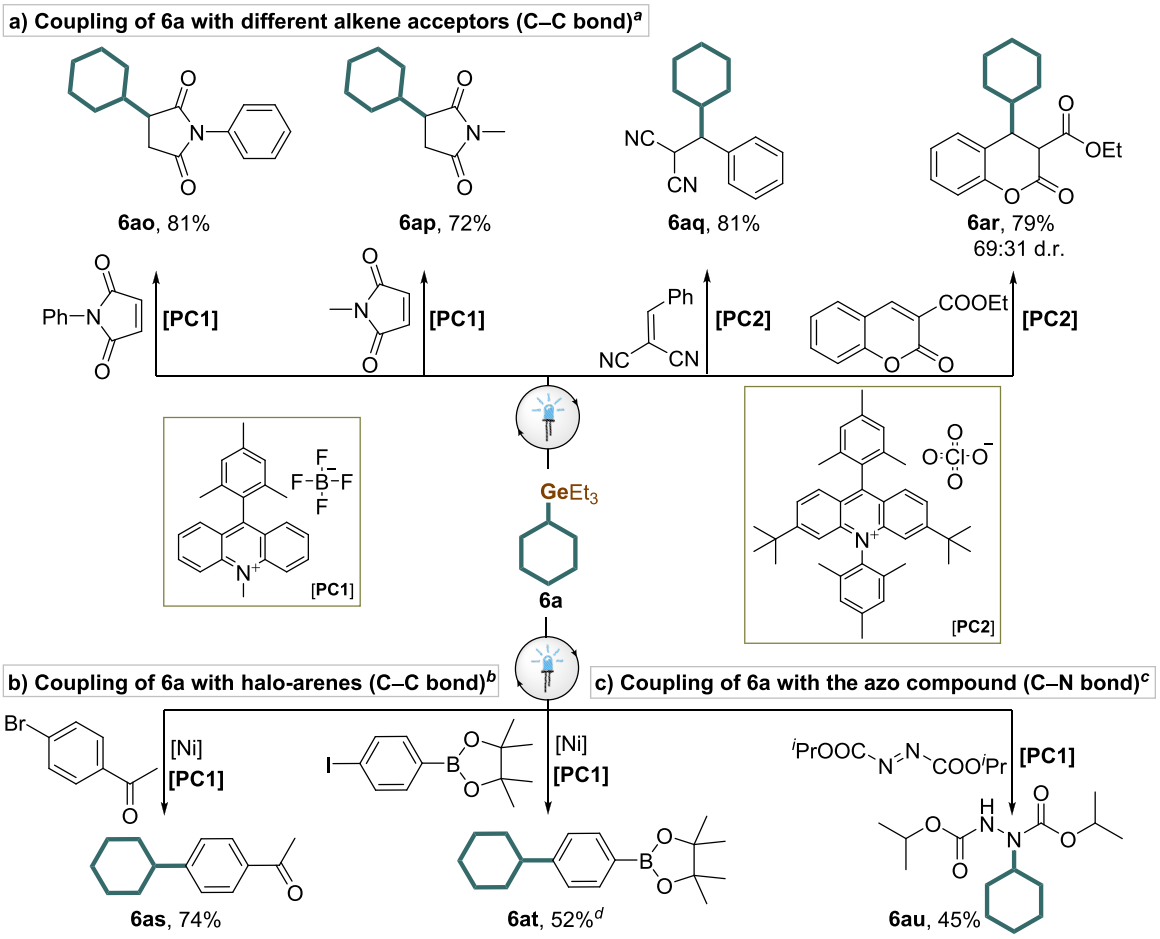

Figure 2. (a–c) Diversification of product **6a**. [a]Reaction conditions for coupling of **6a** with different alkene acceptors: **6a** (0.12 mmol), alkene acceptor (0.1 mmol), [**PC1**] or [**PC2**] (3–10 mol %), MeCN/MeOH (1:1) (1.0 mL), blue LED, and reaction time: 16 h. [b]Reaction conditions for coupling of **6a** with different halo-arenes: **6a** (0.1 mmol), halo-arene (0.2 mmol), $NiCl_2$ (6 mol %), 1,10-phenanthroline (6 mol %), [**PC1**] (5 mol %), MeCN (1.0 mL), blue LED, and reaction time: 24 h. [c]Reaction conditions for coupling of **6a** with the substituted azo compound: **6a** (0.1 mmol), diisopropyl azodicarboxylate (DIAD) (0.2 mmol), [**PC1**] (10 mol %), MeCN/MeOH (1,1) (1.0 mL), blue LED, and reaction time: 16 h. [d]NMR yield.

reaction mixture for the hydrogenation of **5a** over time displayed that the reaction did not require any induction period. The reaction resulted in a 15% NMR yield after 5 min confirming the high activity of catalyst **4** toward hydrogenation. As the time proceeded, the reaction continued steadily with nearly the same reaction rate and resulted in full conversion after 2 h yielding 98% to the corresponding product **6a**. The reaction progress for the hydrogenation of **5b** using catalyst **4** exhibited distinct reactivity in comparison to **5a**. Hydrogenation of **5b** proceeded slowly yielding 2% after 15 min, approximately 7 times slower in comparison to **5a**. The reaction rate increases continuously resulting in a 30% yield after 3 h. Subsequently, the reaction slowed down but reached 64% yield after 19 h. These observations indicated that the hydrogenation of functionalized aromatic germanes is difficult in comparison to non-functionalized germanes.

Furthermore, to prove that the nature of the active catalytic species is heterogeneous during catalysis, the standard catalytic reaction was performed in the presence of mercury, an effective poison for the heterogeneous catalysts. Only the 20% product was obtained under these reaction conditions. Subsequently, the control fractional poisoning experiment with benzothiophene did not show any product formation. These results indicated that the active species in the reaction are heterogeneous. Afterward, we targeted the characterization of the catalytic active species obtained from catalyst **4** after the first catalytic cycle. After the first cycle of the reaction, the catalyst was precipitated, isolated *via* filtration, and analyzed by transmission electron microscopy (TEM) (Figure 1b). TEM imaging showcased the formation of the nanoparticles after completion of the reaction in the two different size ranges of 2.6 ± 0.3 and 3.4 ± 0.4 nm (Figure 1c). The isolated gray precipitate was further used as a catalyst in the next cycle for the hydrogenation of **5a** confirming the product formation with an NMR yield of 86% delivering identical reactivity as catalyst **4**. Energy-dispersive X-ray diffraction (EDX) imaging confirmed that the nanoparticles are composed of Rh and Pt, which indicates the transformation of Nishimura's catalyst into the nanoparticles during the catalytic hydrogenation (Section S10, Supporting Information).

Having an established and efficient method for the preparation of saturated cyclic germanes, we further analyzed their synthetic utility (Figure 2). In this context, we focused on the coupling reactions where saturated organocyclic germanes can serve as a coupling partner by using transition-metal precursors and photocatalysts. We were intrigued by the fact that employing our methodology-saturated carbocycle germanes can be synthesized in one reaction step and can be

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further utilized as coupling partners. At first, we examined the C_{sp2}−C_{sp3} coupling reactions (Giese-type addition) using cyclohexyltriethylgermane (**6a**) as a substrate, *N*-phenylmaleimide as a coupling partner, and Acr^+-Mes as an organic photocatalyst.[34,35] Efficient alkylation of *N*-phenylmaleimide was observed, resulting in an 81% yield (**6ao**). This transformation was also applied for alternative alkene acceptors such as *N*-methylmaleimide, 2-benzylidenemalononitrile, and substituted-coumarin, affirming the yield range of 69−81% (**6ap**−**6ar**). We also demonstrated the cross-coupling reaction between halo-arenes and saturated cyclic germane.[35] The reaction between 1-(4-bromophenyl)ethan-1-one and **6a** in the presence of a nickel precursor and photocatalyst resulted in a 74% yield (**6as**). Similarly, pinacolborane-substituted iodobenzene was also coupled with **6a** yielding 52%, confirming orthogonal reactivity of germane over borane (**6at**). Furthermore, we also developed a new catalytic transformation where **6a** can serve as a coupling partner for the construction of C_{sp3}−N bonds. Under non-optimized reaction conditions, **6a** was coupled with azodicarboxylic ester using an organic photocatalyst confirming the notable C_{sp3}−N bond formation with a yield of 45% (**6au**).

CONCLUSIONS

In conclusion, we have developed a novel catalytic system that can straightforwardly access saturated carbo- and heterocyclic germanes from promptly available and easy-to-synthesize aromatic germanes. To the best of our knowledge, this work represents the synthesis of *cis*-selective functionalized saturated carbocyclic and heterocyclic germane derivatives for the first time. The transformation displayed a remarkably broad reaction scope providing good to excellent yields and moderate to very high *cis*-selectivity while comprising the tolerance of functional groups such as −OR (R = H, CH_3, phenyl, and benzyl), $-CF_3$, −F, borane, and silanes. The overall reaction protocol is found to be atom economical as no side and by-products were formed. The synthesized saturated alkyl germane has shown impressive application in coupling reactions including the advanced strategy of aza-Giese-type addition reaction from the saturated cyclic germanes. In light of the consistent developments and high demands of these vital motifs in various above-discussed applications, we envisage that our protocol has great potential by unlocking the synthesis of a novel 3D chemical space and introducing them into the diverse organic framework.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.2c12062.

Experimental section, a detailed description of synthetic procedures, spectral data, additional information regarding catalyst characterization, and copies of the NMR spectra of the compounds (PDF)

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Notes

The authors declare no competing financial interest.

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