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Low-valent germanium and tin hydrides as catalysts for hydroboration, hydrodeoxygenation (HDO), and hydrodesulfurization (HDS) of heterocumulenes†

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The low-valent germanium and tin hydrides, [LMH; L = {(ArHN)(ArN)-C═N–C═(NAr)(NHAr); Ar = 2,6-Et_2-C_6H_3}; M = Ge; (**Ge-1**), Sn (**Sn-2**)] bearing bis-guanidinato anions are employed as catalysts for chemoselective reduction of heterocumulenes *via* hydroboration reactions. This protocol demonstrates that a wide range of carbodiimides (CDI), isocyanates, isothiocyanates, and isoselenocyanates undergo partial reduction, yielding the corresponding *N*-boryl formamidine, *N*-boryl formamide, *N*-boryl thioformamide, and *N*-boryl selenoformamide products, respectively. Isocyanates and isothiocyanates are further converted into *N*-boryl methyl amines through hydrodeoxygenation (HDO) and hydrodesulfurization (HDS) reactions in the presence of catalyst **Ge-1**. Additionally, catalyst **Sn-2** exhibits excellent inter and intramolecular chemoselectivity over other functional groups. Based on stoichiometric experiments, a plausible catalytic cycle for chemoselective hydroboration of heterocumulenes is proposed.

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Introduction

Main group metals are abundant on Earth, eco-friendly, non-toxic, and more affordable than transition and lanthanide metals. As a result, their application and catalytic properties have garnered significant attention recently.[1] Numerous catalysts based on main group metals(elements) have been extensively employed for the reduction of various unsaturated organic substrates.[1b,2]

Organoboranes play a crucial role as synthetic intermediates in various organic chemical reactions.[3] Boron-containing products have recently attracted attention due to their ability to be transformed into a broad range of functional groups. In this context, there have been numerous reports on hydroboration reactions catalyzed by transition,[4] s-block,[5] and group 13 metals.[6] However, hydroboration reactions catalyzed by low-valent group 14 metals remain limited. Jones and coworkers first pioneered the Ge- and Sn-catalyzed hydroboration of carbonyl compounds.[7] Subsequently, a few additional reports on group 14 metal-catalyzed hydroboration of carbonyl compounds have been published by other research groups.[7,8] Sen and coworkers introduced the pyridylpyrrolido ligand-stabilized Sn complex[8f] for the hydroboration of alkenes and alkynes. Nakata[8e] and Sen[8b] groups have also independently reported the hydroboration of imines using an iminophosphonamido tin(II) complex and an amidinato silane complex, respectively (Scheme 1A).

In 2019, So and coworkers developed a chemo- and regioselective hydroboration reaction using a versatile cationic NHC-silyliumylidene catalyst (Scheme 1B).[9] Subsequently, the Cui group reported the use of cationic silaamidinate germylenes and stannylenes for the hydroboration of pyridines.[10] To our knowledge, there have been three reports on group 14 metal-catalyzed hydroboration of heterocumulenes[11] (Scheme 1C), including CO_2.[11b]

The partial reduction of isocyanates or isothiocyanates produces valuable amides or thioamides, which are key starting materials in biological transformations and the polymer and agrochemical industries.[12] Due to their broad applications, numerous synthetic routes have been established to prepare amides[13] and amines selectively.[14] Traditionally, acid derivatives and amines serve as valuable precursors for forming amide bonds (C–N bonds).[15] Stoichiometric metal reagents have converted heterocumulenes into formamidines,[16] formamides,[17] and thioformamides.[18] Pace and coworkers syn-

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†Electronic supplementary information (ESI) available: ^1H and $^{13}C\{^1H\}$ NMR spectra of compounds **Int A**, **Int A1** and **Int A1′** stoichiometric experiments, and catalytic products. CCDC 2300244. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d3dt04080a

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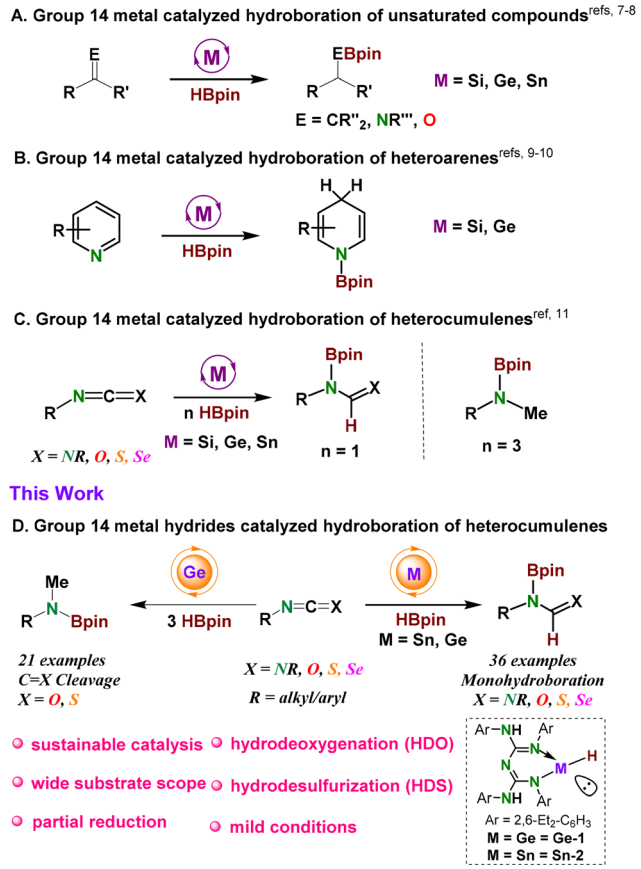


Scheme 1 Group 14 metal-catalyzed hydroboration of unsaturated substrates.

thesized formamides and thioformamides from isocyanates[17b] and isothiocyanates[18f] using the Schwartz reagent stoichiometrically. However, these methods suffer from several drawbacks, including harsh reaction conditions, poor selectivity, low yields, and generation of a large amount of waste.

Therefore, metal-catalyzed selective reduction of heterocumulenes is highly desirable. In this context, CDI hydroboration using transition-[19] and main group metal[5e,19b,20] catalysts has been established. In 2021, our group reported the first example of zinc hydride catalyzed partial reduction of isocyanate to *N*-boryl formamide.[21] Since then, there have been few reports on partial hydroboration of isocyanates using some main group (s-[22] and p-block[11c,23]), transition,[24] and actinide[25] metal-based catalysts.

N-Methyl amines are essential precursors for synthesizing natural products, drugs, and fine chemicals.[26] These *N*-methyl amines have been synthesized using methyl iodide and $(CH_3)_2SO_4$; however, these protocols suffer from issues such as over-methylation and high chemical waste. Subsequently, a few groups reported the metal-catalyzed hydrodeoxygenation (HDO) of isocyanates using three equivalents of pinacolborane (HBpin).[21,22c,23,24b,c,25,27] Our group recently established hydrodesulfurization (HDS) of isothiocyanates to *N*-boryl methyl amine using a bis-guanidinate aluminum hydride complex.[23a]

Herein, we present the synthesis and characterization of bis-guanidinate-stabilized heteroleptic tin(II) chloride [LSnCl; L = {(ArHN)(ArN)C═N–C═(NAr)(NHAr); Ar = 2,6-Et_2-C_6H_3}] (**Sn-1**) and hydride LSnH (**Sn-2**) complexes. Additionally, we report germanium and tin hydride catalyzed reduction of heterocumulenes (CDIs, isocyanates, isothiocyanates, and isoselenocyanates) *via* hydroboration reactions. Furthermore, *N*-boryl methyl amines have been synthesized through HDO of isocyanates and HDS of isothiocyanates (Scheme 1D).

Results and discussion

Synthesis of low valent group 14 metal hydrides

Our group recently reported the synthesis of a bis-guanidinate stabilized low-valent germanium hydride, [LGeH (**Ge-1**); L = {(ArHN)(ArN)-C═N–C═(NAr)(NHAr); Ar = 2,6-Et_2-C_6H_3}], through the reaction of LGeCl with Na[$HBEt_3$] in toluene.[29] Next, we aimed to access low-valent bis-guanidinate Sn(II) complexes. Accordingly, compound LSnCl (**Sn-1**) was prepared by reacting the *in situ* generated lithiated salt of the bis-guanidine ligand with anhydrous $SnCl_2$, yielding 75% *via* a salt metathesis pathway (Scheme 2). The compound LSnH (**Sn-2**) can be readily synthesized by treating LSnCl with a commercially available Alane reagent, achieving a 76% yield through a hydride-halide exchange reaction.

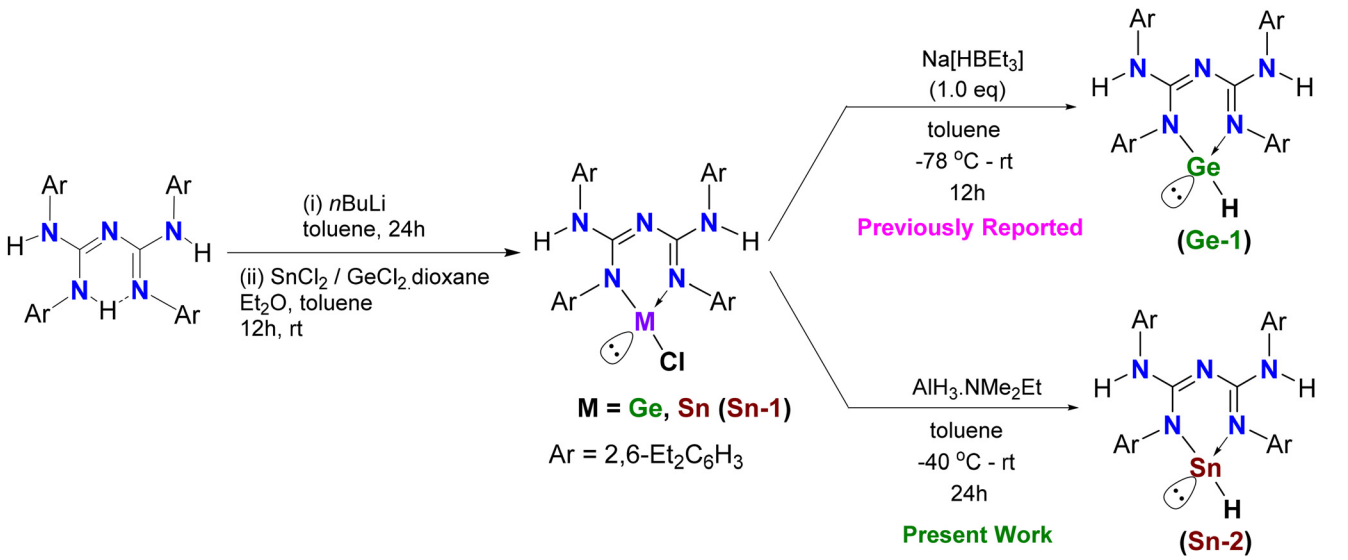
Sn-1 and **Sn-2** are highly sensitive to air and moisture, with melting points of 195–205 °C and 185–195 °C, respectively, indicating their thermal stability. The ^{1}H NMR spectrum of compound **Sn-1** shows resonances such as singlet, triplet, quartet, and multiplets, and their integration values are consistent with their formulation. The ^{119}Sn NMR spectrum also shows a single signal at 245.1 ppm, confirming the successful Sn metal atom incorporation into the ligand moiety.

The ^{1}H NMR spectrum of compound **Sn-2** shows the Sn–H resonance at 14.03 ppm in benzene-d6, which is well in agreement with the previously produced ^{Dipp}NacNac tin(II) hydride; (^{Dipp}Nacnac = [{ArNCMe)$_2$CH}]; (Ar = Dipp = 2,6-di-isopropylphenyl) by the Roesky group.[28] The ^{119}Sn NMR spectrum shows one signal at 205.0 ppm, which confirms the consumption of **Sn-1**. The ^{13}C{^{1}H} NMR spectrum of compounds **Sn-1** and **Sn-2** revealed the N_3C core of the ligand by distinctive signals at 155.8 and 157.1 ppm, respectively. High-resolution mass spectrometry provided further confirmation of both compounds.

Hydroboration of carbodiimide (CDI)

After the successful hydroboration and cyanosilylation of ketones catalyzed by **Ge-1**,[29] we sought to explore the catalytic activities of **Ge-1** and **Sn-2** for the hydroboration of heterocumulenes.

Initially, the hydroboration reaction was carried out using 1 equiv. of *N*,*N*′-diisopropylcarbodiimide (DIC) with 1 equiv. of HBpin at 70 °C in the presence of 10 mol% of catalyst **Ge-1** under neat conditions, resulting in 99% conversion of the desired product after 12 h. Lowering the catalyst loading from



Scheme 2 Synthesis of low-valent Ge(II) and Sn(II) hydrides bearing bis-guanidinate anions.

10 mol% to 8, 6, and 5 mol% still produced quantitative conversion of *N*-boryl formamidine under the same conditions. However, when the catalyst loading was reduced to 3 mol%, the yield was 75% at 70 °C after 12 h. We investigated a wide range of substrates using the optimized reaction conditions (5 mol% catalyst **Ge-1** at 70 °C, neat) (see ESI, Table S1†). In all cases, the progress of the reaction was monitored by ^{1}H NMR analysis. Aliphatic carbodiimides such as *N*,*N*′-di-*tert*-butyl carbodiimide (**1b**), *N*,*N*′-di-cyclohexyl carbodiimide (DCC) (**1c**), and *N*,*N*′-dibenzylcarbodiimide (**1d**) were also converted into the desired *N*-boryl formamidines (**2a–2d**) after 12 h at 70 °C. Various symmetrical *N*,*N*′-diaryl carbodiimide substrates with different alkyl substituents attached at various positions on the aryl group were successfully converted into the corresponding *N*-boryl formamidine products (**2e–2i**) with higher yields. When unsymmetrical aryl CDIs were treated with one equiv. of HBpin using a 5 mol% catalyst **Ge-1** under neat conditions, only one type of regioisomeric *N*-boryl formamidine product (**2j–2m**) was obtained. This product exhibited attachment of the Bpin moiety to the more hindered nitrogen atom of the NCN core, aligning with observations by the Eisen and Hill groups (Table 1).[19a,20g]

Similarly, two symmetrical bis-aryl CDIs (**1n** and **1o**) also gave the corresponding hydroborated products (**2n** and **2o**) when treated with two equiv. of HBpin under the optimized conditions (Table 1). These products were confirmed by ^{1}H NMR spectroscopy, where a singlet resonance peak of NC*H*N appeared in the 7.81–10.12 ppm range.

Hydroboration of isocyanate

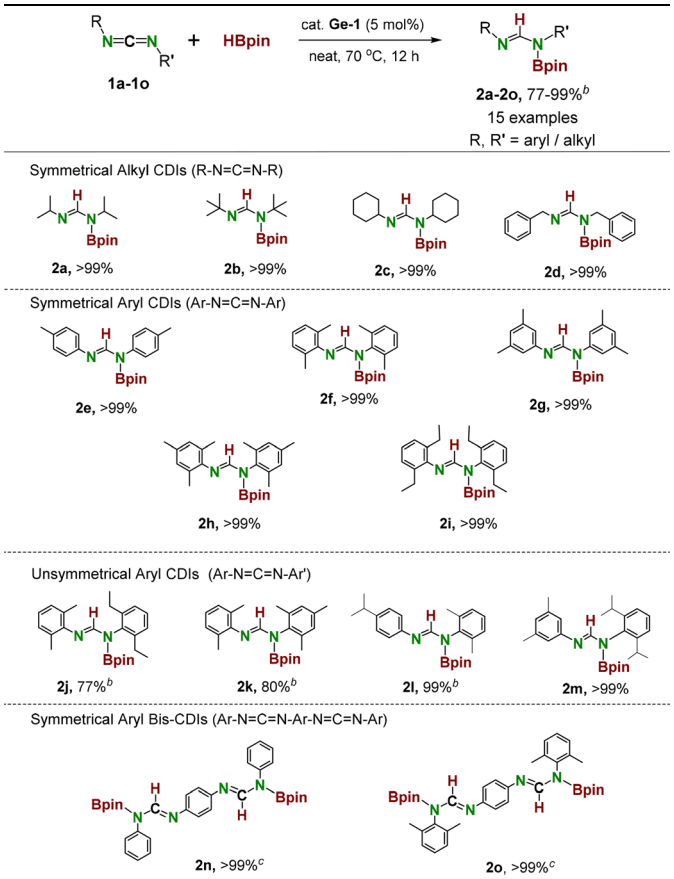
To further demonstrate the potential of the **Ge-1** catalyst, we investigated the hydroboration of isocyanates. While chemoselective products were formed, full reduction products, specifically *N*-boryl methyl amines, were obtained smoothly.

Considering a few examples of metal-catalyzed hydrodeoxygenation (HDO) of isocyanates,[21,22c,23,24b,c,25,27] we began to explore **Ge-1**-catalyzed complete reduction of isocyanates to *N*-boryl methyl amines. The reaction of 1 : 3 stoichiometric amounts of *p*-tolyl isocyanate (**3c**) and HBpin with 6 mol% catalyst under neat conditions at 70 °C gave only *N*-boryl methyl amine (**4c**) in quantitative yield. Lowering the catalyst loading from 6 mol% to 2 mol% gave quantitative conversion under the same reaction conditions. However, at a catalyst loading of 1 mol%, we observed a 70% product yield within 12 h. A very small conversion was noticed in the absence of a catalyst, indicating that the **Ge-1** catalyst is necessary for the HDO of isocyanates. Moreover, using 2 mol% of catalyst in the presence of solvents such as toluene and benzene showed no change in the yield under the optimized reaction conditions. Thus, the optimal reaction conditions were 2 mol% catalyst loading of catalyst **Ge-1** at 70 °C under neat conditions (see ESI, Table S2†).

A vast range of substrates, including aryl (mono and diisocyanate), alkyl (cyclic and acyclic), and long-chain compounds, were fully reduced into desired *N*-boryl methyl amines using the optimized conditions, with bis(boryl)oxide {O(Bpin)$_2$} as a side product.

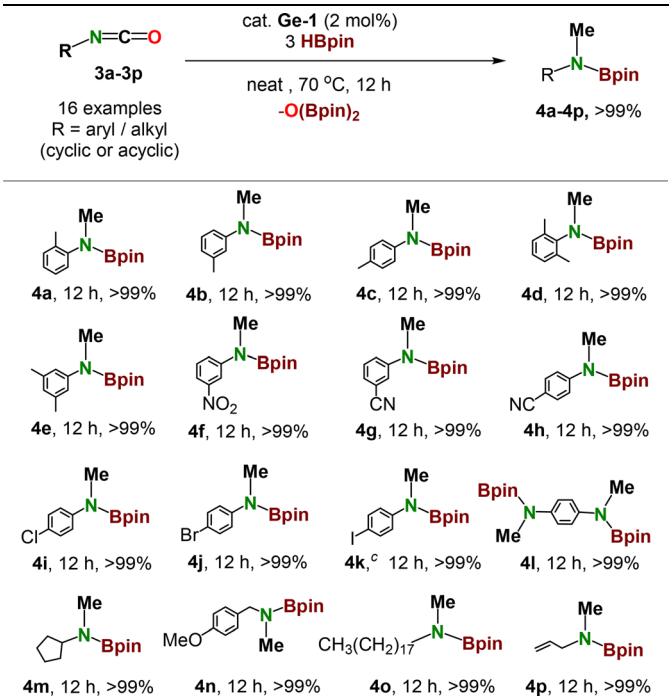
Various mono aryl isocyanates, including electron-donating (**3a–3e**) and electron-withdrawing groups (**3f–3k**), were quantitatively converted into the corresponding *N*-boryl methyl amines (**4a–4e** and **4f–4k**) under optimized conditions. However, 1,4-phenylene diisocyanate (**3l**) was treated with 6 equiv. of HBpin to give a quantitative amount of the corresponding HDO product (**4l**) at 70 °C after 12 h. All cyclic and acyclic groups were also converted into the corresponding *N*-boryl methyl amines (**4m–4p**) using the optimized conditions (Table 2). The phenyl ring's nitro, halide, alkene, and nitrile groups remain unchanged in the present catalytic reac-

Table 1 Substrate scope for mono-hydroboration of carbodiimides using the **Ge-1** complex as a catalyst[a]



[a] Reaction conditions: carbodiimide (0.3 mmol, 1.0 equiv.), HBpin (0.3 mmol, 1.0 equiv.), and cat. **Ge-1** (5 mol%) were placed in a vial under N_2 and stirred at 70 °C for 12 h. The % conversion was examined by ^{1}H NMR spectroscopy based upon the consumption of carbodiimide and the identification of the newly formed characteristic proton (NC*H*N) resonance signal. [b] For **2j**, **2k**, and **2l**, the yield was determined by ^{1}H NMR spectroscopy using nitromethane as an internal standard. [c] For **2n**, **2o**, and HBpin (0.6 mmol, 2.0 equiv.) was used.

Table 2 Substrate scope for HDO of isocyanates using the **Ge-1** complex as a catalyst[a,b]



[a] Reaction conditions: isocyanate (1.0 equiv., 0.3 mmol), HBpin (3.0 equiv., 0.9 mmol), and catalyst **Ge-1** (2 mol%) were placed in a vial and stirred under N_2 at rt or 70 °C for 12 h under neat conditions. [b] The % conversion yield was determined by ^{1}H NMR spectroscopy based on isocyanate consumption and the identified N*Me* signal confirmed the product. $O(Bpin)_2$ is a side-product of hydrodeoxygenation products. [c] For (**4l**), HBpin (6.0 equiv. 1.8 mmol) was used.

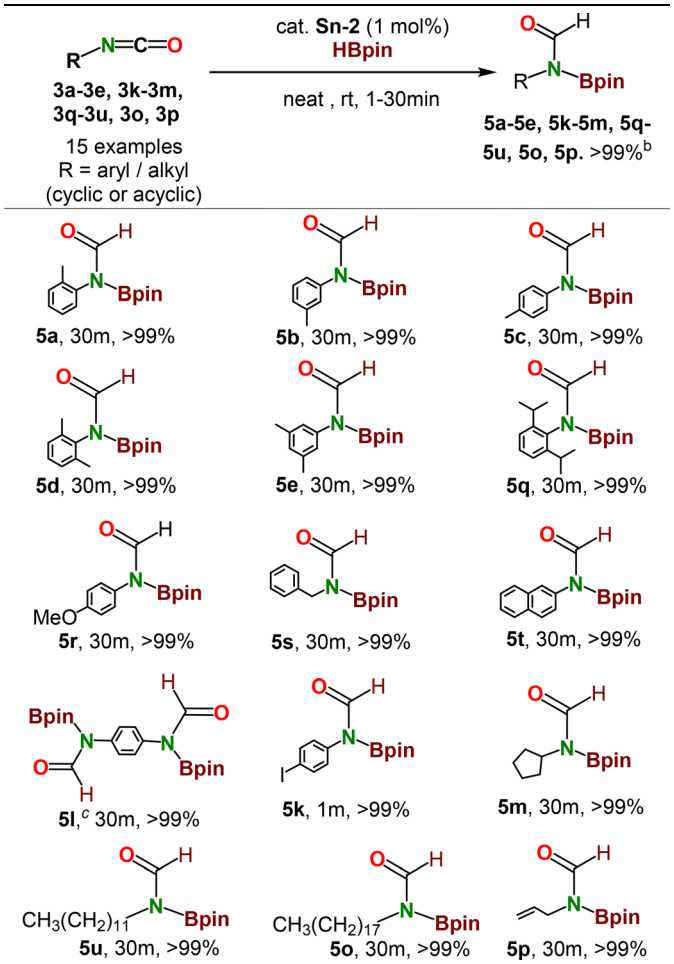
tions. Thus, the catalytic system showed good functional group tolerance.

All the products were characterized by ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopy. The ^{1}H NMR spectra revealed the appearance of a characteristic *N*-boryl methyl amine (NCH_3) peak in the range of 2.48–3.11 ppm, indicating the formation of *N*-boryl methyl amine products.

Inspired by Jones's[7] exceptional findings on the high activity of the tin catalyst for the hydroboration of carbonyls, we decided to test the **Sn-2** catalyst for the hydroboration of isocyanates. Initially, we reduced *p*-tolyl isocyanate (**3c**) using 1 equiv. of HBpin and a catalyst loading (**Sn-2**) at 10 mol%, under neat conditions and at room temperature for 12 hours. Remarkably, this approach achieved a >99% conversion of the isocyanate into the corresponding *N*-boryl formamide (**5c**), as confirmed by NMR analysis. Further reductions in catalyst loading to 5 mol%, 3 mol%, and 1 mol%, with reaction times of up to 30 minutes, while maintaining other conditions unchanged, still resulted in maximum conversion. However, reducing the catalyst loading to 0.5 mol% drastically decreased the conversion to 70% within 1 h. No conversion was observed under catalyst-free conditions, even after 12 h at 80 °C. Additionally, using 1 mol% of the catalyst in benzene solvent showed no change in conversion. Hence, the optimal reaction conditions were determined to be 1 mol% of catalyst loading at room temperature for 30 min (refer to ESI Table S3,† entry 7).

With these optimized conditions in hand, we screened a wide range of isocyanates (alkyl/aryl) and obtained the corresponding *N*-boryl formamides (**5a–5e**, **5k–5m**, **5o**, **5p**, **5q–5u**) in quantitative yields. In addition, compound (**Sn-2**) demonstrated enhanced activity towards the substrates with electron-withdrawing groups, *i.e.*, halide, nitrile, and nitro-substituted groups. These substrates exhibited rapid conversion, sometimes leading to dihydroboration and HDO products within minutes, resulting in a mixture of products under optimized conditions. This behavior can be attributed to the increased electrophilicity of the isocyanate group. Remarkably, with precise control, we successfully synthesized *N*-boryl formamide compound **5k** within a 1-minute reaction time at room temperature (Table 3). However, isocyanates substituted with electron-donating groups (**5a–5e**, **5q**, **5r**) took around 30 minutes

Table 3 Substrate scope for mono-hydroboration of isocyanates using **Sn-2** hydride as a catalyst[a]



[a] Reaction conditions: isocyanate (1.0 equiv., 0.1 mmol), HBpin (1.0 equiv., 0.1 mmol), and catalyst **Sn-2** (1 mol%) were placed in a vial and stirred under N_2 at rt for 1–30 min under neat conditions. [b]The % conversion yield was determined by ^{1}H NMR spectroscopy based on isocyanate consumption and the identified N(C*H*O)signal confirmed the product. [c]For (**5l**), HBpin (2.0 equiv. 0.2 mmol) was used.

to form their desired *N*-borylformamides. Beyond aromatic isocyanates, cyclic aliphatic and long chain isocyanates (**3m**, **3u**, **3o**, **3p**) were also successfully hydroborated into the corresponding formamides (**5m**, **5u**, **5o**, **5p**) with a 99% conversion. Moreover, all the formamide compounds (**5a–5e**, **5k–5m**, **5o**, **5p**, **5q–5u**) were characterized by ^{1}H NMR spectroscopy, showing the signature peak for the NC*H*O moiety within the range of 8.65–9.11 ppm, consistent with reported literature values.

Moreover, compound **5b** was confirmed by solid-state X-ray structural analysis. The N1–C1 and C1–O1 bond distances (1.372(2) and 1.212(2) (Å)) are comparable to the standard N–C single bond and C=O double bond, respectively. Furthermore, the N1–C1–O1 (124.70(16)°) bond angle is acute compared to N=C=O of isocyanate (Fig. 1), confirming the formation of *N*-boryl formamide product **5b**.

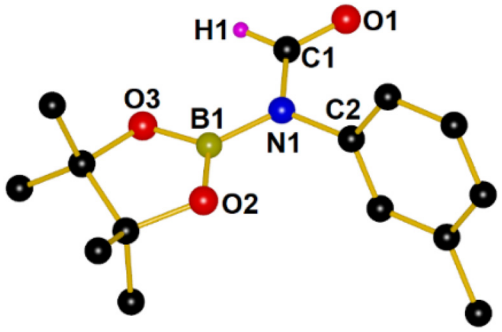


Fig. 1 Molecular structure of **5b**. The thermal ellipsoids are shown at 50% probability, and all the hydrogen atoms (except for H(1)) from structure **5b** are omitted for clarity. Selected bond lengths (Å) and angles (°): for **5b**: O1–C1 1.212(2), N1–C1 1.372(2), N1–B1 1.448(2), N1–C2 1.447(2); O1–C1–N1 124.70(16), C1–N1–B1 121.51(14), C1–N1–C2 118.21(13).

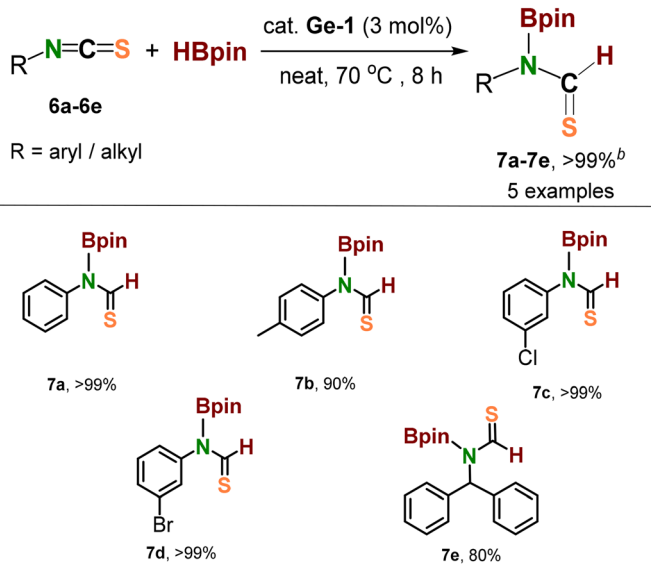
Hydroboration of isothiocyanate

As far as the hydroboration of isothiocyanate to *N*-boryl thioformamide is concerned, only a single example is known.[23a] Thus, we intended to examine the catalytic activity of **Ge-1** with phenyl isothiocyanate (**6a**). Compound **6a**, treated with one equiv. HBpin with 3 mol% of catalyst **Ge-1** was quantitatively converted into corresponding *N*-boryl thioformamide (**7a**) at 70 °C after 8 h (see ESI Table S4†). Using the same conditions, aromatic isothiocyanates (**6b–6d**) with electron-donating and electron-withdrawing substituents were found to deliver the desired products *N*-boryl thioformamide (**7b–7d**) in excellent yields (Table 4). Nonetheless, secondary alkyl isothiocyanate, *i.e.*, benzhydryl isothiocyanate **6e**, yielded the corresponding *N*-boryl thioformamide **7e** in an 80% yield. These products were confirmed by ^{1}H NMR spectroscopy. A single resonance peak of the NC*H*S moiety appeared between 10.15–10.37 ppm.

Next, we aimed for the hydrodesulfurization (HDS) of isothiocyanates with HBpin using catalyst **Ge-1**. We chose *p*-tolyl isothiocyanate as our model substrate. The reaction of *p*-tolyl isothiocyanate with 3 equiv. HBpin with 8 mol% of catalyst **Ge-1** under neat conditions at 80 °C gave *N*-boryl methyl amine an excellent yield after 12 h. No change in the yield was observed after lowering the catalyst loading from 8 mol% to 4 mol%. Negligible conversion was noticed without catalyst **Ge-1** (Table S5†).

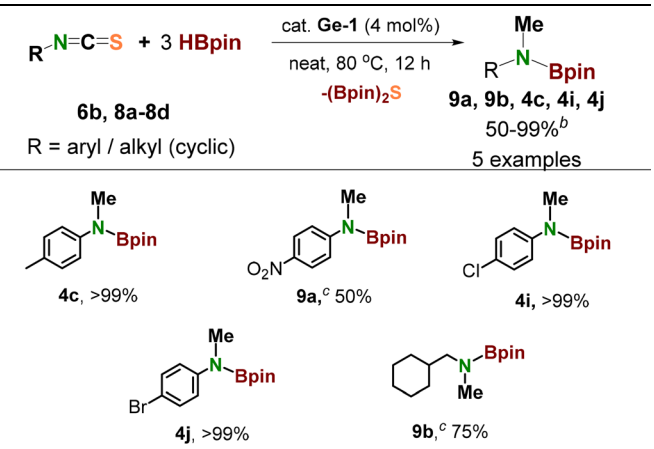
Once the optimized conditions were in hand, we screened various substrates bearing electron-donating (**6a**) and withdrawing substituents on the phenyl ring (–NO_2 (**8a**), –Cl (**8b**), –Br (**8c**)) that produced the respective *N*-boryl methyl amines (**4c**, **9a**, **4i**, **4j**) in yields of up to 99% (except that **8a** gave 50% yield). However, using the above protocol, cyclic alkyl (**8d**) provided **9b** in a moderate yield (Table 5). All the products were characterized by multinuclear NMR spectroscopy. In the ^{1}H NMR spectrum, a singlet resonance peak of the *N*-methyl proton (NCH_3) signal was found in the range of 2.54–3.10 ppm, and the carbon

Table 4 Substrate scope for mono-hydroboration of isothiocyanates using the **Ge-1** complex as a catalyst[a]



[a] Reaction conditions: isothiocyanate (0.3 mmol, 1.0 equiv.), HBpin (0.3 mmol, 1.0 equiv.), and cat. **Ge-1** (3 mol%) were placed in a vial inside the N_2 glove box and stirred for 8 h at 70 °C under neat conditions. [b]Conversion was examined by ^{1}H NMR spectroscopy based upon the consumption of isothiocyanate, and a newly formed characteristic proton (NC*H*S) resonance signal was identified.

Table 5 Substrate scope for hydrodesulfurization of isothiocyanates using the **Ge-1** complex as a catalyst[a]



[a] Reaction conditions: isothiocyanate (0.3 mmol, 1.0 equiv.), HBpin (0.9 mmol, 3.0 equiv.), and cat. **Ge-1** (4 mol%) were placed in a vial inside the N_2 glove box and stirred for 12 h at 80 °C under neat conditions. S(Bpin)$_2$ is found as a side-product in all substrates. [b]The conversion was examined by ^{1}H NMR spectroscopy based on the consumption of isothiocyanate and the newly formed characteristic proton (NMe) resonance signal. [c]For **9a** and **9b** the conversion was determined by ^{1}H NMR spectroscopy using nitromethane as an internal standard.

signal for the (NCH_3) unit appeared in the range of 34.1–35.2 ppm, indicating the formation of *N*-boryl methyl amine products.

Hydroboration of isoselenocyanate

After the successful hydroboration reactions of CDI, isocyanates, and isothiocyanates, we were curious to explore the further reduction of isoselenocyanates.

The reaction of an equimolar amount of 2,6-dimethyl isoselenocyanate (**10a**) and HBpin in the presence of 5 mol% catalyst **Ge-1** at 70 °C for 12 h gave *N*-boryl selenoformamide (**11a**) in quantitative yield (Scheme 3). In the ^{1}H NMR spectrum, the characteristic NC*H*Se moiety signal was found in the downfield region at δ 12.19 ppm, and the distinctive carbon signal for NCHSe was observed at δ 205.2 ppm in the ^{13}C{^{1}H} NMR spectrum, confirming the product.

Stoichiometric experiments

We have studied stoichiometric experiments to establish the germanium and tin hydride-catalyzed hydroboration of heterocumulenes. Initially, a 1 : 1 stoichiometric reaction between catalyst **Ge-1** and DIC was carried out in C_6D_6 at 60 °C in a J. Young valve NMR tube afforded **Int A** after 8 h (Scheme 4), which was confirmed by mass spectrometry (HRMS) and multinuclear NMR spectroscopic methods. Subsequently, the reaction mixture was treated with 1 equiv. of HBpin, yielding catalyst **Ge-1** and **2a** with quantitative yield at rt after 30 min.

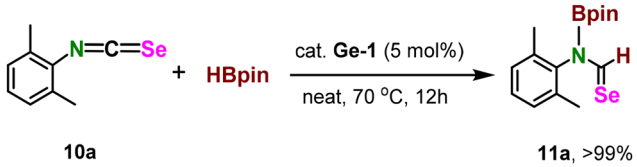
In the next step, catalyst **Ge-1** was mixed with 1.0 equiv. of 2,6-dimethylphenyl isocyanate (**3d**) in C_6D_6 in a J. Young valve NMR tube, forming **Int A1** after 1 h at rt (Scheme 4). Moreover, intermediate **Int A1** was confirmed by NMR and HRMS analyses. Next, a 1 : 1 molar ratio of **Int A1** and HBpin yielded complex **Ge-1** and the *N*-boryl formamide product (**4d**), as confirmed by ^{1}H and ^{13}C{^{1}H} and ^{11}B NMR spectroscopy.

Similarly, we carried out a 1 : 1 stoichiometric reaction of **Sn-2** with 2,6-diisopropylphenyl isocyanate (**3q**) in C_6D_6 in a J. Young valve NMR tube, forming **Int A1′** after 1 h at rt (Scheme 4), confirmed by ^{1}H, ^{13}C{^{1}H} and ^{119}Sn{^{1}H} NMR spectroscopy.

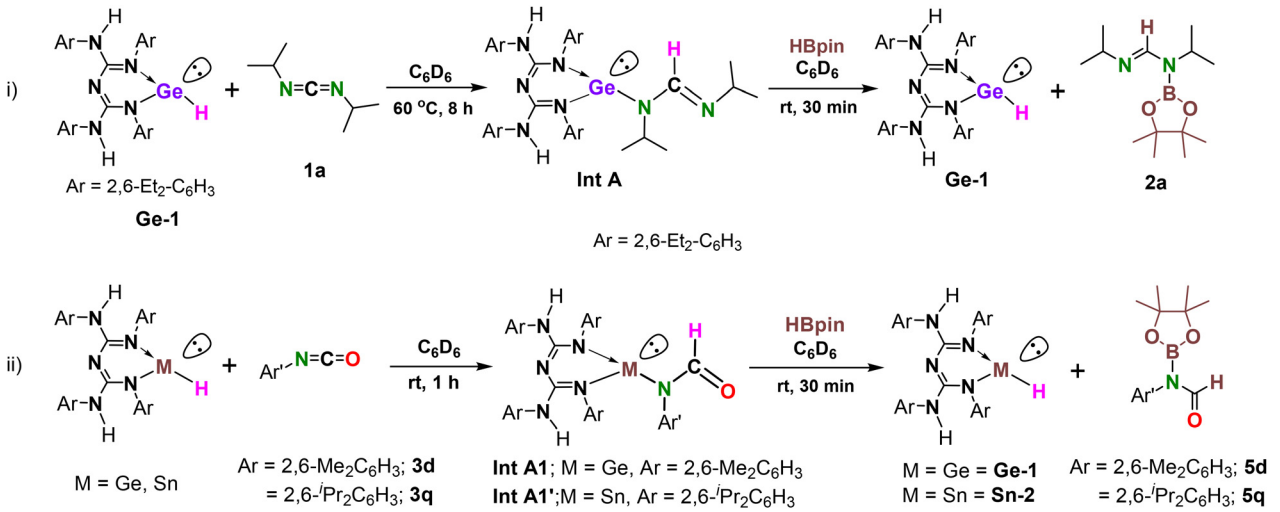
Further reaction of **Int A1′** with 1 equiv. of HBpin afforded complex **Sn-2** and the corresponding formamide **5q**, confirmed by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. A 1 : 1 stoichiometric reaction of (**Sn-2**) with pinacolborane at 80 °C for 12 h resulted in no reaction and left both the reactants unreacted. The outcomes of the control experiments ruled out any hidden boron catalysis.[30]

Catalytic cycle

Based on stoichiometric experiments, we have established a catalytic cycle for the germanium- and tin-catalyzed hydrobora-

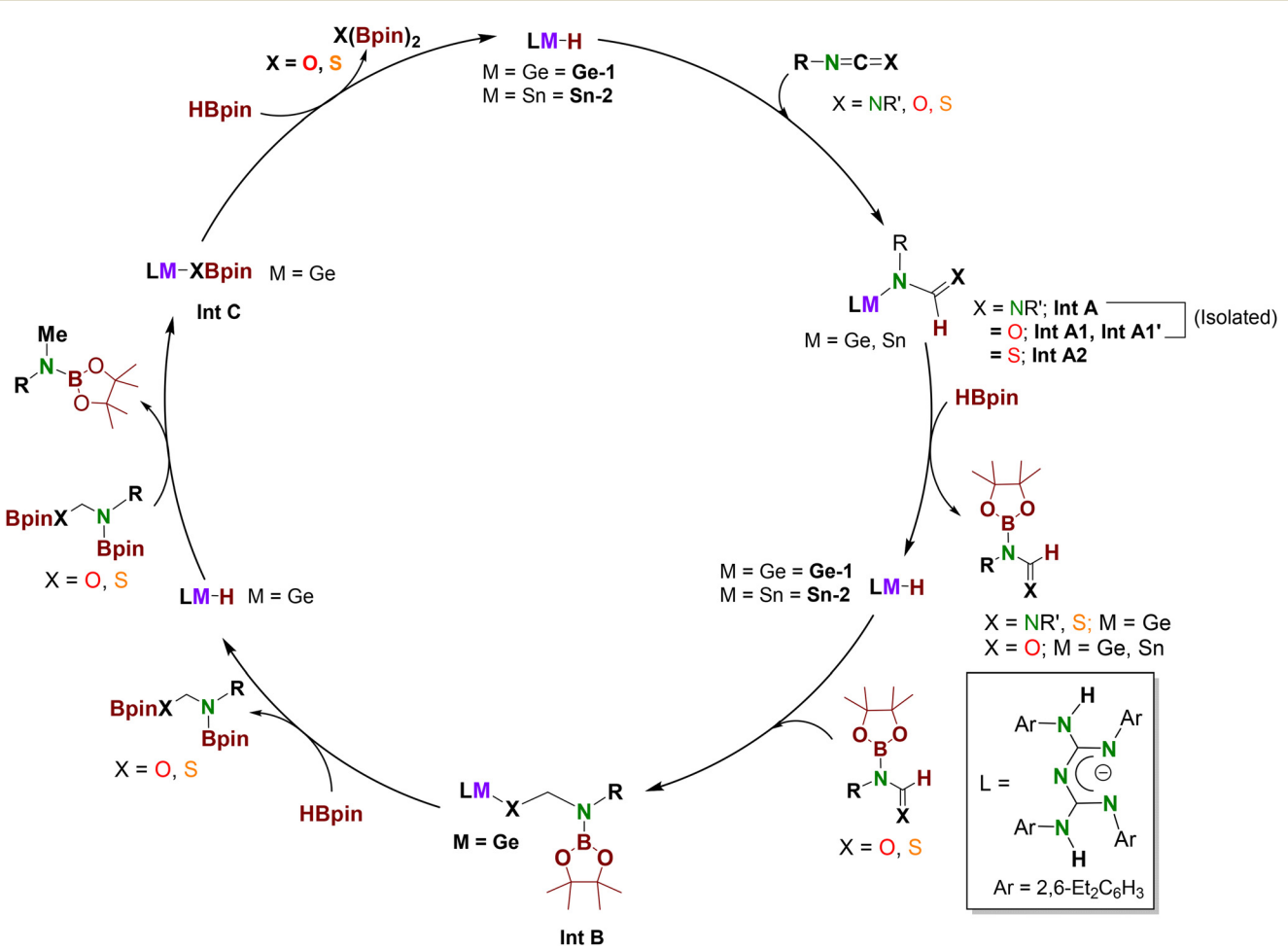


Scheme 3 Monohydroboration of 2,6-dimethyl isoselenocyanate using the **Ge-1** complex as a catalyst.

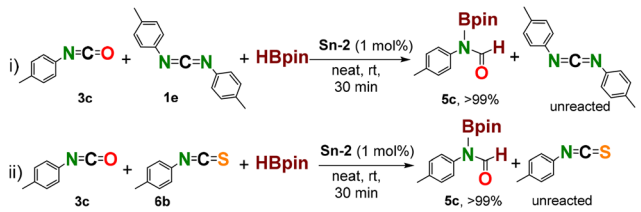


Scheme 4 Stoichiometric experiments.

tion of heterocumulenes. In the first step, the reaction of a 1 : 1 stoichiometric amount of metal hydride (**Ge-1**, **Sn-2**; NCO only) with CDI, NCO, and NCS independently afforded insertion products of bis-guanidinate germanium and tin complexes, **Int A**, **Int A1**, **Int A1′** and **Int A2**, respectively. These products were confirmed by multinuclear NMR and HRMS spec-



Scheme 5 A plausible mechanism for group 14 metal-hydride catalyzed hydroboration of heterocumulenes.



Scheme 6 Intermolecular chemoselective reductions of RNCO *vs.* RNCX (X = NR, S) catalyzed by the **Sn-2** complex.

troscopic analyses. Subsequently, **Int A**, **Int A1**, **Int A1′**, and **Int A2** independently reacted with HBpin to afford *N*-boryl formamidine, *N*-boryl formamide, and *N*-boryl thioformamide, respectively, and regenerate the corresponding metal catalysts. Further *N*-borylated products (except CDI) were treated with a catalyst to produce **Int B**, which reacted with HBpin to yield bis-(boryl) amine and regenerate the catalyst. Next, *N*-boryl methyl amine and **Int C** were formed through the reaction of the catalyst with bis(boryl) amine. Finally, **Int C** reacted with HBpin to generate the catalyst, yielding the side product $X(Bpin)_2$ {X = O, S} and closing the catalytic cycle (Scheme 5).

Intermolecular chemoselective reaction

The reaction of equimolar quantities of *p*-tolyl isocyanate (**3c**), *N*,*N*′-di(*p*-methyl phenyl)carbodiimide (**1e**), and HBpin was carried out with catalyst **Sn-2** (1 mol%) under neat conditions at room temperature for 30 minutes, which yielded the **3c** reduced product, *N*-boryl formamide (**5c**), in quantitative yield, in preference to carbodiimide reduction. Similarly, treating a 1 : 1 molar ratio of *p*-tolyl isocyanate (**3c**) and *p*-tolyl isothiocyanate (**6b**) with one equivalent of HBpin at room temperature for 30 minutes produced *N*-boryl formamide (**5c**) in quantitative yield, demonstrating a preference for **3c** reduction to **5c** over isothiocyanate reduction (Scheme 6).

Conclusion

In conclusion, we have demonstrated, for the first time, that low-valent germanium and tin hydrides can act as catalysts for the chemoselective hydroboration of heterocumulenes. A wide variety of *N*-boryl formamidines, *N*-boryl formamides, *N*-boryl thioformamides, and *N*-boryl selenoformamides were synthesized through the partial reduction of CDIs, isocyanates, isothiocyanates, and isoselenocyanates using HBpin. Additionally, a series of *N*-boryl methyl amines were produced by hydrodeoxygenation (HDO) and hydrodesulfurization (HDS) of isocyanates and isothiocyanates, respectively. Notably, molecular group 14 metal-hydrides proved to be effective catalysts for the partial and complete reduction of heterocumulenes. Furthermore, catalysts **Ge-1** and **Sn-2** exhibited excellent tolerance towards other reducible functional groups. A series of stoichiometric experiments confirmed that hydride species are responsible for all partial and complete reduction reactions of heterocumulenes.

Author contributions

The manuscript was written with contributions from all authors. All authors have approved the final version of the manuscript.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

The authors declare no competing financial interest.

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