NHC-Silyliumylidene Cation-Catalyzed Hydroboration of Isocyanates with Pinacolborane

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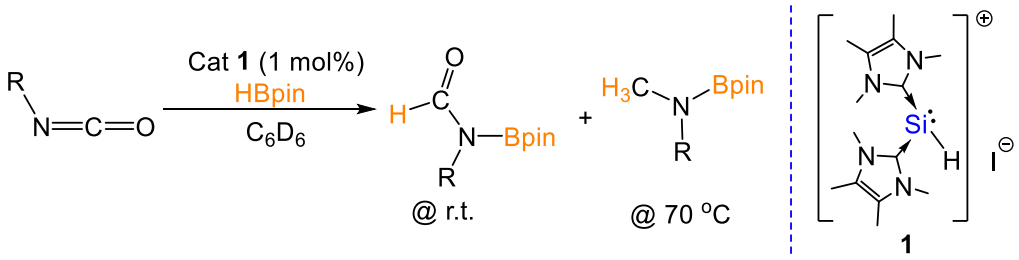
Abstract

The low-oxidation-state silicon-catalyzed hydroboration of isocyanates with pinacolborane (HBpin) using a NHC-silyliumylidene cation catalyst [$(IMe)_2SiH$]I (**1**, IMe = :C{N(Me)C(Me)}$_2$) is described. In the catalysis, the Si lone pair electrons activate isocyanates and the latter react with HBpin to form *N*-boryl formamides at room temperature. Catalyst **1** further activates *N*-boryl formamides at 70 °C, the intermediates of which react with HBpin to form *N*-boryl methylamines and $(pinB)_2O$.

Introduction

Silyliumylidene cations $[R\text{-}Si:]^+$ composing a dual functionality of Lewis acidic silicon cation and silylene are a promising compound to show transition-metal-like reactivity in small molecules activation and catalysis. Müller *et al.* reported a transient mono-substituted arylsilyliumylidene cation to activate the C(sp^2)-H bond of benzene.[1] A stable mono-substituted silyliumylidene cation was isolated by Hinz with the aid of sterically hindered carbazole substituent.[2] The isolation of stable silyliumylidene ions becomes more feasible by coordinating the silicon center with one or two, σ- or π-electron donating ligands.[3-14] Jutzi *et al*. reported a stable η^5-cyclopentadienyl silyliumylidene cation to catalyze the controlled degradation of oligo(ethyleneglycol) diethers.[3,4] Research groups of Driess and Aldridge synthesized two-coordinate β-diketiminato silyliumylidene cations for N-H bond activation.[5,6] Inoue *et al*. showed that a NHC–silyliumylidene cation reduced CO_2 to form CO and activated the C(sp)–H bond of phenylacetylene.[7,8] Kato *et al*. illustrated that labile-base-stabilized silyliumylidene cations activated multiple small molecules and used as a pre-catalyst for catalytic hydroboration of pyridine.[9] We recently reported a NHC-silyliumylidene cation complex $[(IMe)_2SiH]I$ (**1**, IMe = $:C\{N(Me)C(Me)\}_2$) to catalyze hydroboration of carbon dioxide, carbonyl compounds and pyridines using HBpin as well as the N-formylation of primary and secondary amines using $PhSiH_3$.[15,16] However, understanding how a silyliumylidene cation mediating catalysis is still in infancy. To conduct in-depth kinetic and mechanistic studies to unravel the most probable reaction pathway, our attention fell on sterically hindered heteroallene (Scheme 1), namely isocyanates. Herein, we report the first low-oxidation-state-silicon catalyzed hydroboration of isocyanates with HBpin using the NHC-silyliumylidene cation **1** as a catalyst.

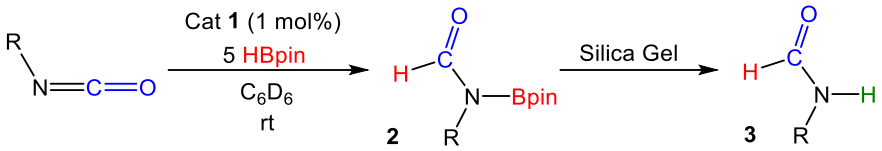


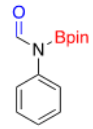
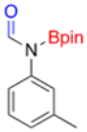
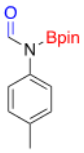
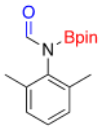
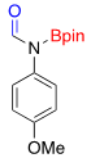
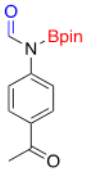
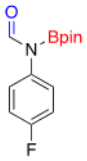
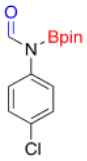
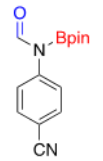
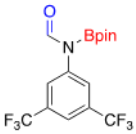
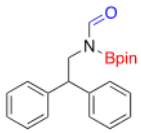
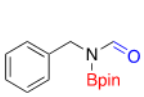
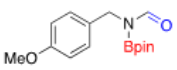
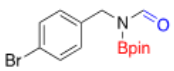
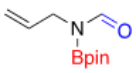
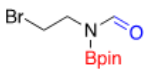
Scheme 1. 1-catalyzed hydroboration of isocyanates

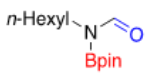
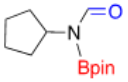
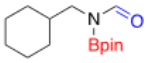
Results and Discussion

First, there was no reaction between catalyst **1** and HBpin, and no reaction between HBpin and isocyanates at room temperature and elevated temperatures (110 °C). Second, 1 mol% of **1** catalyzed selective hydroboration of isocyanates with 5 equiv. of HBpin in C_6D_6 at room temperature (optimized conditions, see the Supporting Information, Table S1) to form *N*-boryl formamides (Table 1). Third, aromatic isocyanates consisting of electron-donating and -withdrawing substituents were quantitatively converted to their *N*-boryl formamides (**2a-2m, 2n-2v**). Strongly electron-withdrawing 2- and 3-nitrophenyl isocyanates (**2s**, **2t**) required heating at 70 °C and 40 °C, respectively. Fourth, both benzylic and alkyl isocyanates were hydroborated quantitatively to their corresponding *N*-boryl formamides (**2w-2ae**). Next, excellent chemoselectivity was displayed in the presence of various reducible substituents such as acetyl-, nitro-, cyano-, halide and alkene functional groups. Their formations were further supported by X-ray crystallography of **3f**, **3h** and **3q** (Fig. S195-197).

Table 1. Scope of *N*-boryl formamide products



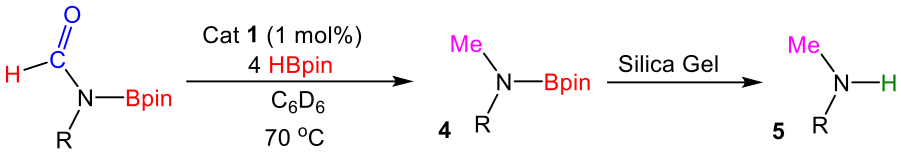
				
2a	**2b**	**2c**	**2d**	**2e**
>99(73)%[d]	>99(74)%	>99(70)%	>99(72)%	>99(70)%
50 h^{-1}	22 h^{-1}	100 h^{-1}	67 h^{-1}	100 h^{-1}
				
2f	**2g**	**2h**	**2k**	**2m**
>99(63)%	>99(76)%	>99(80)%	>99(92)%	>99(93)%
100 h^{-1}	100 h^{-1}	50 h^{-1}	50 h^{-1}	100 h^{-1}
				
2n	**2p**	**2q**	**2r**	**2s**[c]
>99(65)%	>99(78)%	>99(72)%	>99(65)%	>99(73)%
50 h^{-1}	100 h^{-1}	100 h^{-1}	100 h^{-1}	100 h^{-1}
				
2t[b]	**2u**	**2v**[b]	**2w**	**2x**
>99(50)%	>99(71)%	>99(60)%	>99(75)%	>99 %
100 h^{-1}	50 h^{-1}	25 h^{-1}	33 h^{-1}	100 h^{-1}
				
2y	**2z**	**2aa**	**2ab**[b]	
>99%	>99%	>99%	>99%	
100 h^{-1}	100 h^{-1}	67 h^{-1}	25 h^{-1}	

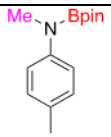
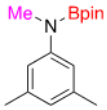
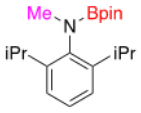
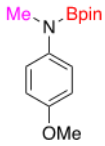
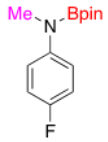
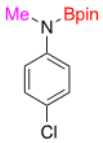
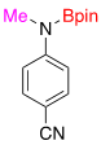
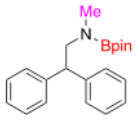
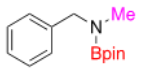
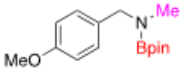
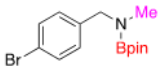
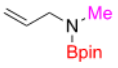
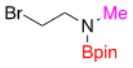
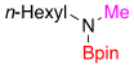
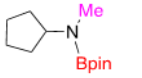
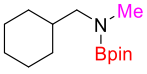
		
2ac[b]	**2ad**[b]	**2ae**[b]
>99%	>99%	>99 %
50 h^{-1}	50 h^{-1}	50 h^{-1}

[a]Reaction conditions: catalyst **1** (1.34 mg, 0.0033 mmol), HBpin (0.24 mL, 1.65 mmol), isocyanates (0.33 mmol), C_6D_6 (0.5 mL), stirred at 25 °C. [b]Reaction conducted at 40 °C. [c]Reaction conducted at 70 °C. [d]Yields were determined by ^{1}H NMR spectroscopy based on isocyanate consumption and appearance of *N*-boryl formamide NC(=O)*H* signal. Isolated yields were reported in parenthesis.

Upon successful generation of the above *N*-boryl formamides, the *in situ* reaction mixtures were heated at 70 ºC to form *N*-boryl methylamines (Table 2). Aromatic *N*-boryl formamides containing electron-donating and -withdrawing groups were hydroborated to generate the corresponding *N*-boryl methylamines (**4a**-**4m**, **4p**-**4v**) along with diborate ether [$(pinB)_2O$]. Second, functional group tolerance to halide, cyano, nitro and alkene substituents was maintained except *N*-boryl 4-acetylphenylformamide **2n** where a mixture of products was observed. Third, sterically hindered **2f**-**2h** required heating at 110°C and **4f**-**4h** formed did not hydrolyze to afford the corresponding methylamines during column chromatography (Fig. S65-67 & 74-76; Fig. S198 for X-ray crystal structure of **4h**). Benzyl (**2w**-**2z**) and alkyl (**2aa**-**2ae**) formamides required prolonged heating at 110 °C to get quantitative conversion.

Table 2. Scope of *N*-boryl methylamine products



				
4a	**4b**	**4c**	**4d**	**4e**
>99(65)%	>99(68)%	>99(82)%	>99(78)%	>99(80)%
25 h^{-1}	4 h^{-1}	33 h^{-1}	33 h^{-1}	33 h^{-1}
				
4f[c,e]	**4g**[c,e]	**4h**[d,e]	**4k**[b]	**4m**
>99(81)%	>99(81)%	>99(64)%	>99(86)%	>99(73)%
5 h^{-1}	4 h^{-1}	5 h^{-1}	8 h^{-1}	50 h^{-1}
				
4p	**4q**	**4r**	**4t**	**4u**
>99(88)%	>99(90)%	>99(86)%	>99(74)%	>99(80)%
50 h^{-1}	50 h^{-1}	50 h^{-1}	50 h^{-1}	50 h^{-1}
				
4v	**4w**[c]	**4x**[c]	**4y**[c]	**4z**
>99(81)%	>99(92)%	>99%	>99%	>99%
50 h^{-1}	5 h^{-1}	4 h^{-1}	4 h^{-1}	4 h^{-1}
				
4aa[c]	**4ab**	**4ac**	**4ad**[c]	**4ae**
>99%	>99(77)%	>99%	>99%	>99%
7 h^{-1}	5 h^{-1}	6 h^{-1}	6 h^{-1}	6 h^{-1}

[a]Reaction conditions: catalyst **1** (1.34 mg, 0.0033 mmol), HBpin (0.24 mL, 1.65 mmol), *N*-boryl formamides (0.33 mmol), C_6D_6 (0.5 mL), stirred at 70 °C. [b]Reaction at 90 °C. [c]Reaction at 110 °C. [d]Reaction at 110 °C with 10 eq. of HBpin. [e]Isolated as *N*-boryl methylamines. [f]Yields were determined by

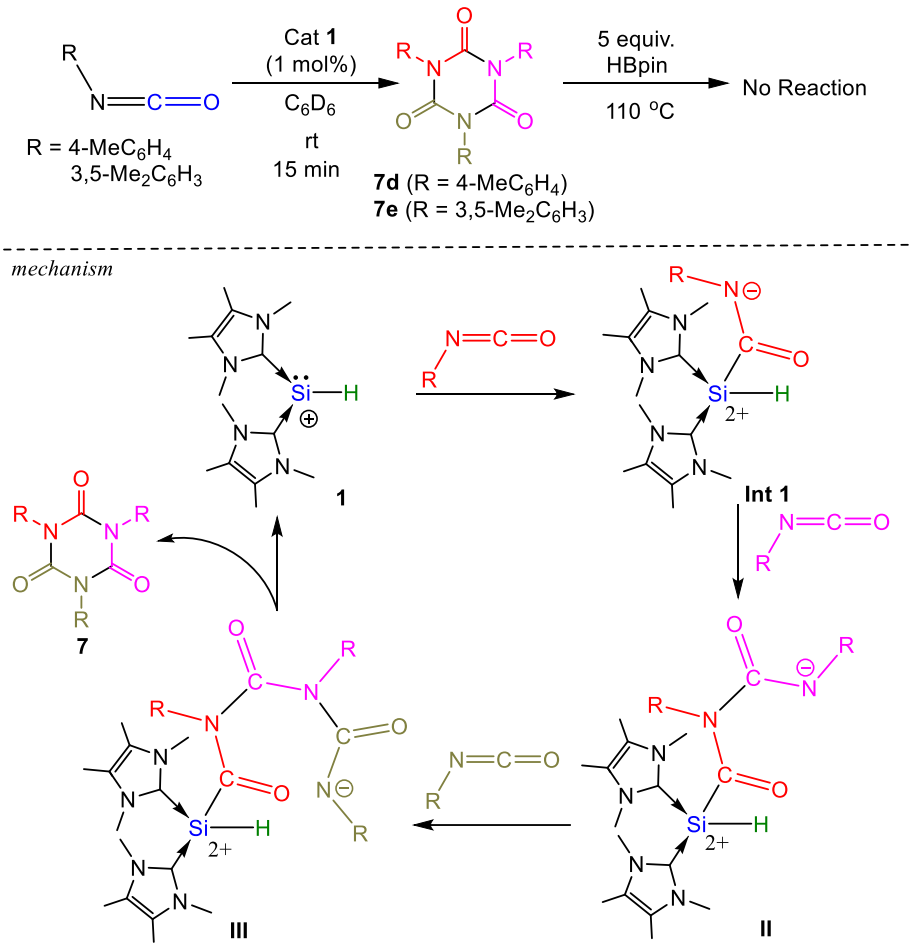
^{1}H NMR spectroscopy based on consumption of *N*-boryl formamide NC(=O)*H* signal and appearance of *N*-boryl methylamine NCH_3 signal. Isolated yields were reported in parenthesis.

In order to shed some light into the practical aspect of our catalytic protocol, a large-scale reaction (3.3 mmol) was carried out. *p*-tolyl isocyanate was fully converted to **2d** (Yield: >99(65)%, TOF: 100 h^{-1}). Upon heating to 70 °C for 3h, **2d** was fully converted to *N*-boryl methylamine **4d** (Yield: >99(70)%, TOF: 33.3 h^{-1}). Both selectivity, yield and TOF were preserved upon upscaling of our catalytic protocol.

In these catalyses, the activity of catalyst **1** in terms of TOF and product yield are better than that of other metal catalysts such as β-diketiminato magnesium,[17] bis(guanidinate) aluminum and zinc dihydride complexes,[18,19] $AgSbF_6$[20] and $Co(acac)_2$[21] (For example, **4m**, [Zn]: yield = >99%, TOF = 4.17 h^{-1}; [Al]: yield = >99 %, TOF = 4.17 h^{-1}; [Co]: yield = 91%, TOF = 0.95 h^{-1}; see Table S4).

As no reaction occurred between catalyst **1** and HBpin or between HBpin and isocyanates, catalyst **1** should activate isocyanate in the first step of catalysis. To support this, **1** catalyzed cyclotrimerization of *p*-tolyl or 3,5-dimethylphenyl isocyanate in C_6D_6 in 15 min to form the corresponding isocyanurates (**7**, Scheme 2, Fig. S200-201). In this reaction, catalyst **1** attacks isocyanate to form **Int1** (Scheme 2). The negatively charged nitrogen center subsequently attacks the second isocyanate to form $[(IMe)_2(H)Si\{C(=O)(NAr)\}_2]$ (**II**), which attacks the third isocyanate to form $[(IMe)_2(H)Si\{C(=O)(NAr)\}_3]$ (**III**). An intramolecular nucleophilic attack of the terminal di-coordinated nitrogen center on the carbon center of the SiCO unit leads to the six-membered aryl isocyanurate **7**. In addition, the corresponding isocyanurate did not react with HBpin at room temperature or 110 °C, indicating that **7** is not an intermediate in the catalysis.

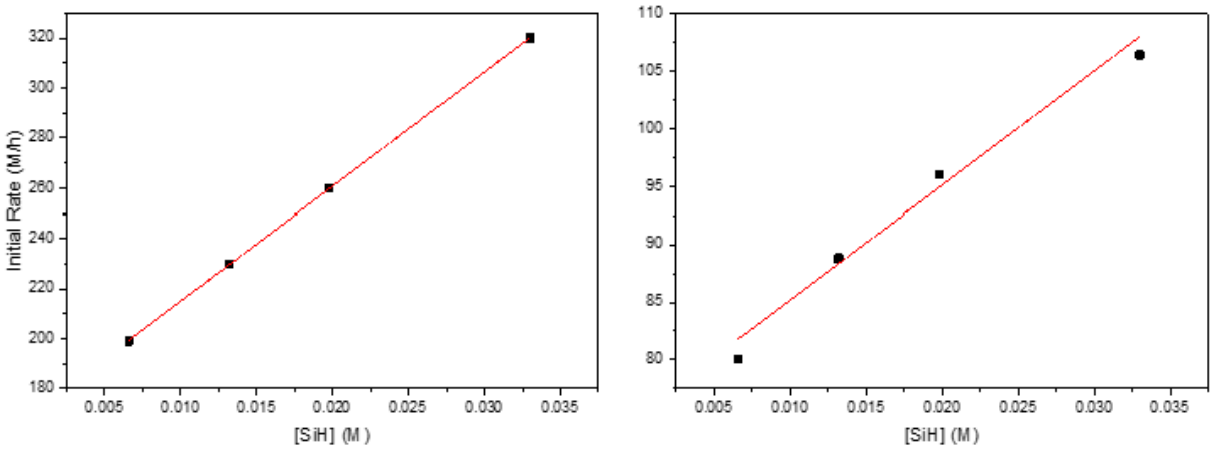
Similar catalytic cyclotrimerization of isocyanate mediated by Lewis bases, namely NHC,[22] *N*-heterocyclic olefin,[23] proazaphosphatrane[24] and 2-phosphaethynolate anion[25] were reported.



Scheme 2. Formation of isocyanurates and its proposed mechanism

In this context, catalyst **1** activates isocyanate, which allows the H-B bond of HBpin to insert into the C-N bond to form *N*-boryl formamide **2** and to regenerate catalyst **1**. It is believed that excess HBpin (5 eqv.) and solvent (C_6D_6) are required to prevent cyclotrimerization of isocyanate. To support this catalytic mechanism, initial rate kinetic studies for the **1**-catalyzed hydroboration of 3,5-dimethylphenyl isocyanate and 5 equiv. of HBpin at room temperature and 70 °C were performed by ^{1}H NMR spectroscopy, where the reaction is first order with respect to

the amount of the isocyanate present for the formation of *N*-boryl formamides and methylamines (Figures 1 & S6).



(a) (b)

Figure 1. Kinetic studies for the **1**-catalyzed hydroboration of 3,5-dimethylphenyl isocyanate to form (a) *N*-boryl formamide and (b) *N*-boryl methyl amine.

DFT calculations (B3LYP-B3(DJ)/def2-SVP, Figure 2) suggest that catalyst **1** mediated the hydroboration and hydrodeoxygenation of isocyanates. The Si lone pair of electrons attacks the carbon center of 3,5-dimethylphenyl isocyanate to form **TS1** via a low kinetic barrier ($\Delta G_{rel}^{\ddagger}$ = 13.5 kcal/mol) whereby electron delocalization results in forming a negatively charged nitrogen center in **Int1** (ΔG_{rel} = 9.1 kcal/mol). It then attacks the boron center of HBpin while the hydride simultaneously attacks the carbonyl group via a 4-membered ring transition state **TS2** ($\Delta G_{rel}^{\ddagger}$ = 27.0 kcal/mol). This yields **Prd1** (ΔG_{rel} = -21.3 kcal/mol) and concurrently regenerates **1**. The calculated kinetic barriers (13.5, 17.9 kcal/mol) are consistent with reaction conditions that room temperature is sufficient to promote the catalysis. The silicon lone pair of electrons then attacks the carbonyl group of **Prd1** via a relatively high kinetic barrier (34.1 kcal/mol) to generate **TS3**

($\Delta G_{rel}^{\ddagger}$ = 12.8 kcal/mol) which explains high reaction temperatures of 70 °C being essential to promote hydrodeoxygenation. The negatively charged oxygen centers of **TS3** coordinates with the second molecule of HBpin to form **Int3** (ΔG_{rel} = -32.8 kcal/mol). The H-B bond then attacks the methine carbon to cleave the C-O bond via **TS4** ($\Delta G_{rel}^{\ddagger}$ = -18.6 kcal/mol), which results in the formation of the Si-N bond in **Int3** and diborate ether $(pinB)_2O$ (ΔG_{rel} = -45.6 kcal/mol). The nitrogen lone pair electrons coordinate with the third HBpin molecule, where the H-B bond simultaneously attacks the methylene moiety to break the Si-C bond via **TS5** ($\Delta G_{rel}^{\ddagger}$ = -29.2 kcal/mol) to form **Prd2** and regenerate catalyst **1** (ΔG_{rel} = -84.4 kcal/mol). The mechanism is different from that mediated by metal hydride catalysts,[18] where the metal-hydride bond inserts into isocyanate to form metal formamidate which is hydroborated by HBpin to form formamide. The latter is further activated by the metal-hydride bond, in which the intermediate is hydroborated by HBpin to form *N*-boryl methylamine and metal boryloxide. Metal boryloxide reacts with HBpin to form the metal hydride catalyst.

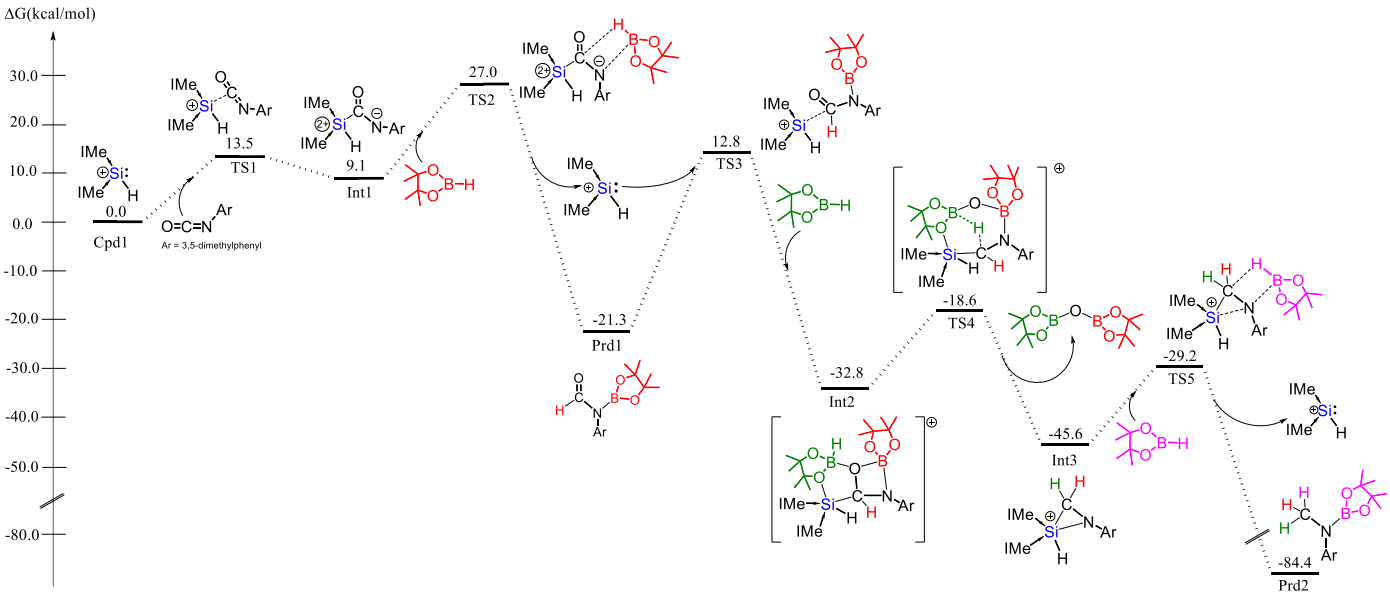


Figure 2. DFT calculations for **1**-catalyzed chemoselective hydroboration of isocyanate using HBpin at the B3LYP-B3(DJ)/def2-SVP level of theory.

In the catalytic hydroboration of unsaturated compounds, Thomas *et al*. argued that nucleophilic catalysts such as metal hydrides decomposed HBpin at above 50 ºC to form BH_3, whereby the latter supersedes the actual catalyst during catalysis.[26] As the **1**-catalyzed hydroboration of isocyanates was performed at 70 ºC to form *N*-boryl methylamines and the reaction therein contained nucleophiles namely catalyst **1**, isocyanates and *N*-boryl formamides, the formation of BH_3 and its role in the catalysis were clarified by ^{11}B NMR spectroscopy. In the reaction of 4-methoxyphenyl isocyanate **1m** with HBpin, TMEDA (1 mol% or 5 equiv.) and catalyst **1** (1 mol%) at 70 ºC, the ^{11}B NMR spectrum showed the formation of trace amount of four-coordinate BH_3 derivatives. Since catalyst **1** and **1m** did not react with HBpin at 70 ºC, *N*-boryl formamide **2m** should be the nucleophile to react with HBpin to form trace amounts of BH_3. The catalytic capability of BH_3 toward hydroboration of isocyanates was subsequently examined. High catalytic loading of $BH_3.SMe_2$ (6.8 mol%) was used to catalyze hydroboration of **1m** with HBpin in C_6D_6 at 70 ºC for 3h, however, the catalytic activity [product yield (49%), TOF (2.41 h^{-1})] is much lower in comparison with **1** (catalytic loading: 1 mol%), indicating that trace amount of BH_3 is not the major catalyst in the catalytic hydroboration and did not deviate the **1**-mediated catalytic mechanism. The above kinetic studies show the same results.

Conclusion

In conclusion, **1** catalyzed metal-free chemoselective hydroboration of isocyanates with HBpin. Kinetic and theoretical studies show that **1** used the Si lone pair of electrons to activate isocyanates and the latter became able to react with HBpin to form *N*-boryl formamides at room temperature. **1** further activated *N*-boryl formamides at 70 ºC and the latter became feasible to react with HBpin to form *N*-boryl methylamines and $(pinB)_2O$.

ASSOCIATED CONTENT

Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org

Experimental procedures and NMR spectra for all compounds, molecular structures of compounds **3f**, **3h**, **3q**, **4h**, **5r**, **7d** and **7e** obtained by X-ray crystallography and DFT calculations (PDF)

Accession Codes

CCDC-2247380 **4h** and CCDC-2247384 **7e** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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SYNOPSIS TOC

A NHC-silyliumylidene cation complex uses its silicon lone pair of electrons to catalyze hydroboration of isocyanates with HBpin to form *N*-boryl formamides at room temperature and *N*-boryl methylamines at 70 °C.