

# Commercially available tin(II) halides as catalysts for the dihydroboration of carbodiimides

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**ABSTRACT:** Dihydroboration of a variety of carbodiimides using pinacolborane (HBpin) is achieved through commercially available tin(II) halides [SnBr<sub>2</sub> (**1**) and SnCl<sub>2</sub> (**2**)] as catalysts at room temperature (21 °C) with short reaction times (0.13 to 6 h).

## INTRODUCTION

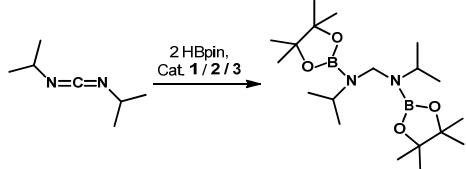
Carbodiimides (R–N=C=N–R) are a unique class of organic compounds containing two C=N bonds (R = alkyl or aryl group). Addition of E–H (E = N, P, O, B, S, C) moiety across the C=N bonds of carbodiimides has gained tremendous interest in the recent years;<sup>1–4</sup> if E is a boron atom, it is the hydroboration of carbodiimides. Due to the presence of two C=N bonds, both monohydroborylated and/or dihydroborylated products can be anticipated. Hill and coworkers showed the monohydroboration of carbodiimides using a  $\beta$ -diketiminato(alkyl)magnesium catalyst,<sup>5</sup> and the group of Eisen reported an organoactinide catalysed monohydroboration of carbodiimides.<sup>6</sup> The group of Ramos has reported the 9-borabicyclo[3.3.1]nonane catalysed monohydroboration of carbodiimides.<sup>7</sup> Dihydroboration is known for only one carbodiimide, *N,N'*-diisopropyl carbodiimide (DIC), and two catalysts can achieve this (a) 1 mol% of magnesium hydridotriphenylborate ([Mg(thf)<sub>6</sub>][HBPh<sub>3</sub>]<sub>2</sub>) precatalyst<sup>8</sup> reported by Okuda and coworkers took 12 h at 60 °C using HBpin for >99% conversion, and (b) 10 mol% of Hill's magnesium tris(pentafluorophenyl)hydridoborate catalyst LMg[HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] consumed 30 h at room temperature or 6 h at 60 °C to achieve >90% conversion (L = HC{(Me)CNDipp}<sub>2</sub>).<sup>9</sup> This discussion divulges that dihydroboration of carbodiimides is difficult to achieve. But, our studies have revealed that commercially available tin(II) halides (halide = Br **1**, Cl **2**) can work as efficient dihydroboration catalysts for a variety of carbodiimides. For example, 0.5 mol% of **1** and **2** dihydroborylated DIC in 8 and 10 min, respectively, at room temperature (21 °C) with 99% conversion and the details are summarized here.

## RESULTS AND DISCUSSION

The reaction of DIC with 2 equivalents of HBpin for 8 min using 0.5 mol% of SnBr<sub>2</sub> (**1**) in hexane, tetrahydrofuran (THF), chloroform-d (CDCl<sub>3</sub>), and toluene gave the desired dihydroborylated carbodiimide (*N,N'*-(diboryl)diisopropylaminal) with a % conversion of 84, 86, 28, and >99, respectively (Table 1; entries 1-4). These reactions revealed that toluene is the suitable solvent. In the optimized solvent, the efficiency of other catalysts SnCl<sub>2</sub> (**2**) and SnI<sub>2</sub> (**3**) was also examined; the former and latter took 10 and 45 min to give >99 and 88% conversions, respectively (Table 1; entries 5-6).

As **3** showed the least efficiency among the studied tin(II) halides, it was not used for further studies.

**Table 1 Optimization of the reaction conditions for the dihydroboration of DIC with HBpin using tin(II) catalysts SnBr<sub>2</sub> (**1**), SnCl<sub>2</sub> (**2**), and SnI<sub>2</sub> (**3**)**

				
E. no.	Catalyst	Solvent	Time (min)	% Con.
1	1	Hexane	8	84
2	1	THF	8	86
3	1	CDCl <sub>3</sub>	8	28
4	1	Toluene	8	>99
5	2	Toluene	10	>99
6	3	Toluene	45	88
7	---	Toluene	60	0
Conditions: DIC (1 mmol), HBpin (2 mmol), room temperature = 21 °C. % Conversion (% Con.) was determined using <sup>1</sup> H NMR spectroscopy (See the Supporting Information (SI) for details).				

No reaction occurred when a tin(II) halide was not used (Table 1; entry 7). The substrate scope was tested using a variety of carbodiimides (Table 2). Reaction of *N,N'*-dicyclohexylcarbodiimide (DCC) with two equivalents of HBpin afforded the dihydroborylated DCC with 99% conversion in the presence of 0.5 mol% of **1** and **2** after 0.25 and 0.42 h, respectively (Table 2; entries 1-2). Thus, in comparison to DIC, DCC required more reaction times. The diaryl carbodiimides required further demanding conditions. Hence, the reaction of *N,N'*-diphenylcarbodiimide (DPC) with two equivalents of HBpin required a catalytic loading of 5 and 10 mol% of compounds **1** and **2** to result in 99% conversions after 3 and 3.5 h, respectively. When methyl groups are present on the *para*-positions of the phenyl groups in DPC (as

in *N,N'*-di-*p*-tolylcarbodiimide, DPTC), the time required [0.25 h (**1**) and 1.5 h (**2**)] for quantitative conversions (with the same catalytic loading used for DPC) were less than those of DPC. *N*-*i*-butyl-*N'*-phenylcarbodiimide (IPC), an unsymmetrical carbodiimide with *i*-Bu and phenyl groups on the nitrogen atoms needed further stringent conditions. With the same catalytic loading of **1** and **2** used for DPC, IPC's reaction with 2 equivalent of HBpin required 5.5 and 6 h for the formation of the corresponding dihydroborylated product, respectively. To check, what happens when one equivalent of HBpin is used, an equimolar reaction of DIC with HBpin was carried out using 1 mol% of catalysts **1** and **2** for 20 min. Analysis of the products after a workup using <sup>1</sup>H NMR spectroscopy revealed the presence of a mixture of monohydroborylated DIC (*N*-borylformamidine), dihydroborylated DIC, and unreacted DIC (Figure 16; see the SI). Same was the result when this reaction was repeated with two other carbodiimides DCC and DPTC. These data reveal that monohydroborylated carbodiimides are initially formed and their conversion to the dihydroborylated carbodiimides is very fast.

**Table 2 Dihydroboration of carbodiimides using catalysts SnBr<sub>2</sub> (**1**) and SnCl<sub>2</sub> (**2**)**

E. no.	R	R'	Cat. (mol%)	Time (h)	% Con.
1	Cy	Cy <sup>a</sup>	<b>1</b> (0.5)	0.25	>99
2	Cy	Cy <sup>a</sup>	<b>2</b> (0.5)	0.42	>99
3	Ph	Ph	<b>1</b> (5)	3	>99
4	Ph	Ph	<b>2</b> (10)	3.5	>99
5	<i>p</i> -tolyl	<i>p</i> -tolyl	<b>1</b> (5)	0.25	>99
6	<i>p</i> -tolyl	<i>p</i> -tolyl	<b>2</b> (10)	1.5	>99
7	<sup><i>i</i></sup> Bu	Ph	<b>1</b> (5)	5.5	>99
8	<sup><i>i</i></sup> Bu	Ph	<b>2</b> (10)	6	>99
Conditions: Carbodiimide (1 mmol), HBpin (2 mmol), solvent = toluene, room temperature = 21 °C. % Conversion was determined using <sup>1</sup> H NMR spectroscopy (See the SI).					

Apart from the NMR spectroscopic characterization of the dihydroborylated carbodiimides (see the SI), structural characterization of the dihydroborylated DPC (*N,N'*-(diboryl)-diphenylaminal) was also performed (Figure 17; see the SI). The N-C-N bond angle (112.79°) indicates that the methylene carbon is sp<sup>3</sup> hybridized and confirms the double reduction of DPC. This is augmented further by the lengths of the N-CH<sub>2</sub> bonds (N2-C1 1.462 Å and N1-C1 1.460 Å) that are comparable to those in *N,N'*-(diboryl)diisopropylaminal (1.4559 Å, 1.4622 Å).<sup>9</sup>

## CONCLUSION

Dihydroboration of a variety of carbodiimides is shown for the first time. Most importantly, the catalysts used are commercially available tin(II) halides and the dihydroboration is achieved at room temperature (21 °C). Currently, the mechanism of the tin(II) halide catalyzed dihydroboration of carbodiimides and the feasibility of extending the utility of tin(II) halides for the hydroboration of other important organic substrates are being investigated in our laboratory.

## ASSOCIATED CONTENT

### Supporting Information

Experimental data, NMR spectra, and crystallographic details. "This material is available free of charge via the Internet at <http://pubs.acs.org>."

### Accession Code

CCDC 1905681 contains the crystallographic data. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto: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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### Notes

The authors declare no competing financial interest.

## REFERENCES

- [1] For examples see: (a) Zhang, W. X.; Xu, L.; Xi, Z. Recent development of synthetic preparation methods for guanidines via transition metal catalysis. *Chem. Commun.* **2015**, 51, 254–265. (b) Xue, M.; Zheng, Y.; Hong, Y.; Yao, Y.; Xu, F.; Zhang, Y.; Shen, Q. Catalytic addition of amines to carbodiimides by bis(diketimate)lanthanide(II) complexes and mechanistic studies. *Dalton Trans.* **2015**, 44, 20075–20086.
- [2] (a) Behrle, A. C.; Schmidt, J. A. R. Insertion reactions and catalytic hydrophosphination of heterocumulenes using  $\alpha$ -metalated *N,N*-dimethylbenzylamine rare-earth-metal complexes. *Organometallics*, **2013**, 32, 1141–1149. (b) Zhang, W. X.; Nishiura, M.; Hou, Z. Alkali-metal-catalyzed addition of primary and secondary phosphines to carbodiimides. A general and efficient route to substituted phosphaguanidines. *Chem. Commun.* **2006**, 3812–3814.
- [3] (a) Imberdis, A.; Lefèvre, G.; Thuéry, P.; Cantat, T. Metal-free and alkali-metal-catalyzed synthesis of isoureas from alcohols and carbodiimides. *Angew. Chem. Int. Ed.*, **2018**, 57, 3084–3088. (b) Liu, H.; Khononov, M.; Fridman, N.; Tamm, M.; Eisen, M. S. Catalytic addition of alcohols into carbodiimides promoted by organoactinide complexes. *Inorg. Chem.*, **2017**, 56, 3153–3157.
- [4] For examples see: Liu, H.; Fridman, N.; Tamm, M.; Eisen, M. S. Catalytic addition of alcohols to carbodiimides mediated by benzimidazolin-2-iminato actinide complexes. *Organometallics* **2017**, 36, 4600–4610. (b) Batrice, R. J.; Eisen, M. S. Catalytic insertion of E–H bonds (E = C, N, P, S) into heterocumulenes by amido-actinide complexes. *Chem. Sci.*, **2016**, 7, 939–944.
- [5] Weetman, C.; Hill, M. S.; Mahon, M. S. Magnesium catalysis for the hydroboration of carbodiimides. *Chem.–Eur. J.*, **2016**, 22, 7158–7162.
- [6] Liu, H.; Kulbitski, K.; Tamm, M.; Eisen, M. S. Organoactinide-catalyzed monohydroboration of carbodiimides. *Chem.–Eur. J.*, **2018**, 24, 5738–5742.
- [7] (a) Ramos, A.; Antiñolo, A.; Hermosilla, F. C.; Fernández-Galán, R.; Diéguez, A. R.; García-Vivó, D. Carbodiimides as catalysts for the reduction of CO<sub>2</sub> with boranes. *Chem. Commun.*, **2018**, 54, 4700–4703. (b) Ramos, A.; Antiñolo, A.; Hermosilla, F. C.; Galán, R. F.; García-Vivó, D. 9-Borabicyclo[3.3.1]nonane: a metal-free catalyst for the hydroboration of carbodiimides. *Chem. Commun.*, **2019**, 55, 3073–3076.
- [8] Mukherjee, D.; Shirase, S.; Spaniol, T. P.; Mashima, K.; Okuda, J. Magnesium hydridotriphenylborate [Mg(thf)<sub>6</sub>][HBPh<sub>3</sub>]<sub>2</sub>: a versatile hydroboration catalyst. *Chem. Commun.*, **2016**, 52, 13155–13158.
- [9] Anker, M. D.; Arrowsmith, M.; Arrowsmith, R. L.; Hill, M. S.; Mahon, M. F. Alkaline-earth derivatives of the reactive [HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>−</sup> Anion. *Inorg. Chem.*, **2017**, 56, 5976–5983.

