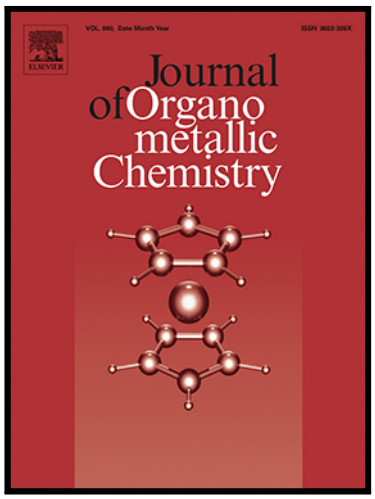


Readily Available Lithium Compounds as Catalysts for the Hydroboration of Carbodiimides and Esters

Milan Kumar Bisai , Kritika Gour , Tamal Das , Kumar Vanka , Sakya S. Sen

PII: S0022-328X(21)00245-X
DOI: https://doi.org/10.1016/j.jorganchem.2021.121924
Reference: JOM 121924

To appear in: *Journal of Organometallic Chemistry*

Received date: 27 March 2021
Revised date: 2 June 2021
Accepted date: 4 June 2021

Please cite this article as: Milan Kumar Bisai , Kritika Gour , Tamal Das , Kumar Vanka , Sakya S. Sen , Readily Available Lithium Compounds as Catalysts for the Hydroboration of Carbodiimides and Esters, *Journal of Organometallic Chemistry* (2021), doi: https://doi.org/10.1016/j.jorganchem.2021.121924

Readily Available Lithium Compounds as Catalysts for the

Hydroboration of Carbodiimides and Esters

Milan Kumar Bisai,[ac] Kritika Gour,[ac] Tamal Das,[bc] Kumar Vanka,*[bc] and Sakya S. Sen*[ac]

[a]*Inorganic Chemistry and Catalysis Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pashan, Pune 411008 (India);* [b]*Physical and Material Chemistry Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pashan, Pune 411008 (India);*

[c]*Academy of Scientific and Innovative Research (AcSIR), Ghaziabad-201002 (India).*

Correspondence should be addressed: ss.sen@ncl.res.in, k.vanka@ncl.res.in

Highlights

(a) The catalytic application of organolithium compounds is very limited due to their high reactivity and aggregation phenomena. However, the paradigm started to shift recently, when the groups of Okuda (J. Am. Chem. Soc. 2016, 138, 10790) and Mulvey (Chem. Eur. J., 2017, 23, 16853) reported the use of organolithium compounds for the hydroboration of aldehydes and ketones. Nonetheless, the catalytic use of organolithium compounds for reduction of more challenging and synthetically useful substrates such as carbodimides, esters etc. is deemed desirable.

(b) Very recently, we have shown the use of organolithium compounds for the hydroboration of aldehydes and ketones (Chem. Commun. 2018, 54, 6843) as well as alkenes and alkynes (Chem. Commun. 2019, 55, 11711). Building upon our previous works, we demonstrate here catalytic hydroboration of ester to alcohol and carbodiimide to imine.

(c) Prior to this work, there are few main-group catalysts reported for the hydroboration of carbodiimdies (See Chart 1 in the manuscript), but no well-defined group 1 complex as a single site catalyst has been used. The same is true for ester hydroboration. This is the first report of the catalytic hydroboration of esters and carbodiimides using single site catalyst based on a *s*-block element.

(d) A thorough DFT studies were carried out to understand the mechanism of carbodiimide hydroboration.

Abstract

Selective and efficient hydroboration of esters and carbodiimides to alcohols and amines by two well-defined and readily accessible lithium complexes, 2,6-di-tert-butyl phenolate lithium (**1a**) and 1,1'-dilithioferrocene (**1b**) are described. A range of aliphatic, aromatic, and cyclic esters with various functional groups were selectively converted into the corresponding boronate esters. Similarly, the single hydroboration of carbodiimides with aliphatic and aromatic substituents on the nitrogen atoms was studied. A possible mechanistic pathway of the hydroboration of carbodiimides with HBpin is proposed using NMR studies and DFT calculations. These reactions are convenient alternatives to stoichiometric hydride reduction or hydrogenation. The employing of lithium complexes is also significant because of the need to find cheap and green alternatives to the noble metal complexes.

Introduction

Hydroboration, the direct formation of X-B bond by formal addition of a borane to a C=X (X=C, N, O) bond, is a powerful synthetic procedure for the reduction of carbonyls, amides, alkynes, alkenes, nitriles etc. Although tremendous progress has been achieved in the field of transition metal catalyzed hydroboration,[1] the rising demand for sustainable chemical processes have led to signuificant focus on the development of hydroboration catalysts involving main-group elements. In this regard, there have been several important discoveries in the design of main-group element based catalytic systems for hydroboration of unsaturated organic substrates.[2] Among the main-group elements, lithium compounds have been neglected, but they could be the alternatives to address today's urgent need to develop new catalysts and processes that are clean,

safe, and efficient. A further impetus for the lithium catalysts comes from their inexpensiveness, ready accessibility, and non-involvement in Schlenk equilibrium unlike their adjacent group 2 elements.[3] Moreover, catalysts based on main-group elements are usually synthesized from their lithium compounds. Hence, the use of lithium compounds as catalysts benefits from the avoidance of the additional salt metathesis step. It is said that Ziegler initially used *n*BuLi to promote his olefin polymerization reaction, but later switched to trialkyl aluminum, presumably due to price advantage.[4] Although the lithium catalysts lost the first round, recent ground-breaking works from the groups of Okuda,[5,6,7] Mulvey,[8,9] Wangelin,[10] and others[11,12,13,14,15] for the hydroboration of aldehydes, ketones, nitriles, and other organic substrates using a range of lithium compounds have brought them back into competition.

We have been actively developing operationally convenient methods for hydroboration using simple and readily accessible main-group compounds.[16,17,18] Over the past three years, our laboratory has reported the use of lithium 2,6-di-tert-butyl phenolate (**1a**) and 1,1'-dilithioferrocene (**1b**) as catalysts for the reduction of aldehydes, ketones, alkenes, alkynes, all three classes of amides.[19,20,21] Herein, we report single-site hydroboration of carbodiimides and esters using HBpin in the presence of **1a** and **1b**. Reduction of esters to the corresponding alcohols is an important transformation in organic chemistry, while the reduction of carbodiimides (R-N=C=N-R) is a practical method for the synthesis of amines without the formation of any by-product.

Results and Discussion

Hydroboration of Carbodiimides. In comparison to aldehydes and ketones, the electrophilicity of the carbodiimide group is considerably low, which makes the hydroboration of carbodiimides a challenging task. Probably because of this reason, very few examples of the hydroboration of

carbodiimides using compounds with main-group elements have been reported. Hill and co-workers described a *β*-diketiminato magnesium alkyl complex, [CH{C(Me)NDipp}$_2$}Mg*n*Bu] (Dipp=2,6-*i*Pr$_2$C$_6$H$_3$), as an effective pre-catalyst for the catalytic hydroboration of carbodiimides with pinacolborane (HBpin).[22] Parkin reported hydroboration of two alkyl carbodiimides (R=*i*Pr and Cy) using a terminal magnesium hydride, [Tism$^{i\text{PrBenz}}$]MgH.[23] Roesky and co-workers reported a alkylaluminum complex, [CH{C(Me)NDipp}$_2$}Al*n*Bu$_2$] as a pre-catalyst for hydroboration of carbodiimides.[24] Subsequently, the same group as well as Nembenna's team studied a series of aluminum compounds as catalysts for the hydroboration of carbodiimides.[25,26] Eisen and co-workers showed monohydroboration of carbodiimides using actinide-methyl complexes of uranium and thorium.[27] 9-borabicyclo[3.3.1]nonane catalyzed hydroboration of carbodiimides was reported by the groups of Ramos and Antinolo.[28] Besides these developments, simple main-group compounds such as SnCl$_2$/SnBr$_2$,[29] KCH$_2$Ph,[30] NaH[31] have been shown to promote/catalyze the hydroboration of carbodiimides. Additionally, dihydroboration of carbodiimides was reported with magnesium hydridotriphenylborate, [Mg(thf)$_6$][HBPh$_3$]$_2$ from the groups of Okuda[32] and magnesium tris(pentafluorophenyl)hydridoborate, [CH{C(Me)NDipp}$_2$}Mg][HB(C$_6$F$_5$)$_3$] from the groups of Hill (Chart 1).[33]

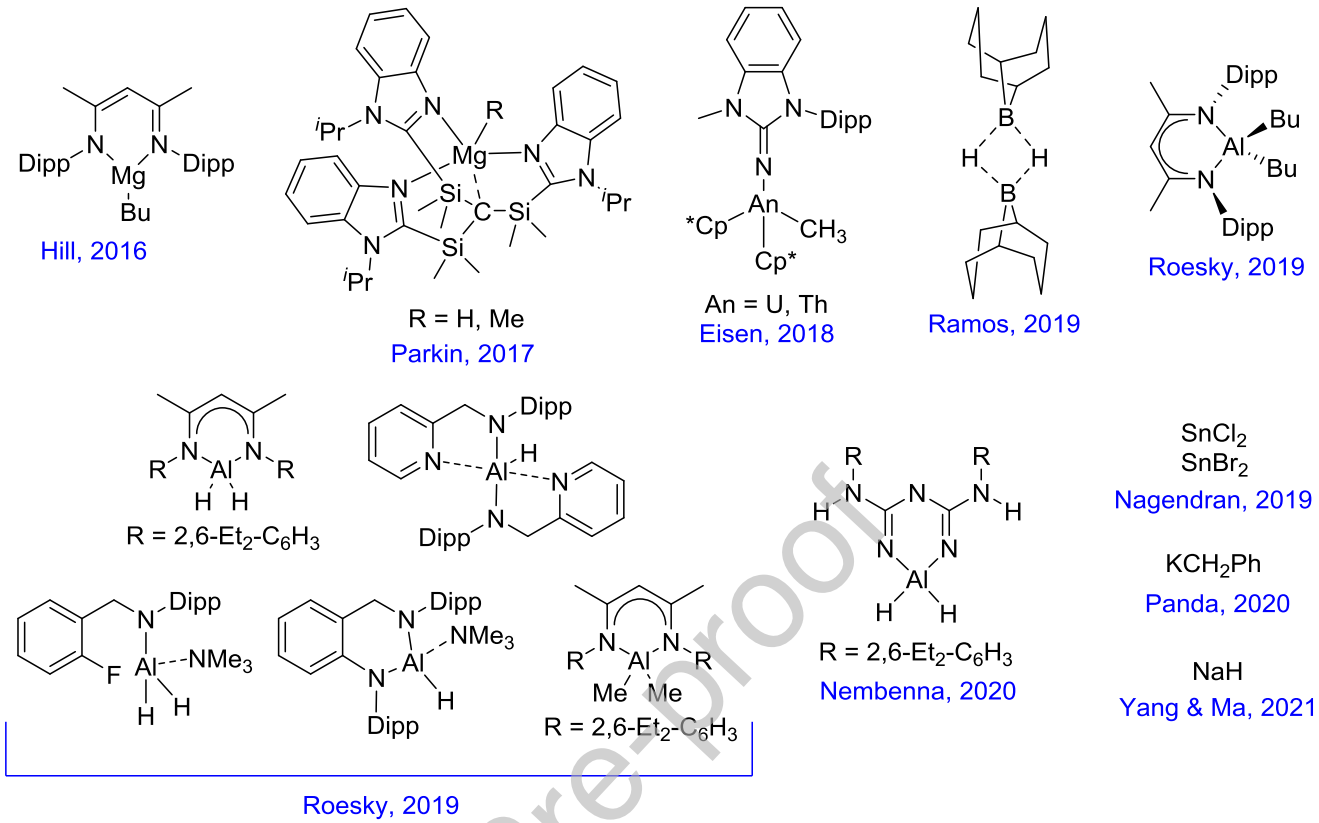


Chart 1. Main group and actinide based catalysts for carbodiimide hydroboration.

We started our investigation with *N*,*N*′-diisopropyl carbodiimide (DIC) (0.25 mmol) in the presence of equimolar amount of HBpin (0.28 mmol, 1.1 eq) at 80 °C in neat condition without any solvent (Table 1), which afforded the desired singly reduced *N*-borylformamidine in excellent yield within 12-15 h (Table 1, entry 6 and entry 13). It is important to point out that the reaction between DIC and HBpin did not afford any product in the absence of catalysts under the same reaction conditions. With the optimized conditions in hand, the scope of the reaction was investigated and product *N*-borylformamidine [$R^1NCHN(BPin)R^1$] was identified through ^1H NMR spectrum with a singlet resonance at δ = 7.90 ppm. Also, other substrates such as *N*,*N*′-di-tert-butylcarbodiimide, N,N'-dicyclohexylcarbodiimide (DCC), and bis(2,6-diisopropylphenyl)carbodiimide provide moderate to good yields of the desired mono hydroboration products under standard reaction conditions (Scheme 1, entries **2-4**). It is worth

mentioning here that, even though DIC performed well at the room temperature (Entry 4 and 10), other substrates underwent very poor conversion under the same reaction condition.

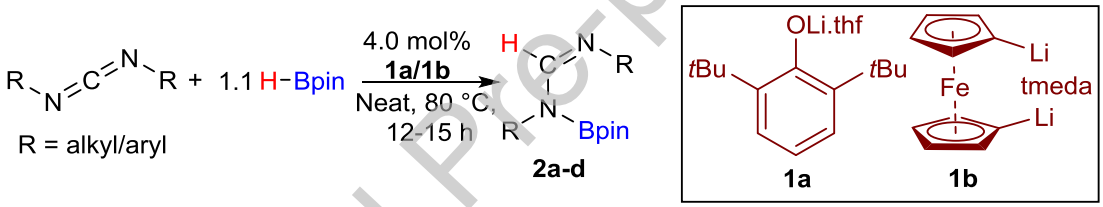
Table 1. Optimization table for hydroboration of *N*,*N*-diisopropyl carbodiimide by **1a** and **1b**. Yields were determined by ^{1}H NMR integration relative to mesitylene. Reaction Scale: 0.25 mmol (carbodiimide) and 0.28 mmol (HBpin) in neat condition. $CDCl_3$ is used as the deuterated solvent.

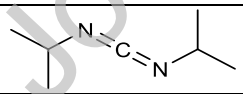
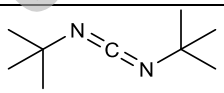
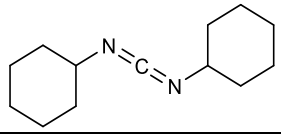
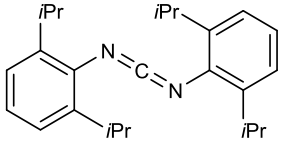
Entry	Catalyst	Catalyst (mol%)	Temp (°C)	Time (h)	NMR Yield (%)
1.	**1a**	3.0	rt	1	20
2.	**1a**	3.0	rt	15	53
3.	**1a**	5.0	rt	13	84
4.	**1a**	5.0	rt	15	90
5.	**1a**	3.0	60	15	66
6.	**1a**	4.0	80	15	92
7.	**1a**	4.0	80	18	>99
8.	**1b**	3.0	rt	1	54
9.	**1b**	5.0	rt	13	87
10.	**1b**	5.0	rt	15	96
11.	**1b**	2.0	80	12	92
12.	**1b**	3.0	80	12	95
13.	**1b**	4.0	80	12	99
14.	**1b**	4.0	60	12	86
15	-	-	rt-120	20	62

The performance of **1a** and **1b** as catalysts is superior to the recently reported *n*BuLi catalyzed carbodiimide hydroboration, where the quantitative conversion of aliphatic carbodiimides (DCC

and DIC) took 24 h at 80 °C and the hydroboration of Dipp-N=C=N-Dipp was reported to take 48 h.[15] Between **1a** and **1b**, the latter is found to be more efficient as it requires less time than the former to achieve the transformation. It is noteworthy that an attempted reaction of *i*PrN=C=N*i*Pr and two equivalents of HBpin afforded 52.0% mono hydroboration and 24.0% double hydroboration product under the same reaction conditions.

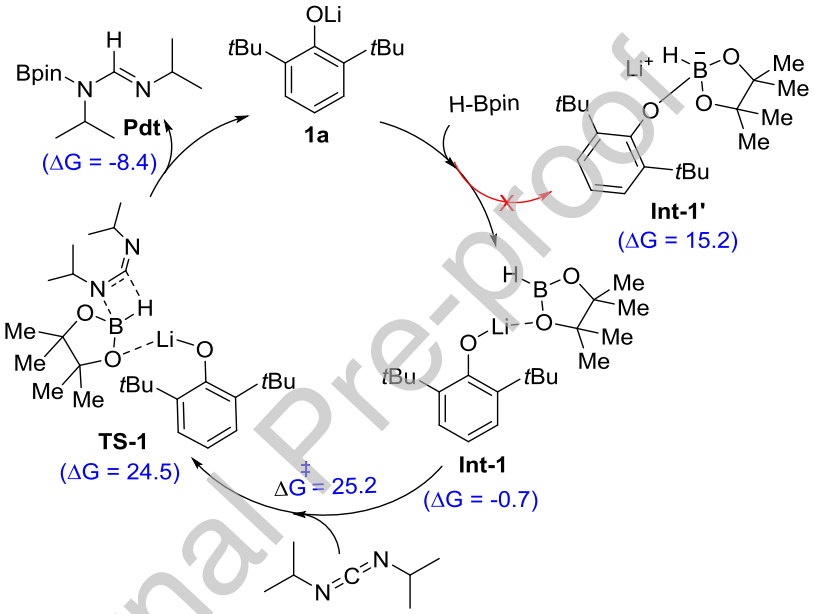
Scheme 1. The scope of hydroboration with carbodiimide substrates. Reaction Scale: 0.25 mmol (carbodiimide) and 0.28 mmol (HBpin). Reaction conditions: 4.0 mol% catalyst, 12-15 h reaction at 80 °C in neat conditions. Superscripts "a" and "b" stand for the catalysts **1a** and **1b** respectively. Yields were determined by ^{1}H NMR integration relative to mesitylene. $CDCl_3$ is used as the deuterated solvent.



Entry	Substrate	Time (h)	Yield Single Hydroboration (%)	Time (h)	Yield Single Hydroboration (%)
		At 80 °C		At room temperature	
1.		15[a]/12[b]	92[a]/99[b]	15	90[a]/96[b]
2.		15[a]/12[b]	30[a]/86[b]	15	3[a]/11[b]
3.		15[a]/12[b]	98[a]/88[b]	15	64[a]/41[b]
4.		15[a]/12[b]	90[a]/67[b]	15	46[a]/0[b]

DFT studies for carbodiimide hydroboration. We have investigated the hydroboration mechanism of carbodiimide only with **1a**. The reaction of **1a** with HBpin gives a peak at δ 4.7 ppm in the ^{11}B NMR, which can be ascribed for a three-coordinated boron atom. However, keeping the NMR tube for a longer time led to the generation of a singlet and a quintet resonance at δ 21.62 and –39.83 ppm, reflecting the formation of a trialkoxyborane [2,6-*t*Bu$_2$-C$_6$H$_3$-OBpin] and BH_4^- anion (See SI, Figure S44). Very recently, Thomas and coworkers divulged the possible role of BH_3 adducts as "true catalysts" in the hydroboration with HBpin of unsaturated substrates using nucleophiles.[34,35] Hence, we have performed the hydroboration of DIC in presence of 10 mol% of TMEDA, however, the reaction afforded 86% yield implying the negligible influence of BH_3 as a hidden catalyst in this reaction (See SI, Figure S45). To obtain additional mechanistic insight, full quantum chemical calculations were done with density functional theory (DFT) at the dispersion corrected PBE/TZVP level of theory. In the first step of the reaction in the presence of catalyst **1a**, a weekly bound complex (**Int-1**) is formed between catalyst **1a** and pinacolborane as stated earlier for the hydroboration of aldehydes, ketones and amides.[19] The formation of **Int-1´** was discarded based on the Gibbs' free energy value of the reaction (15.2 kcal/mol), which is thermodynamically unfavorable. A very similar mechanism was proposed by Pati and Khan in their recent germylene and stannylene catalyzed hydroboration of aldehydes.[36] Now, the carbodiimide approaches towards the B-H bond of the **Int-1**. This is the prelude to the nucleophilic attack by the imide nitrogen of carbodiimide to the boron center of the pinacolborane, with the hydride being transferred from the boron center to the electrophilic sp-hybridized carbon of the imide. This occurs through a four-membered transition state (**TS-1**) and leads to the formation of hydroboration product (**Pdt**) along with the regeneration of the catalyst **1a** (see Scheme 2 and Figure S46 in the SI**)**. The ΔE (-12.1 kcal/mol)

and ΔG (-8.4 kcal/mol) values for this step are significantly negative and the activation energy ($\Delta G^{\#}$) barrier corresponding to the transition state is 25.2 kcal/mol. This is also the slowest step of the overall hydroboration reaction. In this transition state there is a significant amount of B-H bond activation (the B-H bond distance increases to 1.91 Å), which allows the hydride transfer from the boron to the sp-hybridized imide carbon center along with the simultaneous C=N bond cleavage and B-N bond formation.



Scheme 2. The catalytic cycle for the carbodiimide hydroboration by catalyst **1a**. ΔG and $\Delta G^{\ddagger}$ represent the Gibbs free energy of reaction and the barrier, respectively. All values are in kcal/mol.

Hydroboration of esters. Similar to carbodiimides, ester hydroboration with main-group compounds is seldom reported. Sadow and coworkers described $To^{M}MgMe$ (To^{M} = tris(4,4-dimethyl-2-oxazolinyl)phenylborate) catalyzed ester hydroboration.[37] Nembenna and coworkers showed magnesium amide $Mg\{N(SiMe_3)_2\}_2$ and complexes derived from the latter, such as

(iPr$_2$N)C(NAr$_2$)MgN(SiMe$_3$)$_2$ (Ar = 2,6-Me$_2$-C$_6$H$_3$ and 2,6-iPr$_2$-C$_6$H$_3$)[38] and the group of Ma has recently demonstrated the use of a Mg(I) dimer as an efficient pre-catalyst for the hydroboration of a wide range of esters (Chart 2).[39] Apart from main-group elements, the groups of Sadow and Marks independently used lanthanum catalysts for the hydroboration of esters.[40,41] Given the success of hydroboration of carbodiimides, we next turned our attention towards the hydroboration of ester with HBpin. Accordingly, the reaction conditions were optimized to realize the maximum yield.

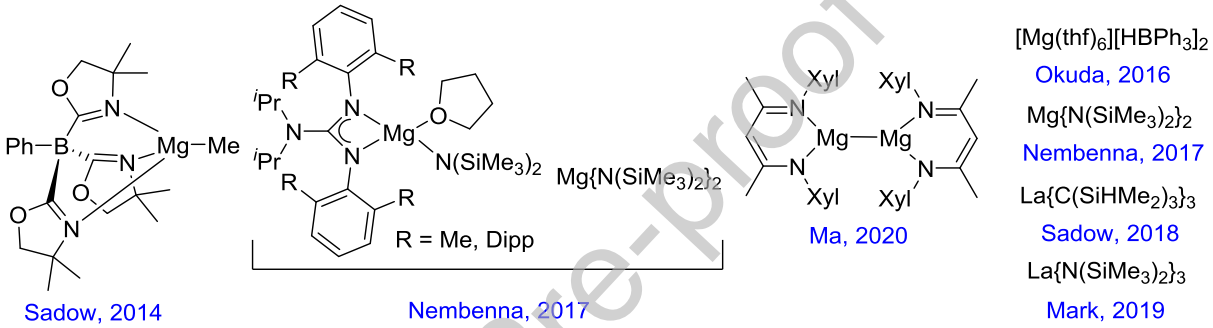


Chart 2. Main group and lanthanide based (pre)catalysts for ester hydroboration.

As seen in Table 2, methyl benzoate was treated with HBpin in the presence of 6 mol% **1a** at room temperature to obtain the corresponding aryloxy boronate ester only in 35% yield (entry 1). With the increase of temperature and time, the reaction yield started to gradually increase (entry 2-5). A high yield of 95% was obtained when the reaction was conducted at 80 °C for 10 h (entry 5). The decrease of mol% of **1a** or reaction time led to drop-off in yield (entry 6 and 7). When we have used **1b** as the catalyst, we observed that it requires less catalyst mol% and reaction time. The highest yields were obtained with 3-4 mol% of **1b** with 10 h reaction time (entry 10 and 11). When the reaction time was reduced to 8 h, there is a yield drop to 88% (entry 12). However, we chose the latter as the optimized condition in order to study the electronic

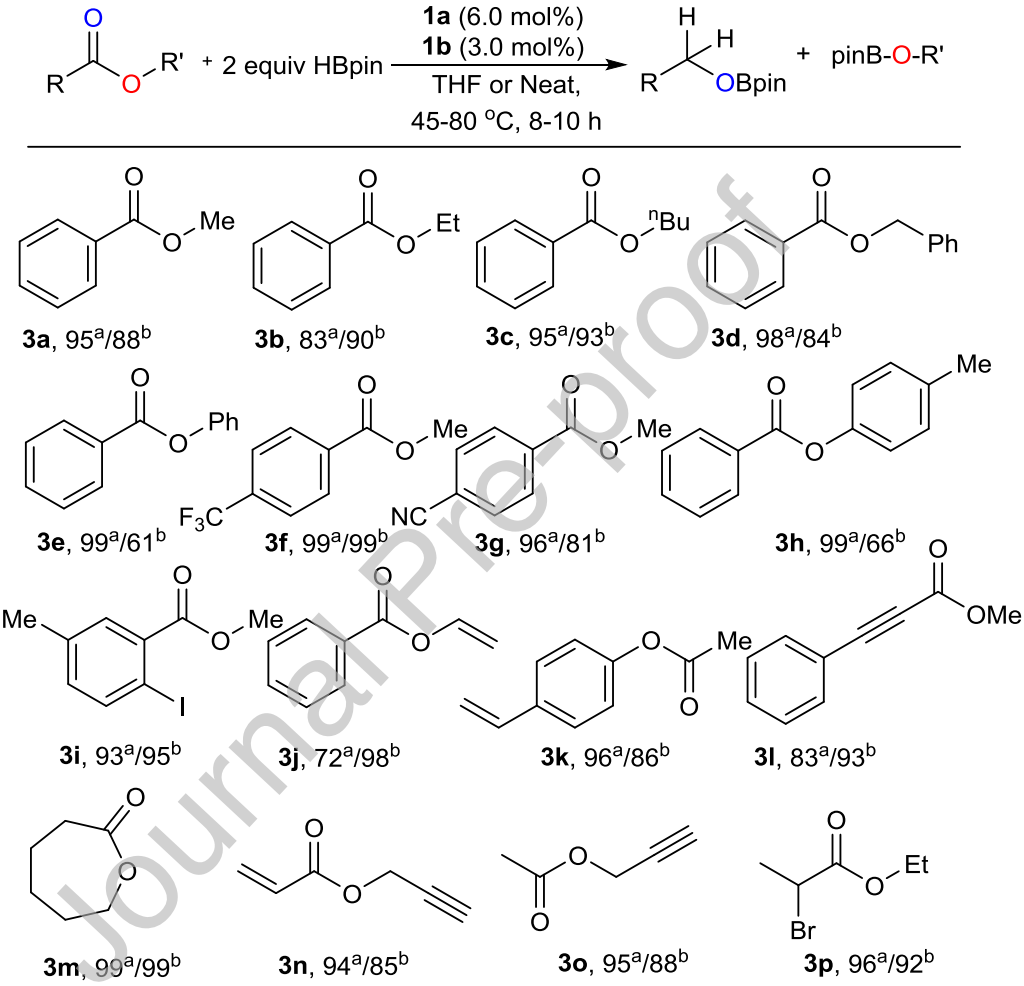
effect of the ester substituents. Unlike carbodiimide hydroboration, we did not perform the DFT studies for the ester hydroboration.

Table 2. Optimization table for the hydroboration of methyl benzoate catalyzed by **1a** and **1b**. Reaction conditions: 3.0-6.0 mol% catalyst, 8-10 h reaction at 45-80 °C temperature in neat condition or in THF solvent (0.5 mL). Yields were determined by ^{1}H NMR integration relative to mesitylene. Reaction Scale: 0.25 mmol (ester) and 0.50 mmol (HBpin). $CDCl_3$ is used as the deuterated solvent.

Entry	Catalyst	Catalyst (mol%)	Solvent	Temperature (°C)	Time (h)	NMR yield (%)
1.	**1a**	6.0	Neat	25	12	35
2.	**1a**	6.0	Neat	60	10	44
3.	**1a**	6.0	THF	60	10	44.5
4.	**1a**	6.0	Neat	80	12	96.5
5.	**1a**	6.0	Neat	80	10	95
6.	**1a**	5.0	Neat	80	10	81
7.	**1a**	6.0	Neat	80	8	73
8.	**1b**	6.0	THF	25	12	98
9.	**1b**	4.0	THF	25	12	83
10.	**1b**	4.0	THF	45	10	>99
11.	**1b**	3.0	THF	45	10	97
12.	**1b**	3.0	THF	45	8	88
13.	**1b**	3.0	THF	45	6	82
14.	**1b**	2.0	THF	45	8	75

Scheme 3. The scope of hydroboration with ester substrates. Reaction Scale: 0.25 mmol (ester) and 0.50 mmol (HBpin). Reaction conditions: 3.0-6.0 mol% catalyst, 8-10 h reaction at 45-80 °C

temperature in neat condition or in THF solvent. Superscripts “a” and “b” are for catalyst **1a** and **1b** respectively (See SI for further details). Yields were determined by ^{1}H NMR integration relative to mesitylene. $CDCl_3$ is used as the deuterated solvent.



Both aliphatic and aromatic esters underwent hydroboration to form corresponding boronate ester in good to excellent yield. Aromatic esters with short to long alkyl chains showed negligible steric influence and provided the desired product in quantitative yields (**3a**-**3e**). Also, aromatic esters with electron-withdrawing or donating substituents at the *o/m/p* positions react

with HBpin and show complete conversion (Scheme 3, **3f**-**3i**) to the respective products. Similarly, the aliphatic esters underwent smooth reduction when treated with HBpin (**3m**-**3p**). The quantitative conversion was documented for the reaction of ε-caprolactone (**3m**) under similar reaction conditions. We did not observe any evidence of polymerization. Chemoselective reduction of esters is very important and quite challenging in the presence of other reducible functional groups in organic synthesis. In this regard, we have demonstrated the hydroboration of esters in the presence of other functional groups such as conjugated or non-conjugated C=C double bonds (**3j**, **3k** and **3n**) and C≡C triple bonds (**3l**, **3n**, and **6o**). Esters with halide substituents (**3i** and **3p**) were also tolerated well. No side reaction with nitrile substituent (**3g**) was observed, indicating the preference for the ester reduction.

Conclusion

In our previous papers, we have demonstrated the use of simple lithium compounds as catalysts for hydroboration of aldehydes, ketones, alkenes, alkynes, primary-tertiary amides. Herein, the scope and mechanism of lithium compound-catalyzed hydroboration of diverse series of esters are studied. The catalyst shows complete selectivity for ester reduction over competing nitrile, alkenes, and alkynes moieties, even at temperatures as high as 60 °C. Besides, the catalysts are very efficient for the hydroboration of carbodiimides with HBpin. We believe that our contributions in employing simple and readily accessible lithium compounds as catalysts and will spur more interest in organolithium chemistry, a land that is undoubtedly worth exploring.[42]

Acknowledgment

This work was supported by Ramanujan Research Grant (SB/S2/RJN-073/2014) and CSIR-Young Scientist Award Contingency Grant (YSA000726). MKB, KG, and TD thank the Council of

Scientific and Industrial Research (CSIR), India for research fellowships. The support and the resources provided by 'PARAM Brahma Facility' under the National Supercomputing Mission, Government of India at the IISER Pune are gratefully acknowledged. We are thankful to the reviewers for their critical feedbacks to improve the quality of the manuscript.

Dedication

This paper is dediated to Prof. Pradeep Mathur on the occasion of his 65th birthday

Supporting Information

General catalytic procedure for the hydroboration of carbodiimides and esters, analytical data of the corresponding borylamines and boronate esters, their representative NMR spectra, and details of theoretical calculations are provided in the supporting information.

[1] For reviews on transition metal complexes catalyzed hydroboration (a) D. S. Matteson, D. S. In The Metal-Carbon Bond; F. R. Hartley, F. R., Ed.; John Wiley & Sons, Inc.: Chichester, U.K., 1987; Vol. 4, pp 307−409. (b) Contemporary Boron Chemistry; M. Davidson, A. K. Hughes, T. B. Marder, K. Wade, Eds.; Royal Society of Chemistry: Cambridge, U.K., 2000; pp 371−472. (c) A. Suzuki, Angew. Chem., Int. Ed. 50 (2011) 6722−6737.

[2] For reviews on main group compound catalyzed hydroboration, see: (a) M. L. Shegavi, S. K. Bose, Catal. Sci. Technol. 9 (2019) 3307–3336. (b) C. C. Chong, R. Kinjo, ACS Catal. 5 (2015) 3238–3259.

[3] J. Intemann, H. Bauer, J. Pahl, L. Maron, S. Harder, Chem. Eur. J. 21 (2015) 11452–11461.

[4] A staff feature, Ind. Eng. Chem. 54 (1962) 50–52.

[5] D. Mukherjee, H. Osseili, T.P. Spaniol, J. Okuda, J. Am. Chem. Soc. 138 (2016) 10790–10793.

[6] H. Osseili, D. Mukherjee, K. Beckerle, T. P. Spaniol, J. Okuda, Organometallics 36 (2017) 3029–3034.

[7] H. Osseili, D. Mukherjee, T. P. Spaniol, J. Okuda, Chem. Eur. J. 23 (2017) 14292–14298.

[8] R. McLellan, A. R. Kennedy, R. E. Mulvey, S. A. Orr, S. D. Robertson, Chem. Eur. J. 23 (2017) 16853–16861.

[9] L. E. Lemmerz, R. McLellan, N. R. Judge, A. R. Kennedy, S. A. Orr, M. Uzelac, E. Hevia, S. D. Robertson, J. Okuda, R. E. Mulvey, Chem. Eur. J. 24 (2018) 9940–9948.

[10] P. Ghosh, A. J. v. Wangelin, Org. Chem. Front. 7 (2020) 960–966.

[11] D. Yan, X. Wu, J. Xiao, Z. Zhu, X. Xu, X. Bao, Y. Yao, Q. Shen, M. Xue, Org. Chem. Front. 6 (2019) 648–653.

[12] Z. Zhu, X. Wu, X. Xu, Z. Wu, M. Xue, Y. Yao, Q. Shen, X. Bao, J. Org. Chem. 83 (2018) 10677–10683.

[13] S. J. Yang, A. K. Jaladi, J. H. Kim, S. Gundeti, D. K. An, Bull. Korean Chem. Soc. 40 (2019) 34–38.

[14] M. Luo, J. Li, Q. Xiao, S. Yang, F. Su, M. Ma, J. Organomet. Chem. 868 (2018) 31–35.

[15] B. Yan, X. He, C. Ni, Z. Yang, X. Ma, ChemCatChem 13 (2021) 851–854.

[16] M. K. Bisai, S. Pahar, T. Das, K. Vanka, S. S. Sen, Dalton Trans. 46 (2027) 2420–2424.

[17] S. Yadav, S. Pahar, S. S. Sen, Chem. Commun. 53 (2017) 4562–4564.

[18] S. Yadav, R. Dixit, M. K. Bisai, K. Vanka, S. S. Sen, 37 (2018) 4576–4584.

[19] M. K. Bisai, T. Das, K. Vanka, S. S. Sen, Chem. Commun. 54 (2018) 6843–6846.

[20] M. K. Bisai, S. Yadav, T. Das, K. Vanka, S. S. Sen, Chem. Commun. 55 (2019) 11711–11714.

[21] M. K. Bisai, K. Gour, T. Das, K. Vanka, S. S. Sen, Dalton Trans. 50 (2021) 2354–2358.

[22] C. Weetman, M. S. Hill, M. F. Mahon, Chem. Eur. J. 22 (2016) 7158–7162.

[23] M. Rauch, S. Ruccolo, G. Parkin, J. Am. Chem. Soc. 139 (2017) 13264−13267.

[24] Y. Ding, X. Ma, Y. Liu, W. Liu, Z. Yang, H. W. Roesky, Organometallics 38 (2019) 3092–3097.

[22] Q. Shen, X. Ma, W. Li, W. Liu, Y. Ding, Z. Yang, H. W. Roesky, Chem. Eur. J. 25 (2019) 11918–11923.

[26] N. Sarkar, S. Bera, S. Nembenna, J. Org. Chem. 85 (2020) 4999–5009.

[24] H. Liu, K. Kulbitski, M. Tamm, M. S. Eisen, Chem. Eur. J. 24 (2018) 5738–5742.

[28] A. Ramos, A. Antinolo, F. Carrillo-Hermosilla, R. Fernandez-Galan, D. Garcia-Vivo, Chem. Commun. 55 (2019) 3073−3076.

[29] P. Mahawar, D. Yadav, D. Singh, M. Kumar Sharma, N. Selvarajan, ChemRxiv. Preprint. https://doi.org/10.26434/chemrxiv.8944970.v1

[30] T. K. Panda, I. Banerjee, S. Sagar, Appl. Organomet. Chem. 24 (2020) e5765.

[31] X. He, B. Yan, C. Ni, Y. Zhao, Z. Yang, X. Ma, Asian J. of Org. Chem. 10 (2021) 196-201.

[32] D. Mukherjee, S. Shirase, T. P. Spaniol, K. Mashima, J. Okuda, Chem. Commun. 52 (2016) 13155–13158.

[33] M. D. Anker, M. Arrowsmith, R. L. Arrowsmith, M. S. Hill, M. F. Mahon, Inorg. Chem. 56 (2017) 5976−5983.

[34] A. D. Bage, T. A. Hunt, S. P. Thomas, Org. Lett. 22 (2020) 4107−4112.

[35] A. D. Bage, K. Nicholson, T. A. Hunt, T. Langer, S. P. Thomas, ACS Catal. 10 (2020) 13479–13486.

[36] R. Dasgupta, S. Das, S. Hiwase, S. Pati, S. Khan, Organometallics 38 (2019) 1429-1435.

[37] D. Mukherjee, A. Ellern, A. D. Sadow, Chem. Sci. 5 (2014) 959–964.

[38] M. K. Barman, A. Baishya, S. Nembenna, Dalton Trans. 46 (2017) 4152–4156.

[39] X. Cao, W. Wang, K. Lu, W. Yao, F. Xue, M. Ma, Dalton Trans. 49 (2020) 2776–2780.

[40] S. Patnaik, A. D. Sadow, Angew. Chem., Int. Ed. 58 (2019) 2505-2509.

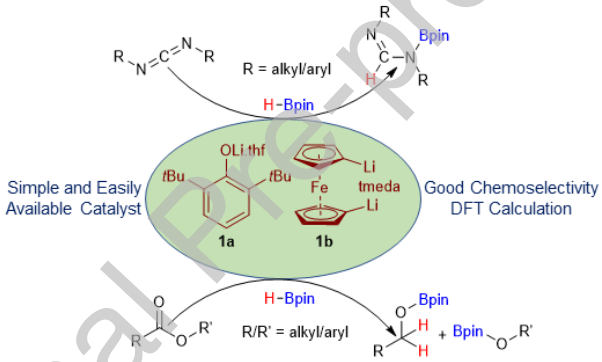
[41] C. J. Barger, A. Motta, V. L. Weidner, T. L. Lohr, T. J. Marks, ACS Catal. 9 (2019) 9015−9024.

[42] V. Capriati, F. M. Perna, A Salomone, Dalton Trans. 43 (2014) 14204–14210.

TOC

for

Readily Available Lithium Compounds as Catalysts for the Hydroboration of Carbodiimides and Esters



We have demonstrated the use of simple and readily available lithium compounds, 2,6-di-tert-butyl phenolate lithium (**1a**) and 1,1'-dilithioferrocene (**1b**) as single site catalysts for hydroboration of diverse esters and carbodiimides in high yields and excellent functional group tolerance. DFT studies have been performed to understand the mechanism of carbodiimide hydroboration.