



HAL
open science

Carbon Dioxide Reduction to Methylamines under Metal-Free Conditions

Enguerrand Blondiaux, Jacky Pouessel, Thibault Cantat

► **To cite this version:**

Enguerrand Blondiaux, Jacky Pouessel, Thibault Cantat. Carbon Dioxide Reduction to Methylamines under Metal-Free Conditions. *Angewandte Chemie International Edition*, 2014, 53 (45), pp.12186-12190. 10.1002/anie.201407357 . hal-01157654

HAL Id: hal-01157654

<https://hal.science/hal-01157654>

Submitted on 31 Jan 2019

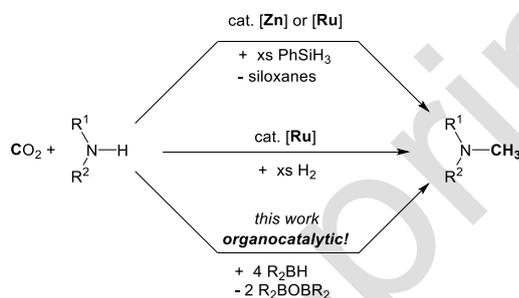
HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

CO₂ Reduction to Methylamines under Metal-Free Conditions**

Enguerrand Blondiaux, Jacky Pouessel and Thibault Cantat*

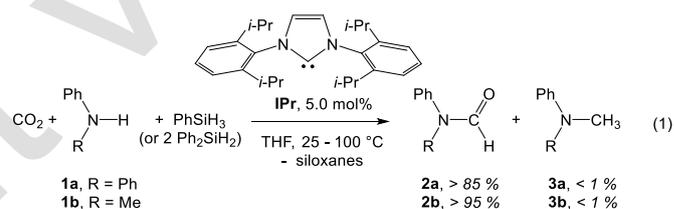
The utilization of CO₂ as a C₁-building block for the production of fuels or chemicals has the advantage of creating added-value, able to mitigate the capture cost of this greenhouse gas.^[1] In this context, increasing research efforts have been devoted to promoting the reduction of CO₂ to formic acid or methanol, because these C₁-molecules can either serve as H₂ carriers or directly as fuels.^[2] In parallel, the scope of organic molecules incorporating a CO₂ molecule has rapidly increased with the discovery of new methodologies to promote the conversion of CO₂ to a variety of heterocycles, carboxylic acids, amides and methylamines.^{[3],[4],[5],[6]} Importantly, the reduction of CO₂ to fuels or functional chemicals both require the use of stable catalysts able to operate under mild conditions, with high turnover numbers (TONs). While, renewable reductants, such as H₂ or electrochemical cells, are required for the large scale recycling of CO₂ to formic acid or methanol, the formation of fine chemicals from CO₂ can also be advantageously achieved with mild hydrides such as hydrosilanes or hydroboranes, which feature a polarized Si-H or B-H bond.^{[7],[8]} In fact, CO₂ transformation to fine chemicals poses different constraints as a large scope and a high chemoselectivity is anticipated for the fixation of CO₂ into functionalized organic molecules. In addition, metal-free catalytic systems are desirable in this strategy, to circumvent the problematic availability, cost and/or toxicity of metal ions.



Scheme 1. Methodologies for the methylation of amines with CO₂.

First unveiled in 2013, the catalytic reduction of CO₂ to methylamines is a promising new method for recycling CO₂ to value added chemicals, as it by-passes the classical methodologies

involving formaldehyde or hazardous alkylating agents such as methyl iodide, dimethylsulfate or dimethylcarbonate.^[9] Using molecular zinc catalysts, our group has indeed shown that CO₂ could serve as an efficient carbon source for the formation of N-CH₃ groups, in the presence of PhSiH₃,^[6a] and Beller *et al.* developed, in parallel, ruthenium catalysts to promote the same transformation (Scheme 1).^[6b] Klankermeyer *et al.* and Beller *et al.* have shown later on that, using Ru complexes, molecular hydrogen could replace the hydrosilane reductant.^[6c, 6d] Nonetheless, the metal catalysts perform at elevated temperatures, ranging from 100 to 150 °C, under elevated pressure, with TONs lower than 100. Furthermore, these new methodologies still suffer from a limited scope and, while aromatic and benzylic N-H bonds are the most active substrates, electron rich secondary aliphatic amines display a low reactivity. In order to overstep these limitations, we describe herein the first metal-free methylation of amines using CO₂ as a carbon source. Using phosphorus bases as catalysts, N-H bonds in aromatic and aliphatic amines are quantitatively methylated, with CO₂ and hydroboranes reductants.



The methylation of amines with CO₂ necessitates the use of catalysts able to promote both the formation of N-C bonds and the 6-electron reduction of CO₂. N-heterocyclic carbenes are thus potential organocatalysts in this transformation. Zhang *et al.* have indeed shown that NHCs are efficient catalysts in the hydrosilylation of CO₂ to methanol and our group has demonstrated that they can also convert amines and CO₂ to formamides, in the presence of hydrosilanes.^[2b, 4a] Nevertheless, reacting diphenylamine (**1a**) or *N*-methylaniline (**1b**) with CO₂, in the presence of PhSiH₃ or Ph₂SiH₂ and 5.0 mol% **IPr**, only afforded the corresponding formamide products **2** and only trace amounts of the expected methylamines **3** were detected at 100 °C by GC/MS analyses (< 1 % yield) (Eq. 1). It is noteworthy that the metal-free reduction of CO₂ to methanol has been recently exemplified using hydroboranes reductants. While Fontaine *et al.* utilized a P/B Frustrated Lewis Pair (FLP) as catalyst, our group showed that N/B FLPs or simple amidine and guanidine bases could serve as potent catalysts for the reduction of CO₂ to methoxyboranes.^[8a-c] We have thus explored the possible use of hydroboranes as reductants in the methylation of amines with CO₂. To our delight, reacting **1a** with CO₂ and 4 equiv. 9-BBN, in the presence of 1.0 mol% **IPr**, affords *N*-methyldiphenylamine in a good 79 % yield, after 15 min at 90 °C (Entry 2, Table 1). This catalytic transformation represents the first example of a metal-free reaction for the direct methylation of amines with CO₂.

[*] E. Blondiaux, Dr. J. Pouessel, Dr. T. Cantat
CEA, IRAMIS, NIMBE, CNRS UMR 3299
91191 Gif-sur-Yvette, France
Fax: (+33) 1.6908.6640
E-mail: thibault.cantat@cea.fr
Homepage: <http://iramis.cea.fr/Pisp/thibault.cantat/index.htm>

[**] For financial support of this work, we acknowledge CEA, CNRS, ADEME, the CHARMMAT Laboratory of Excellence and the European Research Council (ERC Starting Grant Agreement n.336467). T.C. thanks the Fondation Louis D. – Institut de France for its support.

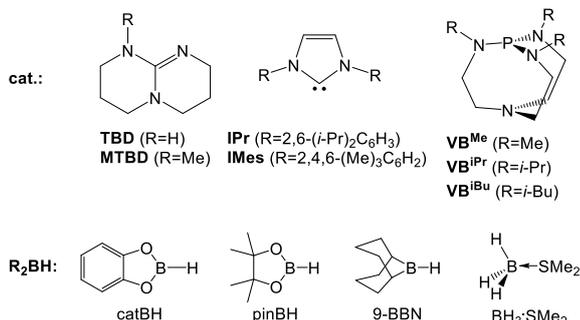
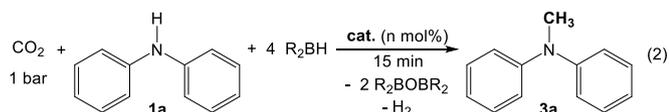


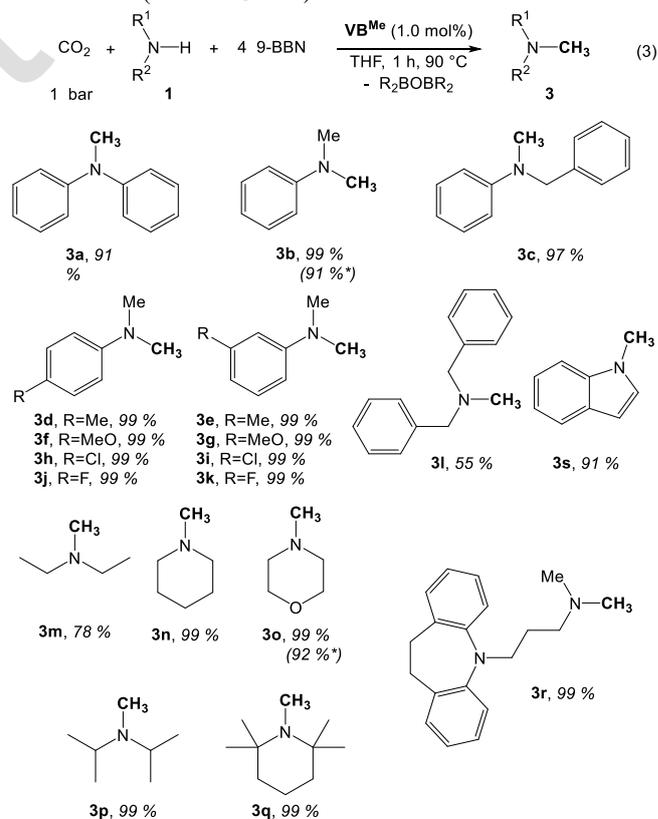
Table 1. Metal-free catalytic methylation of **1a** with CO₂ and hydroboranes, as depicted in Eq. 2.

Entry	Catalyst [mol%]	Borane (R ₂ BH)	Temp [°C]	Solvent	Yield [%] ^[a]
1	–	9-BBN	90	THF	< 1
2	IPr (1.0)	9-BBN	90	THF	79
3	IMes (1.0)	9-BBN	90	THF	52
4	TBD (1.0)	9-BBN	90	THF	59
5	MTBD (1.0)	9-BBN	90	THF	67
6	PPh ₃ (1.0)	9-BBN	90	THF	13
7	P(NEt ₂) ₃ (1.0)	9-BBN	90	THF	43
8	VBⁱBu (1.0)	9-BBN	90	THF	85
9	VBⁱPr (1.0)	9-BBN	90	THF	93
10	VB^{Me} (1.0)	9-BBN	90	THF	91
11	VB^{Me} (1.0)	catBH	90	THF	< 1
12	VB^{Me} (1.0)	pinBH	90	THF	< 1
13	VB^{Me} (1.0)	BH ₃ SMe ₂	90	THF	< 1
14	VB^{Me} (0.1)	9-BBN	90	THF	70
15	VB^{Me} (0.01)	9-BBN	90	THF	4
16	VB^{Me} (1.0)	9-BBN	90	THF	61 ^[b]
17	VB^{Me} (1.0)	9-BBN	90	THF	65 ^[c]
18	VB^{Me} (1.0)	9-BBN	60	THF	57
19	VB^{Me} (1.0)	9-BBN	20	THF	6
20	VB^{Me} (1.0)	9-BBN	90	toluene	83
21	VB^{Me} (1.0)	9-BBN	90	pentane	50

Reaction conditions: amine (0.20 mmol), hydroborane (0.80 mmol), solvent (0.50 mL), CO₂ (1 bar). [a] Yield determined by GC/MS using mesitylene as an internal standard. [b] In the presence of 3 equiv. 9-BBN. [c] For a reaction time of 5 min.

A variety of organic catalysts were then tested so as to improve the efficiency of the methylation of **1a**. Replacing **IPr** with **IMes** significantly lowers the conversion yield of **1a** to **3a** (Entries 2 and 3, Table 1). Interestingly, nitrogen bases, such as **TBD** and **MTBD**, are also catalysts in the methylation of **1a** with CO₂ and 9-BBN and **3a** was obtained in 59–67 % yield, after 15 min at 90 °C (Entries 4 and 5, Table 1). These results are in agreement with our previous findings on the ability of guanidines to promote the 6-electron reduction of CO₂ to methoxyboranes.^[8b] Indeed, nitrogen bases can significantly enhance the reduction capability of hydroboranes by coordination to the boron vacant site. Because phosphorus bases have a high affinity for boron, they were also tested in the methylation of **1a**.^[10] While PPh₃ affords **3a** with a mediocre 13 % yield from CO₂, it is formed in 43 % yield with the more basic P(NEt₂)₃ catalyst (Entries 6 and 7, Table 1). It is well-established that proazaphosphatranes are superbases and Verkade and coworkers have shown that their pK_a values exceed 32 in MeCN and are therefore significantly higher than the pK_a of the P center in classical phosphines (2.7 in PPh₃ and 8.2 in P(NEt₂)₃).^[11] Verkade's superbases have thus been successfully employed in numerous organic transformations,^[11b, 12] yet, their utilization as catalysts in reduction chemistry remains unexplored. Three proazaphosphatranes superbases were tested in the reductive functionalization of CO₂ to

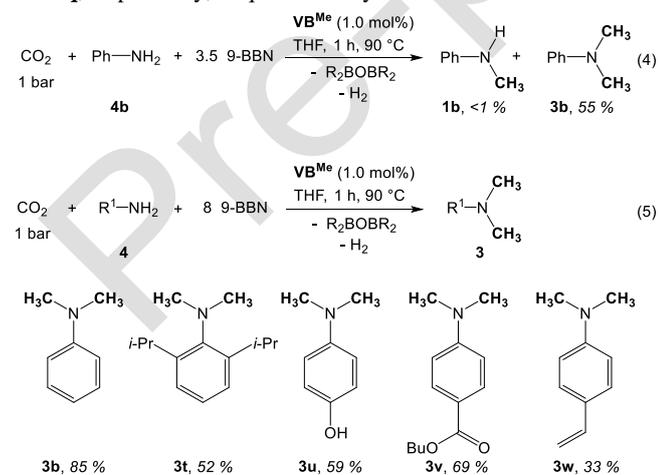
3a, namely **VBⁱBu**, **VBⁱPr** and **VB^{Me}**, which differ by the substitution pattern on the nitrogen atoms of the base (Entries 8–10, Table 1). Importantly, these phosphorus organo-catalysts exhibit a very high catalytic activity and **3a** was obtained in > 85 % yield, after 15 min at 90 °C. **VB^{Me}** and **VBⁱPr** display a similar catalytic activity and **VB^{Me}** was selected as a benchmark catalyst to explore the scope of the reaction depicted in Eq. 2.^[13] While **3a** is obtained in 91 % in the presence of **1a**, 1 bar CO₂ and 4 equiv. 9-BBN, its formation is prohibited by substitution of the reductant with the less reactive catBH and pinBH hydroboranes (Entries 11 and 12, Table 1). Notably, the highly reactive BH₃SMe₂ borane was also found unreactive in this transformation (Entry 13, Table 1). The reaction temperature is an important parameter in the methylation of **1a** and, while the reaction proceeds well above 60 °C, it is inefficient at 20 °C, where 9-BBN was consumed to form CH₃OBBN in place of **3a** (Entries 18 and 19, Table 1). Similarly, decreasing the catalyst loading to 0.1 mol% slightly lowers the conversion yield to **3a** to 70 %, whereas 4 % **3a** are obtained under the same conditions with a loading of 0.01 mol%. The influence of the solvent polarity also has a significant impact on the kinetics of the reaction and **3a** was obtained in 83 and 50 % yield, in toluene and pentane, respectively (Entries 20 and 21, Table 1). As exemplified in Entry 16 (Table 1), the utilization of 4 equiv. 9-BBN is found necessary to achieve a complete methylation of **1a** and, in the presence of 3 equiv. of the hydroborane, **3a** is formed in 61 %. The resulting side-product was identified as the boryl-amine Ph₂N-BBN suggesting that the N-H bond of the substrate undergoes a dehydrogenative borylation, in the early stages of the reaction. This hypothesis was further confirmed by the observation of H₂ evolution in the ¹H NMR spectrum of the crude mixture (δ 4.2 in *ds*-THF).



Scheme 2. Metal-free catalytic methylation of secondary amines with CO₂ and 9-BBN. Reaction conditions: amine (0.20 mmol), hydroborane (0.80 mmol), **VB^{Me}** (0.002 mmol), THF (0.50 mL), CO₂ (1 bar); yield determined by GC/MS using mesitylene as an internal standard, after calibration. (*Isolated yield)

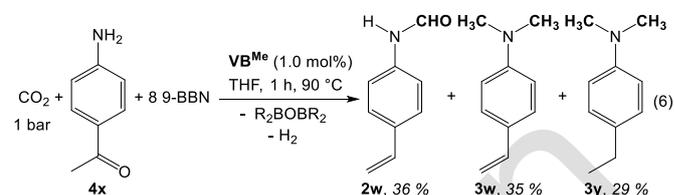
It is of interest to compare the efficiency of this novel metal-free methodology for the conversion of CO₂ to methylamines with the metal-catalyzed versions recently developed by the groups of Beller, Cantat and Klankermeyer, using H₂ and hydrosilanes reductants.^[6a-d] The methylation of *N*-methylaniline **1b** was used as a benchmark substrate by the different groups and the ruthenium and zinc catalysts were found to be active in a 100–150 °C temperature range. The hydrosilylation catalysts exhibit a maximum turnover number (TON) of 49 and a turnover frequency (TOF) of 3.1 h⁻¹ for the complete conversion of **1b** to **3b**.^[6a, 6b] The Ru hydrogenation systems developed independently by Klankermeyer and Beller display similarly performances (TON < 100, TOF < 6.0 h⁻¹) and operate under a pressure of CO₂ (20 bar) and H₂ (60 bar).^[6c, 6d] In comparison, the methylation of **1b** with 1 bar CO₂ and 4 equiv. 9-BBN is quantitative within 10 min at 90 °C, using 0.2 mol% **VB**^{Me}. This result corresponds to a TON of 490 and a TOF of 2934 h⁻¹ and **VB**^{Me} therefore represents the most active catalyst for the methylation of *N*-methylaniline with CO₂ (see SI).

Given the high catalytic activity of **VB**^{Me}, the scope of the methylation of N-H bonds with CO₂ and hydroboranes was explored so as to establish the utility of this new methodology. The methylation of various secondary anilines was investigated using 4 equiv. 9-BBN and 1 bar CO₂, in the presence of 1.0 mol% **VB**^{Me} (Scheme 2). Introduction of electron withdrawing and electron donating groups on the aryl ring of *N*-methylaniline has no major impact on the reactivity of the corresponding aniline derivatives **1b**–**1k**. For example, the *p*-OMe-substituted *N*-methylaniline **1f** (Hammett constant of -0.27) is converted to **3f** in quantitative yield after 1 h at 90 °C, similarly to its *m*-Cl substituted analogue **1i** (Hammett constant of +0.37). This reactivity contrasts with the previous methodologies involving hydrosilanes and H₂, which exhibit a lower reactivity for aniline substrates bearing electron donating groups and are mostly inefficient for aliphatic amines.^[6] Importantly, **VB**^{Me} is also able to promote the methylation of secondary aliphatic amines in quantitative yields. As depicted in Scheme 2, diethylamine, piperidine and morpholine are converted to the corresponding methylamines **3m**, **3n** and **3o** in excellent yields (> 78 %). Notably, the method also shows a very high tolerance to steric congestion and bulky substrates, such as diisopropylamine and 2,2,6,6-tetramethylpiperidine, afford the methylated products **3p** and **3q**, respectively, in quantitative yield within 1 h.

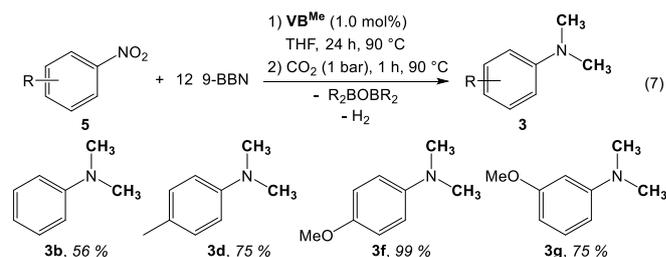


Because secondary amines readily undergo methylation in the presence of CO₂ and 9-BBN, it is noteworthy that the mono-methylation of primary amines is disfavoured and primary amines are directly converted to their dimethylated product, in the presence of **VB**^{Me}. In fact, addition of 3.5 equiv. 9-BBN to a THF solution of aniline (**4b**), in the presence of 1.0 mol% **VB**^{Me} and 1 bar CO₂,

affords **3b** in 55 % yield (Eq. 4). No trace of the mono-methyl derivative **1b** was observed by ¹H NMR spectroscopy and GC/MS analysis and 45 % of the unreacted substrate **4b** was recovered at the end of the reaction. In consequence, in the presence of 8 equiv. 9-BBN, aniline was transformed to **3b** in 85 % yield and dimethylation of the bulky 2,6-diisopropylaniline provides **3t** in 52 % yield, in a single operation.

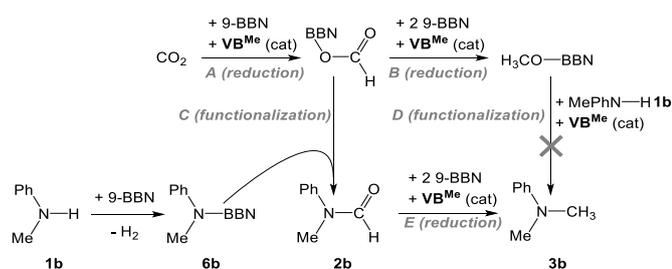


Ideally, the formation of a N-CH₃ functionality in fine chemicals is expected to tolerate a variety of additional functional groups and the chemoselectivity of the metal-free methylation of amines was thus assessed. As discussed thereabove, the **VB**^{Me}/9-BBN is compatible with the presence of halogen groups, including Cl and F substituents. Importantly, the presence of a hydroxyl group in **4u** does not prohibit the methylation of the NH₂ group and **3u** was obtained in 59 % yield. Because the methylation methodology proceeds under reductive conditions, it is remarkable that oxidizing functional groups such as esters and alkenes are well tolerated. Indeed, although aniline **4v** features an oxidizing aromatic ester group, it is converted to **3v** in 69 % yield, without concomitant reduction of the ester function. Similarly, the vinyl-substituted aniline **4w** provides an entry to **3w**. Importantly, although the methylation of indole **1s** resulted in the concomitant reduction of the cyclic C=C bond in the presence of [Ru(triphos)(tmm)]/HNTf₂ and CO₂/H₂,^[6c] indole **3s** is obtained in 91 % yield with the present methodology (Scheme 2). Yet, **VB**^{Me}/9-BBN appears to be a potent system for hydroboration of ketones and methylation of **4x** results in the formation of a mixture of reduction products among which dimethylamines **3w** and **3y** were obtained in 35 and 29 % yield, respectively (Eq. 6). The formation of the vinyl derivative **3w** is puzzling as it suggests that the **VB**^{Me}/9-BBN system is able to promote the deoxygenation of acetophenone derivatives to styrenes and this reaction is currently under scrutiny in our laboratories.



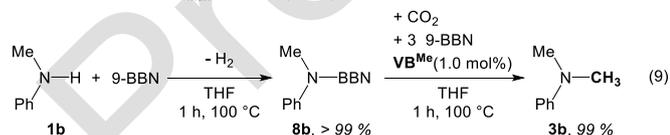
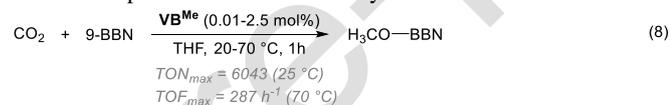
Finally, the high reduction potential of **VB**^{Me}/9-BBN was utilized to promote the methylation of nitroarenes *via* a one-pot reduction of the nitro group and subsequent methylation of the resulting N-B linkages under an atmosphere of CO₂. As exemplified in Eq. 7, this two-step procedure enables the formation of dimethylamines **3b**, **3d**, **3f** and **3g** from the corresponding nitroarenes **5** in good to excellent yields, ranging 56 to 99 %.

Different pathways can account for the formation of methylamines from CO₂, amines and hydroboranes, which are represented in Scheme 3. The catalytic reduction of CO₂ to the methoxyborane CH₃OBBN can first precede the formation of the C-N bond (steps A and B in Scheme 3). Indeed, we found that proazaphosphatrane superbases are highly efficient catalysts in the hydroboration of CO₂ (see SI). In fact, **VB**^{Me} exhibits a maximum TON of 6043 (TOF of



Scheme 3. Proposed pathways for the catalytic methylation of **1b** with CO₂ and 9-BBN.

31 h⁻¹ at RT and 287 h⁻¹ at 70 °C) for the reduction of CO₂ with 9-BBN and is therefore the most active metal-free catalyst for this transformation, so far (see Eq. 8 and SI). Nonetheless, CH₃OBBN is a poor electrophile and no trace of methylamine **3b** could be observed upon reaction of 1 equiv. **1b** with CH₃OBBN, in the presence or absence of VB^{Me} and/or 9-BBN (step D). In fact, **1b** readily undergoes a dehydrogenative N-B coupling in the presence of 9-BBN, at 100 °C, to afford borylamine **6b**. The complete conversion of **6b** to **3b**, in the presence of 3 equiv. 9-BBN and 1.0 mol% VB^{Me} confirms the possible implication of a N-B linkage in the methylation of amines (Eq. 9). In addition, as suggested by the formation of **2w**, formamides are also possible intermediates in the formation of the methylamine product and this hypothesis was verified by the successful reduction of *N*-formyl-*N*-methylaniline (**2b**) to **3b** with 9-BBN. A plausible route thus involves the reduction of CO₂ to a formoxyborane intermediate HCOOBBN (step A), which serves as an electrophile to facilitate the formation of the C-N bond and afford a formamide intermediate (step C). Reduction of the R₂N-COH formamide with 9-BBN then yields the methylamine R₂N-CH₃ (step E). Importantly, in this mechanism, the efficiency of the methylation of the N-H bond is directly governed by the relative rates of the formylation of the amine with the formoxyborane (step C) and the reduction of HCOOBBN to the unproductive methoxyborane end-product (step B). This mechanism thus accounts for the influence of the reaction temperature on the efficiency of the methylation of the amine, because step C is favored at higher temperature (> 60 °C). As exemplified in Entry 19 of Table 1, methylation of diphenylamine **1a** is unproductive at 20 °C and the quantitative formation of methoxyborane CH₃OBBN was observed in place of the desired methylamine **3a**.



In conclusion, we have developed an unprecedented metal-free method for the methylation of N-H bonds with CO₂. Using hydroboranes as reductants, this transformation enables the methylation of a large scope of substrates, including basic secondary aliphatic amines, with a high chemoselectivity. The success of this approach relies on proazaphosphatrane superbases which are utilized for the first time as reduction catalysts. The potential of these organocatalysts in reduction chemistry is currently under investigation in our group.

Experimental Section

Detailed descriptions of experimental methods and results are given in the Supporting Information.

Received: ((will be filled in by the editorial staff))

Published online on ((will be filled in by the editorial staff))

Keywords: Carbon dioxide · Organocatalysis · Reduction · Boranes · Amines

- [1] M. Aresta, *Carbon dioxide as a chemical feedstock*, Wiley-VCH Verlag GmbH, **2010**.
- [2] a) P. G. Jessop, T. Ikariya, R. Noyori, *Chem. Rev.* **1995**, *95*, 259-272; b) S. N. Riduan, Y. Zhang, J. Y. Ying, *Angew. Chem. Int. Ed.* **2009**, *48*, 3322-3325; c) A. E. Ashley, A. L. Thompson, D. O'Hare, *Angew. Chem. Int. Ed.* **2009**, *48*, 9839-9843; d) R. Tanaka, M. Yamashita, K. Nozaki, *J. Am. Chem. Soc.* **2009**, *131*, 14168-14169; e) C. Federsel, A. Boddien, R. Jackstell, R. Jennerjahn, P. J. Dyson, R. Scopelliti, G. Laurenczy, M. Beller, *Angew. Chem. Int. Ed.* **2010**, *49*, 9777-9780; f) S. Wesselbaum, T. vom Stein, J. Klankermayer, W. Leitner, *Angew. Chem. Int. Ed.* **2012**, *51*, 7499-7502; g) K. Motokura, D. Kashiwame, A. Miyaji, T. Baba, *Org. Lett.* **2012**, *14*, 2642-2645; h) A. Goeppert, M. Czaun, J.-P. Jones, G. K. Surya Prakash, G. A. Olah, *Chem. Soc. Rev.* **2014**.
- [3] a) F. J. Fernandez-Alvarez, A. M. Aitani, L. A. Oro, *Catal. Sci. Tech.* **2014**, *4*, 611-624; b) A. Tlili, X. Frogneux, E. Blondiaux, T. Cantat, *Angew. Chem. Int. Ed.* **2014**, *53*, 2543-2545.
- [4] a) C. Das Neves Gomes, O. Jacquet, C. Villiers, P. Thuery, M. Ephritikhine, T. Cantat, *Angew. Chem. Int. Ed.* **2012**, *51*, 187-190; b) O. Jacquet, C. D. Gomes, M. Ephritikhine, T. Cantat, *J. Am. Chem. Soc.* **2012**, *134*, 2934-2937; c) K. Motokura, N. Takahashi, D. Kashiwame, S. Yamaguchi, A. Miyaji, T. Baba, *Catal. Sci. Tech.* **2013**, *3*, 2392-2396.
- [5] a) M. Khandelwal, R. J. Wehmschulte, *Angew. Chem. Int. Ed.* **2012**, *51*, 7323-7326; b) O. Jacquet, C. Das Neves Gomes, M. Ephritikhine, T. Cantat, *ChemCatChem* **2013**, *5*, 117-120.
- [6] a) O. Jacquet, X. Frogneux, C. Das Neves Gomes, T. Cantat, *Chem. Sci.* **2013**, *4*, 2127-2131; b) Y. Li, X. Fang, K. Junge, M. Beller, *Angew. Chem. Int. Ed.* **2013**, *52*, 9568-9571; c) K. Beydoun, T. vom Stein, J. Klankermayer, W. Leitner, *Angew. Chem. Int. Ed.* **2013**, *52*, 9554-9557; d) Y. Li, I. Sorribes, T. Yan, K. Junge, M. Beller, *Angew. Chem. Int. Ed.* **2013**, *52*, 12156-12160; e) X. Cui, X. Dai, Y. Zhang, Y. Deng, F. Shi, *Chem. Sci.* **2014**, *5*, 649-655; f) X. Frogneux, O. Jacquet, T. Cantat, *Catal. Sci. Tech.* **2014**, *4*, 1529-1533.
- [7] a) S. Chakraborty, J. Zhang, J. A. Krause, H. Guan, *J. Am. Chem. Soc.* **2010**, *132*, 8872-8873; b) S. Chakraborty, Y. J. Patel, J. A. Krause, H. Guan, *Polyhedron* **2012**, *32*, 30-34; c) S. Chakraborty, J. Zhang, Y. J. Patel, J. A. Krause, H. Guan, *Inorg. Chem.* **2013**, *52*, 37-47; d) S. Bontemps, L. Vendier, S. Sabo-Etienne, *Angew. Chem. Int. Ed.* **2012**, *51*, 1671-1674; e) S. Bontemps, S. Sabo-Etienne, *Angew. Chem. Int. Ed.* **2013**, *125*, 10443-10445; f) M. J. Sgro, D. W. Stephan, *Angew. Chem. Int. Ed.* **2012**, *51*, 11343-11345; g) R. Shintani, K. Nozaki, *Organometallics* **2013**, *32*, 2459-2462.
- [8] a) M.-A. Courtemanche, M.-A. Légaré, L. Maron, F.-G. Fontaine, *J. Am. Chem. Soc.* **2013**, *135*, 9326-9329; b) C. Das Neves Gomes, E. Blondiaux, P. Thuéry, T. Cantat, *Chem. Eur. J.* **2014**, *20*, 7098-7106; c) T. Wang, D. W. Stephan, *Chem. Commun.* **2014**, *50*, 7007-7010; d) T. Wang, D. W. Stephan, *Chem. Eur. J.* **2014**, *20*, 3036-3039.

- [9] a) M. F. Ali, B. M. El Ali, J. G. Speight, *Handbook of Industrial Chemistry: Organic Chemicals*, McGraw-Hill Education, **2005**; b) P. Weissermel, H.-J. Arpe, *Industrial Organic Chemistry*, Wiley-VCH, **1997**.
- [10] It was recently shown that phosphines are also efficient organocatalysts in the hydroboration of CO₂ to methoxyboranes. See ref [8c] and C. Gomes, E. Blondiaux, T. Cantat, Patent App. PCT/IB2014/060356 and FR1352996, filed April 4-2013.
- [11] a) L. Chen, A. J. Poë, *Coord. Chem. Rev.* **1995**, *143*, 265-295; b) P. B. Kisanga, J. G. Verkade, R. Schwesinger, *J. Org. Chem.* **2000**, *65*, 5431-5432.
- [12] a) C. Lensink, S. K. Xi, L. M. Daniels, J. G. Verkade, *J. Am. Chem. Soc.* **1989**, *111*, 3478-3479; b) J. G. Verkade, *Acc. Chem. Res.* **1993**, *26*, 483-489; c) J. G. Verkade, *Coord. Chem. Rev.* **1994**, *137*, 233-295; d) J. G. Verkade, P. B. Kisanga, *Tetrahedron* **2003**, *59*, 7819-7858; e) V. R. Chintareddy, K. Wadhwa, J. G. Verkade, *J. Org. Chem.* **2009**, *74*, 8118-8132; f) K. Wadhwa, V. R. Chintareddy, J. G. Verkade, *J. Org. Chem.* **2009**, *74*, 6681-6690; g) K. Wadhwa, J. G. Verkade, *J. Org. Chem.* **2009**, *74*, 5683-5686; h) V. R. Chintareddy, A. Ellern, J. G. Verkade, *J. Org. Chem.* **2010**, *75*, 7166-7174; i) S. M. Raders, J. G. Verkade, *J. Org. Chem.* **2010**, *75*, 5308-5311; j) B. Chatelet, L. Joucla, J. P. Dutasta, A. Martinez, V. Dufaud, *Chem. Eur. J.* **2014**, *20*, 8571-8574; k) B. Chatelet, L. Joucla, J.-P. Dutasta, A. Martinez, K. C. Szeto, V. Dufaud, *J. Am. Chem. Soc.* **2013**, *135*, 5348-5351.
- [13] It is noteworthy that replacing **IPr** with **VB^{Me}** in Eq. 1 affords formamides **2** and formation of **3** was not observed.