Carbon Dioxide Reduction to Methylamines under Metal-Free Conditions

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CO_2 Reduction to Methylamines under Metal-Free Conditions**

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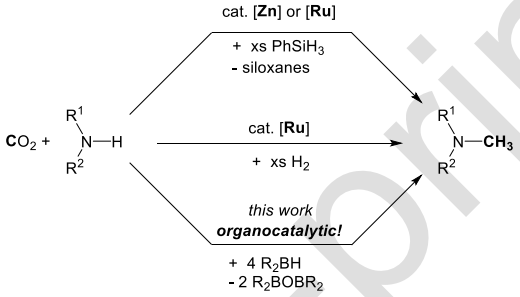
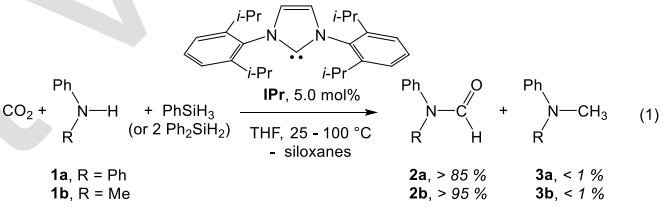
The utilization of CO_2 as a C_1–building block for the production of fuels or chemicals has the advantage of creating added–value, able to mitigate the capture cost of this greenhouse gas.[1] In this context, increasing research efforts have been devoted to promoting the reduction of CO_2 to formic acid or methanol, because these C_1–molecules can either serve as H_2 carriers or directly as fuels.[2] In parallel, the scope of organic molecules incorporating a CO_2 molecule has rapidly increased with the discovery of new methodologies to promote the conversion of CO_2 to a variety of heterocycles, carboxylic acids, amides and methylamines.[3],[4],[5],[6] Importantly, the reduction of CO_2 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 H_2 or electrochemical cells, are required for the large scale recycling of CO_2 to formic acid or methanol, the formation of fine chemicals from CO_2 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, CO_2 transformation to fine chemicals poses different constraints as a large scope and a high chemoselectivity is anticipated for the fixation of CO_2 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 CO_2.

First unveiled in 2013, the catalytic reduction of CO_2 to methylamines is a promising new method for recycling CO_2 to value added chemicals, as it by-passes the classical methodologies involving formaldehyde or hazardous alkylating agents such as methyliodide, dimethylsulfate or dimethylcarbonate.[9] Using molecular zinc catalysts, our group has indeed shown that CO_2 could serve as an efficient carbon source for the formation of N–CH_3 groups, in the presence of $PhSiH_3$,[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 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 CO_2 as a carbon source. Using phosphorus bases as catalysts, N–H bonds in aromatic and aliphatic amines are quantitatively methylated, with CO_2 and hydroboranes reductants.



The methylation of amines with CO_2 necessitates the use of catalysts able to promote both the formation of N–C bonds and the 6–electron reduction of CO_2. 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 CO_2 to methanol and our group has demonstrated that they can also convert amines and CO_2 to formamides, in the presence of hydrosilanes.[2b, 4a] Nevertheless, reacting diphenylamine (**1a**) or *N*–methylaniline (**1b**) with CO_2, in the presence of $PhSiH_3$ or Ph_2SiH_2 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 CO_2 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 CO_2 to methoxyboranes.[8a-c] We have thus explored the possible use of hydroboranes as reductants in the methylation of amines with CO_2. To our delight, reacting **1a** with CO_2 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 CO_2.

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

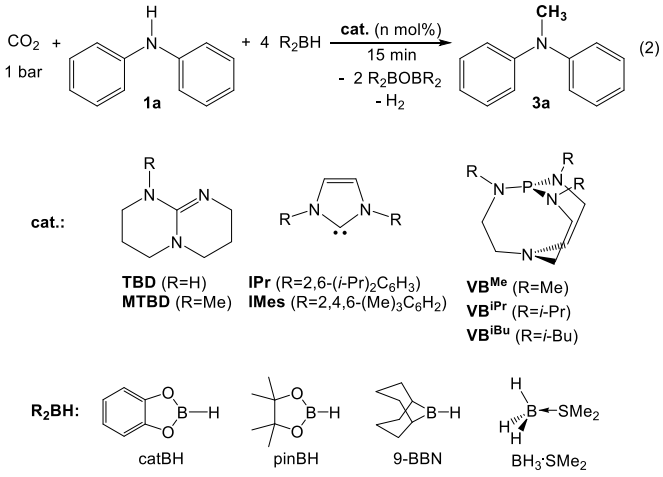
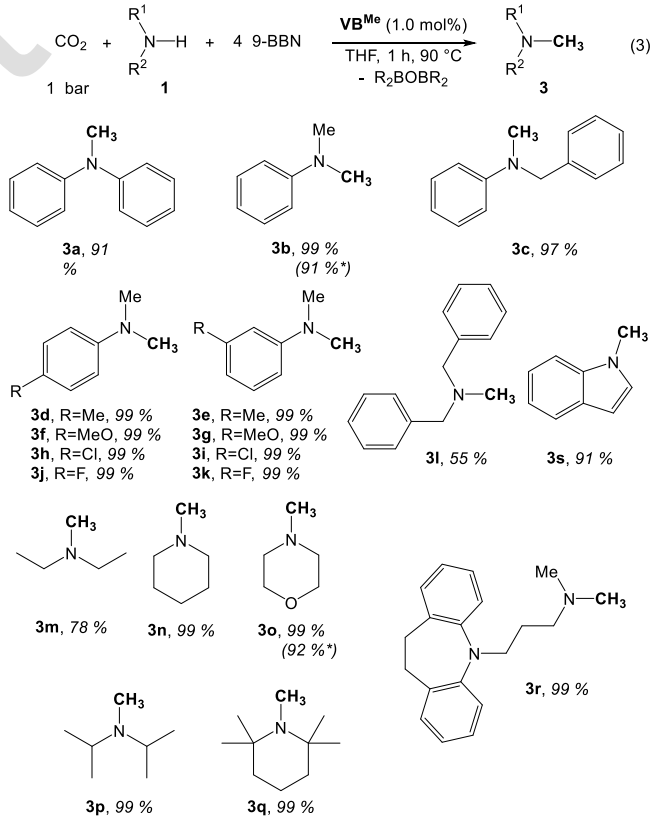


Table 1. Metal–free catalytic methylation of **1a** with CO_2 and hydroboranes, as depicted in Eq. 2.

Entry	Catalyst [mol%]	Borane (R_2BH)	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	**VB^{iBu}** (1.0)	9–BBN	90	THF	85
9	**VB^{iPr}** (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), CO_2 (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.

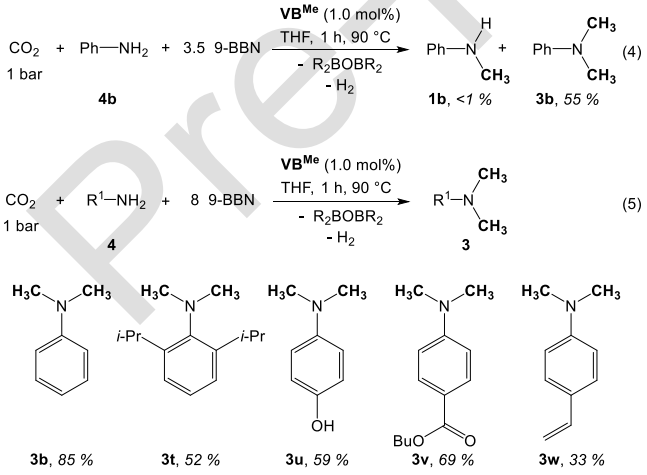
A variety of organic catalysts were then tested so as to improve the efficiency of the methylation of **1a**. Replacing **IPr** with **IMes** significantly lowers the conversion yield of **1a** to **3a** (Entries 2 and 3, Table 1). Interestingly, nitrogen bases, such as **TBD** and **MTBD**, are also catalysts in the methylation of **1a** with CO_2 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 CO_2 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 PPh_3 affords **3a** with a mediocre 13 % yield from CO_2, it is formed in 43 % yield with the more basic $P(NEt_2)_3$ catalyst (Entries 6 and 7, Table 1). It is well–established that proazaphosphatranes are superbases and Verkade and coworkers have shown that their pKa values exceed 32 in MeCN and are therefore significantly higher than the pKa of the P center in classical phosphines (2.7 in PPh_3 and 8.2 in $P(NEt_2)_3$).[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 proazaphosphatrane superbases were tested in the reductive functionalization of CO_2 to **3a**, namely **VB^{iBu}**, **VB^{iPr}** 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 **VB^{iPr}** 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 CO_2 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 BH_3·SMe_2 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 unefficient at 20 °C, where 9–BBN was consumed to form CH_3OBBN 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 Ph_2N–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 H_2 evolution in the ^1H NMR spectrum of the crude mixture (δ 4.2 in d_8-THF).



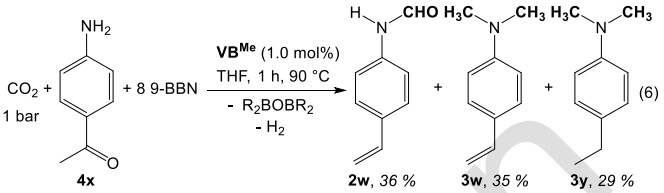
Scheme 2. Metal–free catalytic methylation of secondary amines with CO_2 and 9–BBN. Reaction conditions: amine (0.20 mmol), hydroborane (0.80 mmol), **VB^{Me}** (0.002 mmol), THF (0.50 mL), CO_2 (1 bar); yield determined by GC/MS using mesitylene as an internal standard, after calibration. (*Isolated yield)

It is of interest to compare the efficiency of this novel metal–free methodology for the conversion of CO_2 to methylamines with the metal–catalyzed versions recently developed by the groups of Beller, Cantat and Klankermeyer, using H_2 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 CO_2 (20 bar) and H_2 (60 bar).[6c, 6d] In comparison, the methylation of **1b** with 1 bar CO_2 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 CO_2 (see SI).

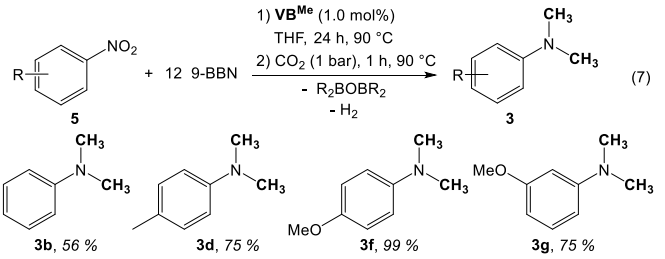
Given the high catalytic activity of **VB^{Me}**, the scope of the methylation of N–H bonds with CO_2 and hydroboranes was explored so as to establish the utility of this new methodology. The methylation of various secondary anilines was investigated using 4 equiv. 9–BBN and 1 bar CO_2, in the presence 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 H_2, 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 CO_2 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 CO_2, affords **3b** in 55 % yield (Eq. 4). No trace of the mono–methyl derivative **1b** was observed by ^{1}H 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.

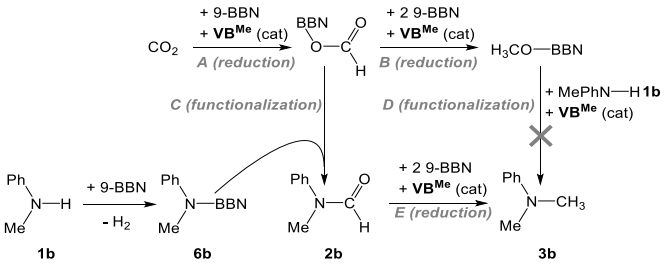


Ideally, the formation of a N–CH_3 functionality in fine chemicals is expected to tolerate a variety of additional functional groups and the chemoselectivity of the metal–free methylation of amines was thus assessed. As discussed thereabove, the **VB^{Me}**/9–BBN is compatible with the presence of halogen groups, including Cl and F substituents. Importantly, the presence of a hydroxyl group in **4u** does not prohibit the methylation of the NH_2 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)]/$HNTf_2$ and CO_2/H_2,[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.



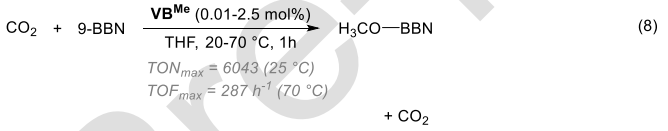
Finally, the high reduction potential of **VB^{Me}**/9–BBN was utilized to promote the methylation of nitroarenes *via* a one-pot reduction of the nitro group and subsequent methylation of the resulting N–B linkages under an atmosphere of CO_2. As exemplified in Eq. 7, this two-step procedure enables the formation of dimethylamines **3b**, **3d**, **3f** and **3g** from the corresponding nitroarenes **5** in good to excellent yields, ranging 56 to 99 %.

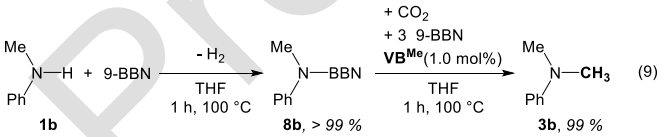
Different pathways can account for the formation of methylamines from CO_2, amines and hydroboranes, which are represented in Scheme 3. The catalytic reduction of CO_2 to the methoxyborane CH_3OBBN can first precede the formation of the C–N bond (steps A and B in Scheme 3). Indeed, we found that proazaphosphatrane superbases are highly efficient catalysts in the hydroboration of CO_2 (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 CO_2 and 9–BBN.

31 h^{-1} at RT and 287 h^{-1} at 70 °C) for the reduction of CO_2 with 9–BBN and is therefore the most active metal–free catalyst for this transformation, so far (see Eq. 8 and SI). Nonetheless, CH_3OBBN is a poor electrophile and no trace of methylamine **3b** could be observed upon reaction of 1 equiv. **1b** with CH_3OBBN, in the presence or absence of $\mathbf{VB^{Me}}$ 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% $\mathbf{VB^{Me}}$ 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 CO_2 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 R_2N–COH formamide with 9–BBN then yields the methylamine R_2N–CH_3 (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 CH_3OBBN 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 CO_2. 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.

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[13] It is noteworthy that replacing **IPr** with **VB^{Me}** in Eq. 1 affords formamides **2** and formation of **3** was not observed.