# ORGANOMETALLICS

# Selective N-Methylation of Aliphatic Amines with CO<sub>2</sub> and Hydrosilanes Using Nickel-Phosphine Catalysts

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**S** Supporting Information

ABSTRACT: A method using CO<sub>2</sub> and PhSiH<sub>3</sub> for the methylation of primary and secondary aliphatic amines catalyzed by Ni (0) complexes was developed, selectively producing the monomethylated products in moderate to good yields. For that purpose, two catalysts were used: [(dippe)- $Ni(\mu-H)]_2$  and the commercially available  $Ni(COD)_2/dcype$ , both of which were rather efficient in this process. With a slight experimental modification, the reaction allowed the production of monomethylated ureas in good yields by using low amounts of PhSiH<sub>3</sub>. On the basis of the experimental



## INTRODUCTION

The development of catalytic processes for the utilization of carbon dioxide, a greenhouse gas, is of growing interest in chemistry.<sup>1</sup> Carbon dioxide is an abundant, nontoxic, nonflammable, cheap, and renewable carbon source and therefore an advantageous C1 building block. Various methodologies for chemical transformation of CO<sub>2</sub> to valuable chemicals have been made to replace phosgene-based routes, by the catalytic incorporation of CO<sub>2</sub> into organic substrates for their derivatization. One of the simplest reactions is the insertion of  $CO_2$  (e.g., to obtain carbamates,<sup>2</sup> carboxylate allyl derivates,<sup>3</sup> acetic acid,<sup>4</sup> dialkyl carbonates,<sup>5</sup> polypyrones,<sup>6</sup> lactones,<sup>7</sup> and polyurethanes).<sup>8</sup> Nevertheless, the scope of organic molecules directly produced from CO<sub>2</sub> remains very strait, and only a small number of commercial processes exist, such as the production of urea (Bosch-Meiser process) and the synthesis of cyclic carbonates, polycarbonates, and salicylic acid (Kolbe-Schmitt synthesis).<sup>1c,9</sup> Interestingly, these reactions result in the functionalization of CO<sub>2</sub> without a significant reduction of the carbon oxidation state. Indeed, multielectron chemical reduction of CO<sub>2</sub> is indisputably the greatest difficulty facing CO<sub>2</sub> recycling, because highly active and inexpensive catalysts are required to activate the stable CO2 molecule and promote its reduction. With regard to this, recent important developments in the conversion of carbon dioxide into formates, methanol (methoxides), and methane, using relatively mild reducing agents (e.g., hydrosilanes, boranes, and  $H_2)$  and a suitable catalyst, have been reported. $^{9c,f,10}$  Also of interest is the design of efficient catalytic systems able to both reduce and functionalize  $CO_2$  to form new bonds such as C-C, C-O, and C-N, expanding the use of carbon dioxide as a C1-feedstock for the production of fine chemicals.<sup>10k,l,11</sup> In this context, the C-N bond formation derived from CO<sub>2</sub> and amines is of great interest due to the importance of N-containing compounds in

the chemical industry, such as methyl-amines and urea derivatives. Methyl-substituted amines have been widely used as key intermediates in the manufacture of pharmaceuticals, agrochemicals, dyes, formulation agents, and polymers, or used as solvents.<sup>12</sup> The most common methodology for amine methylation in industry uses toxic formaldehyde as the C1 source,<sup>13</sup> whereas in laboratories, hazardous methylation reagents like methyl iodide and dimethyl sulfate still prevail.<sup>14</sup> Consequently, the application of safe and sustainable reagents is highly desired. Considering this, during the past decade dimethyl carbonate and methanol have been presented as interesting "green" alternatives.<sup>14b,15</sup> Very recently, Cantat,<sup>101,16</sup> Beller,<sup>17</sup> and Leitner<sup>18</sup> and co-workers reported that CO<sub>2</sub> could act as a methylating reagent with the use of Zn/NHC (Cantat) or Ru/phosphine catalysts and hydrosilane or hydrogen gas as reducing reagents (Beller and Leitner et al.). The 6-electron reduction of CO2 with the formation of a N-C bond was unknown until 2013, and only the above-mentioned catalytic systems are currently known. Despite these great achievements, the Ru/phosphine catalyst requires high CO<sub>2</sub> pressures (30 bar)<sup>17b</sup> to carry out the methylation. Hence, research regarding new, cheap, metal catalysts able to perform such a process under milder conditions is still relevant. Herein, we disclose a nickel/phosphine catalytic system able to perform the monomethylation of primary and secondary aliphatic amines, employing CO<sub>2</sub> and hydrosilanes as methyl group sources.

## RESULTS AND DISCUSSION

Following our interest in the reduction of CO<sub>2</sub> with Et<sub>3</sub>SiH catalyzed by the  $[(dippe)Ni(\mu-H)]_2$  complex (A), we obtained the reduction products of CO<sub>2</sub>, 3s and 4s, which can be

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Scheme 1. Reduction of CO<sub>2</sub> Catalyzed by  $[(dippe)Ni(\mu-H)]_2$ 

Et <sub>3</sub> Si—H	+ co	$\begin{array}{c} [(dippe)Ni(\mu-H)]_2\\ \underline{1 \ mol \ \%}\\ THF, 80^{\circ}C, \ 22h \end{array}$	Et <sub>3</sub> Si <sup></sup> O <sup></sup> SiEt <sub>3</sub>	+	Et <sub>3</sub> Si <sup>O</sup> CH <sub>2</sub> SiEt <sub>3</sub>	+ Et₃Si∽ <sup>O</sup> ∼CH₃ +	со
1s Conv: 50 %	1 at	lm	2s 35 %		3s 12 %	45 3 %	

envisaged as intermediates in the  $CO_2$  reduction toward methane formation (Scheme 1).<sup>19</sup>

Therefore, in order to improve the yields of **3s** and **4s** and even complete the reduction of CO<sub>2</sub> to methane, we decided to assess the use of PhSiH<sub>3</sub>. However, we found that CO<sub>2</sub> was unreactive under a variety of reaction conditions; for example, CO<sub>2</sub> was unreactive using a mixture of PhSiH<sub>3</sub> and [(dippe)-Ni( $\mu$ -H)]<sub>2</sub> (5% mol) at different temperatures (80 to 120 °C) in a variety of solvents (THF, toluene, MeCN, and dioxane). The improved version of the reaction in Scheme 1 is depicted in Scheme 2, where Et<sub>3</sub>B was required to produce silyl formate (Et<sub>3</sub>SiOCOH).<sup>19</sup> Performing the reaction with PhSiH<sub>3</sub> instead of Et<sub>3</sub>SiH allowed the complete recovery of unreacted PhSiH<sub>3</sub>.

Scheme 2. Hydrosilylation of CO<sub>2</sub> with Et<sub>3</sub>SiH Catalyzed by  $[(dippe)Ni(\mu-H)]_2$ .



Therefore, due to the unexpected lack of reactivity for the same systems using PhSiH<sub>3</sub>, we investigated the reaction of carbon dioxide with benzylamine in the presence of PhSiH<sub>3</sub> and  $[(dippe)Ni(\mu-H)]_2$  as a model system. The reaction was assessed under different reaction conditions, and the results for these experiments are summarized in Table 1.

All reactions were monitored by GC/MS, and the following products were found: N-methylbenzyl-amine (1b), N-methyl-N,N'-dibenzylurea (1c), N,N'-dibenzylformimidamide (1d), N,N'-dibenzylurea (1e), N-benzylformamide (1f), and benzy-lisocyanate (1g). The complete conversion of 1a was achieved using toluene after 20 h at 100 °C, producing N-methyl-N,N'-dibenzylurea (1c) in 80% yield (entry 6). In general, both solvents were suitable for this reaction; however, toluene provided the best conversions and selectivity toward the methylated products (1b and 1c). Lowering the reaction

temperature to 80 °C resulted in a low conversion of 1a in both toluene and THF (entries 1 and 4, Table 1). Additionally, the reaction time influences the conversion (entries 2 and 3). Dibenzylurea (1e), *N*-benzylformamide (1f), and benzylisocyanate (1g) can be envisaged as intermediates in the catalytic methylation of amines.

To increase the yield of *N*-methylbenzylamine (1b), we decided to use higher amounts of  $PhSiH_3$  (4 and 6 equiv) but otherwise use reaction conditions for entry 6 in Table 1 (Scheme 3).

As can be seen in Scheme 3, the use of higher amounts of  $PhSiH_3$  in the methylation reaction of 1a increased the yield of *N*-methylbenzylamine (1b). These preliminary results established that the nickel complex (A) is an efficient catalyst for the selective monomethylation of aliphatic amines; control experiments under similar conditions but in the absence of (A) did not produce any product.

Thus, we decided to extend the study to other nickel catalytic systems for the methylation of amines using  $CO_2$  and  $PhSiH_3$ . We turned our attention to the  $Ni(COD)_2/dcype$  (**B**) system, and the main results for these experiments are summarized in Table 2.

The results displayed in Table 2 show that commercially available  $Ni(COD)_2/dcype$  (B) is as good a catalyst as complex (A) and therefore of more practical use. Having at hand both active catalytic systems, we then assessed the scope of the methylation of a variety of primary aliphatic amines, and relevant results are in Tables 3 and 4.

The methylation reaction of aliphatic amines with 2 eq of  $PhSiH_3$  using catalysts (A) and (B) (Table 3) yielded a distribution of products with a reasonable selectivity toward the corresponding *N*-methyl-*N*,*N'*-urea (product c); both catalysts produced, in general, similar conversions. Surprisingly, aniline exhibited low reactivity (Table 3, entry 7), which was unexpected, considering previous reports where the authors argued that the high reactivity of aromatic amines is because the aromatic ring promotes the reduction of the corresponding

Table 1. Catalytic N-Methylation of Benzylamine with CO<sub>2</sub> and PhSiH<sub>3</sub><sup>a</sup>

NH <sub>2</sub>	+ CO2	$\overbrace{ 2 \text{ eq PhSiH}_3}^{[(\text{dippe})\text{Ni}(\mu-\text{H})]_2}$	NH - CH <sub>3</sub> +	O N H CH <sub>3</sub> +	<b>₩</b>	`N → (	©_₽_₽_₽	0+0	∧ <sub>N</sub> <sup>O</sup> H +	N=C=C
1a	P <sub>atm</sub>		1b	10	1d	I	1e		1f	1g
entry	solvent	T (°C)	<i>t</i> (h)	conv. of 1a (%)	1b (%)	1c (%)	1d (%)	1e (%)	1f (%)	1g (%)
1	THF	80	20	39	-	-	-	13	_	26
2	THF	100	12	70	-	22	_	20	3	25
3	THF	100	20	93	4	69	-	17		3
4	toluene	80	20	55	6	38	_	7	_	4
5	toluene	100	12	81	9	61	3	-	8	-
6	toluene	100	20	100	11	80	6	3	-	-

<sup>*a*</sup>All reactions were carried out in a Schlenk flask equipped with a Rotaflo valve using 5 mL of solvent. Reaction conditions: mol ratio of 0.04:1:2 of  $[(dippe)Ni(\mu-H)]_2$ , benzylamine, and PhSiH<sub>3</sub>, respectively, and 1 atm of CO<sub>2</sub> were used. Conversions and yields were determined by GC/MS analysis of the crude mixture.

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NH <sub>2</sub> + 0	CO <sub>2</sub> ((dippe)Ni 4 mol Tolue P <sub>atm</sub> 100 °C,	$ \begin{array}{c} (\mu - H)]_2 \\ \stackrel{\text{(}\mu - H)]_2}{\longrightarrow} & \begin{array}{c} & & \\ $	• • • • • • • • • • • • • • • • • • •	Id	P P N N N N N N N N N N N N N N N N N
Conv. 100 %	4 eq Ph	nSiH <sub>3</sub> 66 %	22 %	3 %	9 %
Conv. 100 %	6 eq Pl	1SiH <sub>3</sub> 69 %	25 %	6 %	

Table 2. N-Methylation of Benzylamine Catalyzed with  $[(dippe)Ni(\mu-H)]_2$  and  $[Ni(COD)_2]/dcype^a$ 

NH <sub>2</sub> +	CO <sub>2</sub>	Catalyst n PhSiH <sub>3</sub> Toluene 100 °C, 20 h	NH CH <sub>3</sub> +	O N CH <sub>3</sub> N	+	N N N	+	
1a	' atm		1b	1c		1d		1e
entry	ca	talyst	conv. of <b>1a</b> (%)	eq of PhSiH <sub>3</sub>	1b (%)	1c (%)	1d (%)	1e (%)
1	<sup>b</sup> [(dippe	$)Ni(\mu-H)]_2$	100	2	11	80	6	3
2			100	4	66	22	3	9
3	<sup>c</sup> [Ni(CO	D) <sub>2</sub> ]/dcype	100	2	6	82	9	3
4			100	4	64	27	-	9

"All reactions were carried out in a Schlenk flask equipped with a Rotaflo valve using 5 mL of solvent. Reaction conditions. <sup>b</sup>Mol ratio of 0.01:0.25:0.5 or 1 of  $[(dippe)Ni(\mu-H)]_2$ , benzylamine, and PhSiH<sub>3</sub>, respectively, and 1 atm of CO<sub>2</sub> were used. <sup>c</sup>Mol ratio of 0.01:0.01:0.25:0.5 or 1 of  $[Ni(COD)_2]$ , dcype, benzylamine, and PhSiH<sub>3</sub>, respectively, and 1 atm of CO<sub>2</sub> were used. Conversions and yields were determined by GC/MS analysis of the crude mixture.

formamide.<sup>101,17b,20</sup> Hence, the lower reactivity of aniline can be explained by the lower basicity of aromatic amines, compared with aliphatic amines; this is included in the corresponding mechanistic proposal depicted in Scheme 4 (vide infra).<sup>21</sup>

The results for the methylation reaction using 4 eq of PhSiH<sub>3</sub> are displayed in Table 4. As a general trend, aliphatic amines were methylated to yield the corresponding *N*-methylated amine (b) in increased but moderate yields, along with three other byproducts (products c, d, and e). Again, both catalysts gave rather similar yields and product distribution. The use of amines gave full conversion with the exception of aniline, entry 7. To note, the *N*,*N*-dimethylated amines were not detected in any case (i. e., the current methodology allows selective monomethylation of primary aliphatic amines).

Considering the results, we proposed a mechanism that considers consecutive methylation of N–H bonds using  $CO_2$  and hydrosilanes, depicted in Scheme 4. The proposed mechanism for the  $L_n$ M-catalyzed process include the following considerations: (i) even though it is a very well-known process, <sup>9c,e,g,10j,m,n,19,22</sup> the reduction of  $CO_2$  with PhSiH<sub>3</sub> to generate the corresponding silver formate (R<sub>3</sub>SiOCOH) or methoxysilane (R<sub>3</sub>SiOCH<sub>3</sub>) was not considered because  $CO_2$  was stable in the presence of PhSiH<sub>3</sub> and the used nickel catalysts. Moreover, both silver formate and methoxysilane species are electrophiles known to react with amines to yield formamides and methylamines, respectively;<sup>23</sup> (iii) the formation of carbamic acid from amines and  $CO_2$  has been documented;<sup>21,24</sup> and (iv) the electrophile isocyanate is considered a key reaction intermediate.<sup>24a,h</sup>

Considering the above, the initial step involves an oxidative addition of  $PhSiH_3$  over Ni(0) to yield **1C** followed by the reaction with the carbamic acid generated in situ to produce the formamide intermediate **2C** along with silanol, then **2C** is further reduced to generate the corresponding methylated

product  $(\mathbf{b})$ ,<sup>101</sup> and later, a condensation of  $\mathbf{b}$  and 1 eq of isocyanate gives the *N*-methyl-*N'*,*N*-urea (c). The isocyanate (g) can be formed either by dehydration of carbamic acid or by dehydrogenation of **2C**. Isocyanate (g) may then react with 1 eq of amine to generate the corresponding urea (**3C**), followed by reduction to yield **d**.

Finally, we assessed the reactivity of secondary aliphatic amines under similar conditions; key results are in Table 5. The use of dibenzylamine was rather informative, since reactivity drops dramatically to yield only 42% of conversion at 150 °C in toluene, with 35% yield of methy-dibenzylamine. The low reactivity observed in secondary amines can be related to steric factors and cancellation of pathways invoking isocyantes for amine methylation.

#### CONCLUSIONS

In summary, we have developed a general protocol for the catalytic *N*-methylation of primary and secondary aliphatic amines using CO<sub>2</sub> as a C1 source and PhSiH<sub>3</sub> as a reducing agent, using nickel-based catalysts  $[(dippe)Ni(\mu-H)]_2$  and the commercially available Ni(COD)<sub>2</sub>/dcype. The monomethylation of aliphatic amines proceeds under relatively mild conditions (atmospheric pressure of CO<sub>2</sub>), in moderate to good yields. This methodology demonstrates for the first time that nickel compounds are efficient catalysts in the selective *N*-methylation of amines using CO<sub>2</sub>. The monomethylated ureas were also obtained in good yields by using an appropriate amount of PhSiH<sub>3</sub>. Finally, we proposed a possible mechanistic reaction for these transformations, based on experimental observations concerning the product distribution.

#### EXPERIMENTAL SECTION

**General Considerations.** Unless otherwise noted, all operations were carried out in a MBraun glovebox (<1 ppm of  $H_2O$  and  $O_2$ ) or

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Table 3. Catalytic Methylation o	of Primary Aliphatic Amines 1	Using CO <sub>2</sub> and 2 eq of PhSil	H <sub>3</sub> Catalyzed by [(d	lippe)Ni(µ-H)]₂ and
$[Ni(COD)_2]/dcype^a$				

R-NH <sub>2</sub> +	CO <sub>2</sub> CO <sub>2</sub> Toluene P. 100 °C. 20 h	→ <sup>R</sup> NH + <sup>R</sup> CH <sub>3</sub>	O NN, R + ⊢ _ H + CH <sub>3</sub>	N R	N <sup>∠R</sup> + H	O R∖N H N∕R	+ R	NH +	N=C=C R
а	Fatm 100 0,20 m	b	C	d		е		f	g
Entry	R-NH <sub>2</sub>	Catalyst <sup>b,c</sup>	Conv. of a (%)	b (%)	с (%)	d (%)	e (%)	f (%)	g (%)
1	NH <sub>2</sub>	b[(dippe)Ni(µ-H)]2	100	11	80	6	3		
	~	<[Ni(COD)2]/dcype	100	6	82	9	3		
2		[(dippe)Ni(µ-H)]2	76	9	42		15	10	
		[Ni(COD)2]/dcype	69	15	36		18		
3	$\square$	[(dippe)Ni(µ-H)] <sub>2</sub>	100	5	66	10	13		6
	✓ `NH₂	[Ni(COD)2]/dcype	100	3	76		21		
4		[(dippe)Ni(µ-H)] <sub>2</sub>	100	2	71	12	15		
	F	[Ni(COD)2]/dcype	100		69	13	18		
5	NH <sub>2</sub>	[(dippe)Ni(µ-H)] <sub>2</sub>			53		25		
	N	[Ni(COD)2]/dcype	85	4	58		22		
6	$H_2N$	[(dippe)Ni(µ-H)] <sub>2</sub>	87	3	72		10	2	
	o	[Ni(COD)2]/dcype	85	5	67			13	
7	NH <sub>2</sub>	[(dippe)Ni(µ-H)] <sub>2</sub>		4	31		13		
		[Ni(COD)2]/dcype	54	5	40		9		

"All reactions were carried out in a Schlenk flask equipped with a Rotaflo valve using 5 mL of solvent. Reaction conditions. <sup>b</sup>Mol ratio of 0.01:0.25:0.5 of  $[(dippe)Ni(\mu-H)]_2$ , benzylamine, and PhSiH<sub>3</sub>, respectively, and 1 atm of CO<sub>2</sub> were used. <sup>c</sup>Mol ratio of 0.01:0.01:0.25:0.5 [Ni(COD)<sub>2</sub>], dcype, benzylamine, and PhSiH<sub>3</sub>, respectively, and 1 atm of CO<sub>2</sub> were used. Conversions and yields were determined by GC/MS analysis of the crude mixture.

by using high-vacuum and standard Schlenk techniques under argon atmosphere. Toluene was dried and distilled over sodium. Dioxane and THF were dried and distilled from dark-purple solutions of sodium/ketyl benzophenone. Deuterated solvents for NMR experiments were purchased from Cambridge Isotope Laboratories and stored over 3 Å molecular sieves in the glovebox. Compound  $[(dippe)Ni(\mu-H)]_2$  was prepared according to the reported procedure.<sup>25</sup> The bisphosphine ligand, dippe (1,2-bisdiisopropylphosphino)ethane, was synthesized according to the reported methods.<sup>26</sup>  $[Ni(COD)_2]$  (COD = 1,5-cyclooctadiene) and dcype (1,2-bis-dicyclohexylphosphino)ethane were purchased from Stream Chemical and stored in the glovebox. All other chemicals and filter aids were reagent grade and were used as received. Carbon dioxide was supplied by Air Products and Chemicals Inc. (purity > 99.99%) and used without further purification. All reagents for the catalytic reactions were loaded in the glovebox using Schlenk flasks equipped with Rotaflo high vacuum stopcocks and further loaded with CO2. The crude reaction mixtures for each catalytic run were immediately analyzed by GC/MS. GC/MS determinations were

performed using an Agilent 5975C system equipped with a 30 m DB-5MS capillary (0.32 mm i.d.) column.

General Procedure for the Reaction of CO<sub>2</sub>, PhSiH<sub>3</sub>, and [(dippe)Ni(µ-H)]<sub>2</sub>. A typical methodology was as follows: a 25 mL Schlenk flask, equipped with Rotaflo valve and with an inner magnetic stirring bar, was loaded into the glovebox with a solution of  $[(dippe)Ni(\mu-H)]_2$  (6.4 mg, 0.01 mmol) in THF (5 mL) and PhSiH<sub>3</sub> (108 mg, 1 mmol). A color change from wine red to brown was immediately observed. The solution was stirred for 10 min, and then a CO<sub>2</sub> stream was bubbled at room temperature for 10 min. Then the flask was closed and heated in an oil bath at 80 °C for 1 h. After this time, the heating was stopped, and the flask was vented into the hood. An aliquot of the reaction mixture was immediately analyzed by GC/MS; only the unreacted PhSiH<sub>3</sub> was observed. This methodology was followed using toluene, dioxane, and acetonitrile instead of THF at a variety of temperatures (80, 100, and 120 °C) and reaction times (1 and 20 h), using 5 mol % of catalyst:  $[(dippe)Ni(\mu-H)]_2$  (6.4 mg, 0.01 mmol) and PhSiH<sub>3</sub> (22 mg, 0.2 mmol).

**Reaction of CO<sub>2</sub>, PhSiH<sub>3</sub>, Et<sub>3</sub>B Catalyzed by**  $[(dippe)Ni(\mu-H)]_2$ . A 25 mL Schlenk flask equipped with a Rotaflo valve and a magnetic

R-NH <sub>2</sub> +	CO <sub>2</sub>	Cataly 4 eq Ph Tolue	yst <u>ISiH<sub>3</sub></u> R <sub>NH</sub> + ne CH <sub>3</sub>	O R、N N <sup>~</sup> R H CH <sub>3</sub>	+	R <sub>N</sub> R	+	O R <sub>N</sub> N_N_R H H
а	Patm	100 °C,	b	С		d		е
Entry	R-N	H <sub>2</sub>	Catalyst <sup>b,c</sup>	Conv. of a (%)	b (%)	с (%)	d (%)	e (%)
1		∕_ <sub>NH₂</sub>	<sup>b</sup> [(dippe)Ni(μ-H)] <sub>2</sub>	100	66	22	3	9
	, , , , , , , , , , , , , , , , , , ,		c[Ni(COD)2]/dcype	100	64	27		9
2	$\sim$	 ^_ <sub>NH2</sub>	[(dippe)Ni(µ-H)] <sub>2</sub>	100	45	15	12	28
		-	[Ni(COD)2]/dcype	100	49	27		24
3	3		[(dippe)Ni(μ-H)] <sub>2</sub>	100	51		32	17
		NП <sub>2</sub>	[Ni(COD)2]/dcype	100	55		31	14
4	$\bigcap$	NH <sub>2</sub>	[(dippe)Ni(µ-H)] <sub>2</sub>	100	59	19	10	12
	F		[Ni(COD)2]/dcype	100	61	22	7	10
5		`NH <sub>2</sub>	[(dippe)Ni(μ-H)] <sub>2</sub>	100	43	17		40
	<sup>∼</sup> N <sup>∞</sup>		[Ni(COD)2]/dcype	100	61	6		33
6		)	[(dippe)Ni(μ-H)] <sub>2</sub>	100	58	27		15
	o		[Ni(COD)2]/dcype	100	69	13		18
7	$\bigcap$	 	[(dippe)Ni(µ-H)] <sub>2</sub>	65	33	18		24
			[Ni(COD)2]/dcype	71	37	25		19

<sup>*a*</sup>All reactions were carried out in a Schlenk flask equipped with a Rotaflo valve using 5 mL of solvent. Reaction conditions. <sup>*b*</sup>Mol ratio of 0.01:0.25:1 of  $[(dippe)Ni(\mu-H)]_2$ , benzylamine, and PhSiH<sub>3</sub>, respectively, and 1 atm of CO<sub>2</sub> were used. <sup>*c*</sup>Mol ratio of 0.01:0.01:0.25:1  $[Ni(COD)_2]$ , dcype, benzylamine, and PhSiH<sub>3</sub>, respectively, and 1 atm of CO<sub>2</sub> were used. Conversions and yields were determined by GC/MS analysis of the crude mixture.

stirrer was charged in the glovebox with a solution of [(dippe)Ni( $\mu$ -H)]<sub>2</sub> (6.4 mg, 0.01 mmol) in THF (5 mL), PhSiH<sub>3</sub> (108 mg, 1 mmol), and Et<sub>3</sub>B (9.8 mg, 0.1 mmol). A color change from wine red to brown and effervescence were observed. The reaction mixture was stirred for 10 min, and then a CO<sub>2</sub> stream was bubbled at room temperature for 10 min. After that, the flask was closed, followed by heating in an oil bath at 80 °C for 1 h. Then, the flask was vented in a hood and analyzed by GC/MS; unreacted PhSiH<sub>3</sub> and traces of Ph<sub>2</sub>SiH<sub>2</sub> and Ph<sub>3</sub>SiH were observed. The very same procedure was followed using toluene or dioxane instead of THF at different temperatures (80, 100, and 120 °C) and times (1 and 20 h).

Typical Procedure for the *N*-Methylation of Amines Catalyzed by  $[(dippe)Ni(\mu-H)]_2$ . A 25 mL Schlenk flask equipped with a Rotaflo valve and a magnetic stirrer was charged in the glovebox with a solution of  $[(dippe)Ni(\mu-H)]_2$  (6.4 mg, 0.01 mmol) in toluene (5 mL), amine (0.25 mmol), and PhSiH<sub>3</sub> (108.2 mg, 1 mmol or 54.1

mg, 0.5 mmol). A color change from wine red to brown and effervescence were observed. The reaction mixture was stirred for 10 min, and then a  $CO_2$  stream was bubbled at room temperature for 10 min. After that, the flask was closed followed by heating in an oil bath at 100 °C for 20 h. After this time, the reaction mixture was cooled down to room temperature, and the flask was vented in a hood, exposed to air, and analyzed by GC/MS.

Typical Procedure for the *N*-Methylation of Amines Catalyzed by  $[Ni(COD)_2]/dcype$ . In a typical experiment,  $[Ni-(COD)_2]$  (2.8 mg, 0.01 mol) and dcype (4.3 mg, 0.01) were dissolved in 5 mL of dry toluene in a 25 mL Schlenk flask equipped with a Rotaflo valve and a magnetic stirrer and then amine (0.25 mmol) and PhSiH<sub>3</sub> (108.2 mg, 1 mmol or 54.1 mg, 0.5 mmol) were added, leading to formation of a brown yellow solution. The reaction mixture was stirred for 10 min. Then a  $CO_2$  stream was bubbled at room temperature for 10 min. After that, the flask was closed and then

Scheme 4. Mechanistic Proposal for the Methylation of Primary Aliphatic Amines by Nickel Complexes



Table 5. Catalytic Methylation of Secondary Aliphatic Amines Using  $CO_2$  and 4 eq of PhSiH<sub>3</sub> Catalyzed by  $[Ni(COD)_2]/dcype^a$ 

$\bigcirc$	NH + la'	$CO_{2} \xrightarrow{4 \text{ mol }\%} Solvent$ $P_{atm}$ $P_{atm}$ $N(COD)_{2}//dcype$ $4 \text{ mol }\%$ $4 \text{ eq PhSiH}_{3}$ $Solvent$ $20h, T$	N CH <sub>3</sub> Ib'	+	le'
entry	solvent	<i>T</i> (°C)	conv. of Ia' (%)	Ib' (%)	Ic' (%)
1	THF	100	20	20	_
2	toluene	100	35	24	11
3	toluene	150	42	35	7

"All reactions were carried out in a Schlenk flask equipped with a Rotaflo valve using 5 mL of solvent. Reaction conditions: mol ratio of 0.01:0.25:1 [Ni(COD)<sub>2</sub>], dcype, benzylamine, and PhSiH<sub>3</sub>, respectively, and 1 atm of CO<sub>2</sub> were used. Conversions and yields were determined by GC/MS analysis of the crude mixture.

heated in an oil bath at 100  $^{\circ}$ C for 20 h. After this time, the reaction mixture was cooled down to room temperature, and the flask was vented in a hood, exposed to air, and analyzed by GC/MS.

## ASSOCIATED CONTENT

## **S** Supporting Information

Selected GC/MS determinations and crystallographic data for 1,3-bis(4-fluorobenzyl)urea. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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