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## COMMUNICATION

# Iron-catalyzed hydrosilylation of CO<sub>2</sub>: CO<sub>2</sub> conversion to formamides and methylamines

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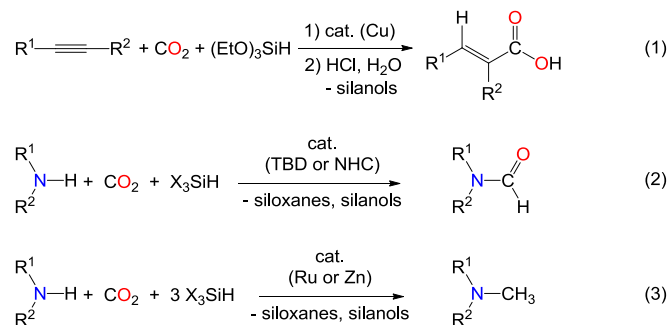
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**Catalytic hydrosilylation of CO<sub>2</sub> is an efficient and selective approach to form chemicals. Herein, we describe the first iron-catalysts able to promote the reductive functionalization of CO<sub>2</sub> using hydrosilanes as reductants. Iron(II) salts supported by phosphine donors enable the conversion of CO<sub>2</sub> to formamide and methylamine derivatives, under mild reaction conditions.**

Catalytic hydrosilylation reactions are attractive alternatives to classical reduction methods with hydrogen or metal-hydrides, because they usually operate under mild conditions with superior chemoselectivity.<sup>1</sup> Indeed, hydrosilanes possess a reduction potential similar to H<sub>2</sub> and a Si-H bond that is kinetically more reactive because of its polarity and lower bond dissociation energy (92 kcal mol<sup>-1</sup> in SiH<sub>4</sub> vs 104 kcal mol<sup>-1</sup> in H<sub>2</sub>).<sup>2</sup> In addition, they circumvent the problematic sensitivity of aluminium and boron hydrides to moisture. As a result, catalytic hydrosilylation can achieve highly chemo- and regio-selective transformations of a wide range of carbonyl groups such as ketones, carboxylic acids, esters, amides and ureas.<sup>3</sup> Importantly, in 1981, Hirai *et al.* extended hydrosilylation strategies to reduce CO<sub>2</sub>, using RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> as a catalyst,<sup>4</sup> and a variety of organic and organometallic catalysts have been shown to promote the direct hydrosilylation of CO<sub>2</sub> since then.<sup>5</sup> CO<sub>2</sub> reduction to formic acid and methanol has limited economical interest, because these molecules are produced at low cost and on large scales that are incompatible with the availability of hydrosilanes. In contrast, CO<sub>2</sub> conversion to fine and bulk chemicals has the advantage of creating added value for niche applications. In this respect, the unique reducing properties of hydrosilanes have been exemplified, over the last 4 years, with the design of novel catalytic transformations to convert CO<sub>2</sub> to carboxylic acids, formamides and methylamines (Scheme 1).<sup>6</sup> These new advances have motivated the search for novel efficient catalysts, able to facilitate the hydrosilylation of CO<sub>2</sub>.<sup>5b-e, 5g, 5i, 5j, 7</sup> From another standpoint, remarkable efforts have recently demonstrated the potential of iron complexes, as earth abundant and cost efficient metal catalysts in hydrosilylation reactions.<sup>8</sup> For example, Sortais, Darcel *et al.* have utilized well-defined iron carbene complexes for the chemoselective reduction of esters to aldehydes.<sup>9</sup> In 2009, Beller *et al.* and Nagashima *et al.* showed independently that iron carbonyl

complexes were potent hydrosilylation catalysts for the reduction of amides to amines.<sup>10</sup> Recently, our group reported the first examples of ureas reduction to formamides, using iron complexes as hydrosilylation catalysts.<sup>3k</sup> Yet, so far, iron catalysts have never been utilized in CO<sub>2</sub> hydrosilylation reactions and, herein, we describe the first iron complexes able to promote the reductive functionalization of CO<sub>2</sub> using hydrosilanes. In this contribution, Fe<sup>II</sup> salts supported by phosphine donors are shown to catalyze the conversion of CO<sub>2</sub> to formamide and methylamine derivatives, under mild reaction conditions.

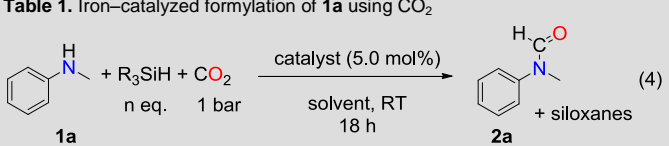


**Scheme 1.** Reductive functionalization of CO<sub>2</sub> to  $\alpha,\beta$ -unsaturated carboxylic acids, formamides and methylamines, using hydrosilanes reductants.

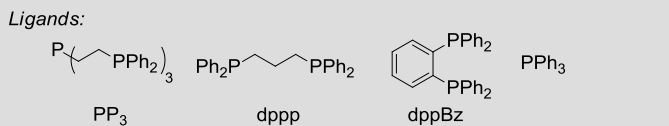
Using CO<sub>2</sub> and hydrosilanes for the formylation of amines affords an attractive entry to formamides and this transformation was unveiled for the first time in 2012, in our laboratories (Eq. 2 in Scheme 1).<sup>6b, 6d</sup> This catalytic reaction was found to be robust and a large scope of N-H bonds in amines, anilines, hydrazines and N-heterocycles were successfully formylated with hydrosilanes, such as PhSiH<sub>3</sub>, Ph<sub>2</sub>SiH<sub>2</sub>, (EtO)<sub>3</sub>SiH or polymethylhydrosiloxane (PMHS). Interestingly, while organic catalysts (guanidines and N-heterocyclic carbenes (NHCs)) were originally utilized, Baba *et al.* showed that copper(II) diphosphine complexes were also active catalysts in this transformation.<sup>7</sup> As such, the formylation of N-methylaniline (**1a**) with CO<sub>2</sub> and phenylsilane was selected as a benchmark reaction to test the catalytic activity of a variety of iron complexes in CO<sub>2</sub>

hydrosilylation. In the presence of a catalytic amount of FeCl<sub>2</sub>, FeCl<sub>3</sub>, Fe(SO<sub>4</sub>)<sub>7</sub>H<sub>2</sub>O, Fe(acac)<sub>2</sub> or Fe(acac)<sub>3</sub> (5.0 mol%), addition of 1 equiv. PhSiH<sub>3</sub> to a THF solution of **1a** under an atmosphere of CO<sub>2</sub> (1 bar) led to no reaction and the starting materials were recovered unreacted after 18 h at 100 °C. Notably, Beller *et al.* have shown that iron(II) phosphine complexes are able to promote the hydrogenation of the kinetically stable CO<sub>2</sub> molecule to formate derivatives<sup>11</sup> and we found recently that Fe(acac)<sub>2</sub> in combination with tris[2-(diphenylphosphino)ethyl]phosphine (PP<sub>3</sub>) can catalyze the hydrosilylation of organic ureas to formamides.<sup>3k</sup> Supporting phosphine ligands were therefore screened so as to form complexes with Fe(acac)<sub>2</sub> and generate active catalysts in the formylation of **1a** (Entries 1–6, Table 1 and SI). While PPh<sub>3</sub>, 1,3-bis(diphenylphosphino)propane (dppp), 1,1'-bis(diphenylphosphino)ferrocene (dppf), 1,2-bis(diphenylphosphino)benzene (dppBz) and 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (XantPhos) did not improve the reactivity of Fe(acac)<sub>2</sub>, an equimolar mixture of PP<sub>3</sub> (5.0 mol%) and Fe(acac)<sub>2</sub> allowed for the quantitative conversion of **1a** to its formamide **2a**, at RT after 18 h (Entry 1, Table 1). After usual work-up aimed at eliminating the siloxanes by-products, **2a** was successfully isolated in 92% yield. Importantly, the presence of both Fe(acac)<sub>2</sub> and the supporting ligand is necessary to obtain a catalytic activity in the conversion of **1a** to **2a** (Entries 2 and 3). Replacing Fe(acac)<sub>2</sub> with Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O lowers the conversion yield to 13% (Entry 7, Table 1).

**Table 1.** Iron-catalyzed formylation of **1a** using CO<sub>2</sub>



**Ligands:**



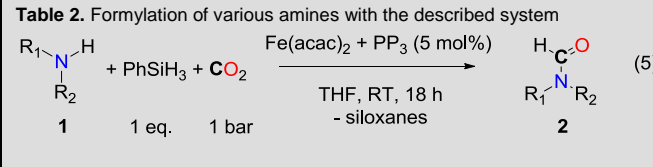
Entry <sup>[a]</sup>	Catalyst <sup>[a]</sup>	Solvent	R <sub>3</sub> SiH (n)	Yield <sup>[b]</sup> (%)
1	Fe(acac) <sub>2</sub> + PP <sub>3</sub> (1:1)	THF	PhSiH <sub>3</sub> (1)	> 95 (92) <sup>[c]</sup>
2	Fe(acac) <sub>2</sub>	THF	PhSiH <sub>3</sub> (1)	<1
3	PP <sub>3</sub>	THF	PhSiH <sub>3</sub> (1)	<1
4	Fe(acac) <sub>2</sub> + PPh <sub>3</sub> (1:4)	THF	PhSiH <sub>3</sub> (1)	<1
5	Fe(acac) <sub>2</sub> + dppp (1:2)	THF	PhSiH <sub>3</sub> (1)	<1
6	Fe(acac) <sub>2</sub> + dppBz (1:2)	THF	PhSiH <sub>3</sub> (1)	<1
7	Fe(BF <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O + PP <sub>3</sub> (1:1)	THF	PhSiH <sub>3</sub> (1)	13
8	Fe(acac) <sub>2</sub> + PP <sub>3</sub> (1:1)	CH <sub>3</sub> CN	PhSiH <sub>3</sub> (1)	> 95
9	Fe(acac) <sub>2</sub> + PP <sub>3</sub> (1:1)	CH <sub>2</sub> Cl <sub>2</sub>	PhSiH <sub>3</sub> (1)	> 95
10	Fe(acac) <sub>2</sub> + PP <sub>3</sub> (1:1)	toluene	PhSiH <sub>3</sub> (1)	63
11	Fe(acac) <sub>2</sub> + PP <sub>3</sub> (1:1)	1,4-dioxane	PhSiH <sub>3</sub> (1)	48
12	Fe(acac) <sub>2</sub> + PP <sub>3</sub> (1:1)	THF	Et <sub>3</sub> SiH (3)	<1
13	Fe(acac) <sub>2</sub> + PP <sub>3</sub> (1:1)	THF	TMDS	<1


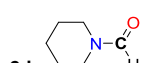

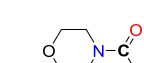

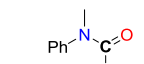

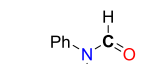
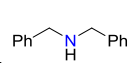
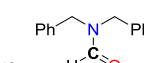
(1.5)				
14	Fe(acac) <sub>2</sub> + PP <sub>3</sub> (1:1)	THF	PMHS (3)	<1 <sup>[d]</sup>

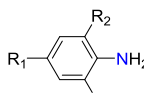
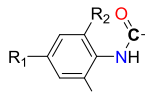

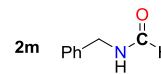

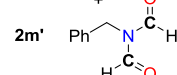
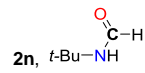

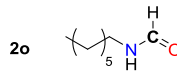
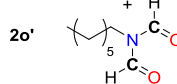

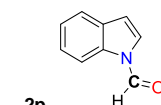

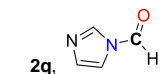

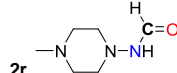

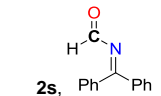

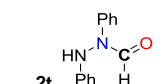

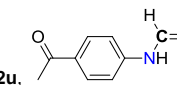

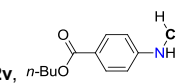

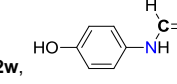
[a] Reaction conditions: *N*-methylaniline (**1a**, 0.250 mmol), hydrosilane R<sub>3</sub>SiH (3 eq. Si-H), catalyst (0.0125 mmol, 5.0 mol%), solvent (0.7 mL), CO<sub>2</sub> (1 bar), 18 h, RT; [b] Determined by GC/MS using mesitylene as internal standard, after calibration; [c] isolated yield; [d] 70 °C.

It is noteworthy that the polarity of the solvent has a significant impact on the activity of the iron catalytic system. While toluene and 1,4-dioxane ( $\epsilon_0 < 2.4$ ) impair the formylation of **1a**, polar solvents with a dielectric constant  $\epsilon_0$  greater than 7.5 (THF, CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>CN) lead to the quantitative formation of **2a** (Entries 1, 8–11 in Table 1). CO<sub>2</sub> reductive functionalization to **2a** also depends on the nature of the reductant and less reactive hydrosilanes such as Et<sub>3</sub>SiH, 1,1,4,4-tetramethyldisiloxane (TMDS) and PMHS are unreactive in equation 4, even at 70 °C (Entries 12–14, Table 1). As a result, Fe(acac)<sub>2</sub>+PP<sub>3</sub> is superior to 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) which operates at 100 °C and affords **2a** in a modest 39% yield after 24 h with 1 equiv. PhSiH<sub>3</sub>.<sup>6b</sup> For comparison, low catalyst loadings of Cu(OAc)<sub>2</sub> + 1.5 dppBz (0.07 mol%) were shown to convert **1a** to **2a** in 87% yield after 30 h at 80 °C. In fact, the catalytic activity of the iron(II) system resembles that of free NHCs, that are able to promote the formylation of N-H bonds of amines, anilines, hydrazines and hydrazones, at room temperature.<sup>6d</sup>

**Table 2.** Formylation of various amines with the described system



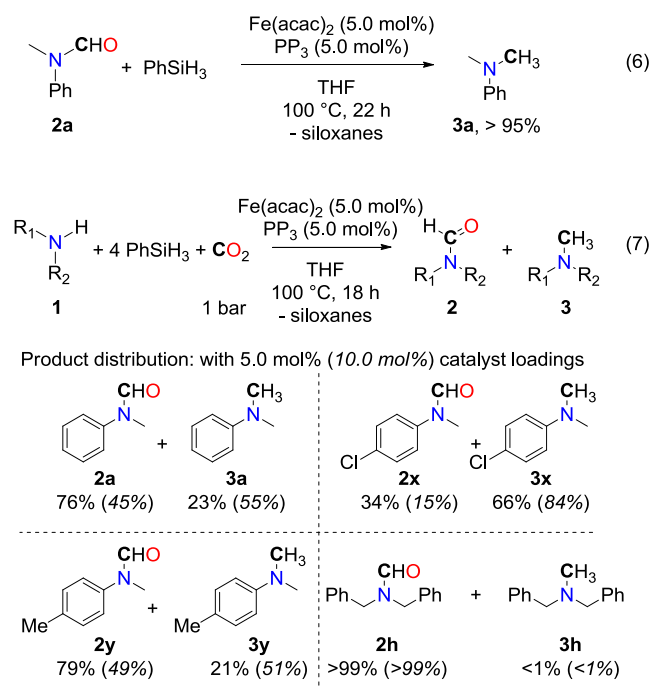
Entry <sup>[a]</sup>	Substrate (1)	Product (2)	Yield <sup>[b]</sup> (%)
1	<b>1b</b> , Et <sub>2</sub> NH	<b>2b</b> , Et-NH-C(=O)-H	> 95
2	<b>1c</b> , <i>i</i> -Pr <sub>2</sub> NH	<b>2c</b> , <i>i</i> -Pr-NH-C(=O)-H	40
3	<b>1d</b> , 	<b>2d</b> , 	> 95
4	<b>1e</b> , 	<b>2e</b> , 	> 95
5	<b>1f</b> , 	<b>2f</b> , 	> 95
6	<b>1g</b> , 	<b>2g</b> , 	<1
7	<b>1h</b> , 	<b>2h</b> , 	> 95

8	 1i R <sub>1</sub> =H, R <sub>2</sub> =H, R <sub>3</sub> =H 1j R <sub>1</sub> =H, R <sub>2</sub> =iPr, R <sub>3</sub> =iPr 1k R <sub>1</sub> =OMe, R <sub>2</sub> =H, R <sub>3</sub> =H 1l R <sub>1</sub> =Cl, R <sub>2</sub> =H, R <sub>3</sub> =H	 2i R <sub>1</sub> =H, R <sub>2</sub> =H, R <sub>3</sub> =H 2j R <sub>1</sub> =H, R <sub>2</sub> =iPr, R <sub>3</sub> =iPr 2k R <sub>1</sub> =OMe, R <sub>2</sub> =H, R <sub>3</sub> =H 2l R <sub>1</sub> =Cl, R <sub>2</sub> =H, R <sub>3</sub> =H	79 38 34 62
9	1m, 	 +  2m' 	76/17
10	1n, <i>t</i> -BuNH <sub>2</sub>		70
11	1o, 	 + 	45/25
12	1p, 		<1
13	1q, 		<1
14	1r, 		24
15	1s, 		8
16	1t, 		26
17	1u, 		65
18	1v, <i>n</i> -BuO 		58
19	1w, 		<1

[a] Reaction conditions: amine (0.250 mmol), PhSiH<sub>3</sub> (0.250 mmol), catalyst (0.0125 mmol), solvent (0.7 mL), CO<sub>2</sub> (1 bar), 18 h, RT. [b] Determined by GC/MS using mesitylene as internal standard, after calibration. [c] isolated yield.

The scope of active amine substrates in the iron(II) catalyzed formylation reaction was then explored (Eq. 5 and Table 2). Using 5.0 mol% of Fe(acac)<sub>2</sub>+PP<sub>3</sub> with PhSiH<sub>3</sub>, aliphatic secondary amines **1b**, **1d**, **1e** and **1h** proved to be highly active in this reaction, providing quantitative conversions to the desired formamides, after 18 h at RT under 1 bar CO<sub>2</sub> (Entries 1,3,4,7, Table 2). Under the same conditions, the sterically hindered di-*iso*-propylamine **1c** was successfully converted to **2c** in a modest 40% yield determined by GC/MS (Entry 2, Table 2). Nonetheless, while **1a** is an active substrate, the presence of two aromatic rings on the nitrogen atom completely shuts down the formylation of the N–H in **1g** (Entry 6, Table 2). This reaction can also be applied with good success to convert primary amines; and formanilide **2i** was obtained in a good 79% conversion from aniline **1i** (Entry 8, Table 2). Despite the presence of two *iso*-propyl substituents at the  $\alpha$ -position, **1j** was transformed to **2j** in 38% conversion. Interestingly, the introduction of an electron donating group at the *para* position of aniline hampers the formylation rate and *p*-anisidine **1k** afforded **2k** in a modest 34% yield, while conversions greater than 62% were observed starting from aniline (**1i**) or *p*-chloroaniline (**1l**). In contrast to the results obtained with NHCs, the bis-formylated products are not observed when aniline derivatives are reacted with PhSiH<sub>3</sub> and CO<sub>2</sub>, in the presence of Fe(acac)<sub>2</sub> + PP<sub>3</sub>.<sup>6d</sup> Yet, starting with aliphatic primary amines, a competition between the mono- and the bis-formylation appears and, although the mono-formamides **2m** and **2o** are obtained as major products from benzylamine (**1m**) and *n*-heptylamine (**1o**), respectively, significant amounts of **2m'** and **2o'** were also detected (up to 25%) (Entries 9, 11, Table 2). This product distribution was left unchanged after longer reaction times (36 h). For sterically hindered substrates such as *tert*-butylamine **1n**, no trace of bis-formylated product was detected (entry 10) and the formamide was obtained in a good 70% GC yield.

The N–H bonds in less basic substrates such as imidazoles (**1q**) or indoles (**1p**) are reluctant to formylation (Entries 12 and 13). Benzophenone imine (**1s**) and aliphatic and aromatic hydrazines (**1r** and **1t**) display a low reactivity and the corresponding formyl products were obtained in low yields, ranging 8 to 26% (Entries 14–16, Table 2). An important advantage of hydrosilylation over classical reduction methods (with hydrogen or metal-hydrides) is the enhanced chemoselectivity, enabled by the use of a mild and polarized hydrosilane reductant. This benefit translates well in the present iron-catalyzed formylation of amines and **1u** and **1v** are successfully formylated to **2u** and **2v**, respectively, with no reduction of the additional ketone or ester functionality (Entries 17 and 18, Table 2). Nevertheless, the system is incompatible with the presence of a hydroxyl group (Entry 19, Table 2).



**Scheme 2.** Iron-catalyzed reduction of **2a** to **3a** and methylation of *N*-methylanilines.

In 2013, we have designed a novel catalytic reaction to utilize CO<sub>2</sub> as a C<sub>1</sub>-building block in the methylation of amines.<sup>6c</sup> Using zinc catalysts and hydrosilanes as reductants, CO<sub>2</sub> was shown to undergo a complete deoxygenation *via* a 6-electron reduction pathway coupled to the formation of a C–N bond (Eq. 3 in Scheme 1). Shortly afterwards, Beller *et al.* reported an efficient ruthenium phosphine catalyst for this transformation.<sup>12</sup> Both the Zn and Ru catalytic systems operate at 100°C with PhSiH<sub>3</sub>. From a mechanistic standpoint, it was shown that the zinc-catalyzed methylation of N–H bonds involves two steps with opposite electronic demand at the nitrogen centre and the amine substrate is first converted to its formamide, which is subsequently hydrosilylated to the corresponding methylamine. In order to evaluate the potential of Fe(acac)<sub>2</sub>+PP<sub>3</sub> in the catalytic methylation of amines with CO<sub>2</sub>, the reduction of formamide **2a** was first tested, in the presence of a stoichiometric amount of PhSiH<sub>3</sub>. As depicted in Eq. 6 (Scheme 2), the iron catalyst can promote the quantitative hydrosilylation of formamide **2a** to **3a**, albeit at 100 °C. As a consequence, raising the reaction temperature to 100 °C enables the utilization of the iron catalyst in the direct methylation of *N*-methylaniline with CO<sub>2</sub>. In fact, using 1 bar CO<sub>2</sub> and 4 equiv. PhSiH<sub>3</sub>, Fe(acac)<sub>2</sub>+PP<sub>3</sub> (5.0 mol%) is able to convert directly **1a** to *N,N*-dimethylaniline (**3a**) in 23% yield, after 18 h (Eq. 7, Scheme 2). As such, the iron catalyst exhibit a somewhat lower activity than the zinc carbene or ruthenium phosphine complexes utilized previously by Cantat *et al.* and Beller *et al.*, respectively.<sup>6c, 12</sup> As expected, formamide **2a** accumulates in the methylation of **1a** and its reduction to **3a** is rate limiting. Increasing the catalyst loading to 10.0 mol% is beneficial to the conversions to methylamines and **3a**, **3x** and **3y** are obtained in good yields, ranging from 51 to 84%, from **1a**, **1x** and **1y**, respectively (Eq. 7, Scheme 2). Under the same conditions, the aliphatic di-benzylamine (**1h**) yields selectively formamide **2h**. Although modest, the catalytic activity of Fe(acac)<sub>2</sub>+PP<sub>3</sub> in the methylation of amines establishes the potential of iron complexes to promote the 6-electron reduction of CO<sub>2</sub> and further efforts are underway in our

laboratories to improve the catalytic activity of the iron system and to utilize inexpensive hydrosilanes, such as PMHS and TMDS, in this transformation.

## Conclusions

In the search for earth abundant and cost efficient catalysts for the reduction of CO<sub>2</sub>, we have reported herein the first examples of iron catalysts able to promote the hydrosilylation of CO<sub>2</sub>. Iron(II) salts supported by a tetra-phosphine ligand are able to transform CO<sub>2</sub> to formamides, in the presence of amines and PhSiH<sub>3</sub>, at room temperature. The reaction is chemoselective and tolerant to ketone and ester functionalities. At 100°C, the catalytic system is also active in the methylation of aniline derivatives.

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## Notes and references

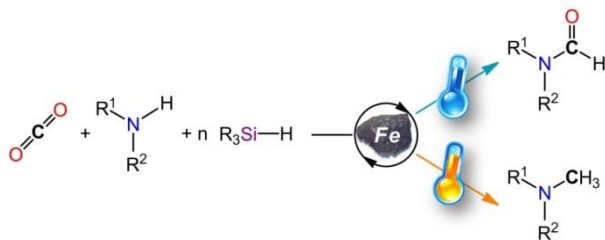
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† Electronic supplementary information (ESI) available: General experimental details, synthetic procedures and data for **2r** and **2v**. For ESI see DOI: 10.1039/b000000x/

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## GRAPHICAL ABSTRACT



Catalytic hydrosilylation of CO<sub>2</sub> is an efficient and selective approach to form chemicals. Herein, we describe the first iron-catalysts able to promote the reductive functionalization of CO<sub>2</sub> using hydrosilanes as reductants. Iron(II) salts supported by phosphine donors enable the conversion of CO<sub>2</sub> to formamide and methylamine derivatives, under mild reaction conditions.