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Iron-catalyzed hydrosilylation of CO₂: CO₂ conversion to formamides and methylamines†

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Catalytic hydrosilylation of CO₂ is an efficient and selective approach to form chemicals. Herein, we describe the first iron catalysts able to promote the reductive functionalization of CO₂ using hydrosilanes as reductants. Iron(II) salts supported by phosphine donors enable the conversion of CO₂ 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.¹ Indeed, hydrosilanes possess a reduction potential similar to H₂ and a Si–H bond that is kinetically more reactive because of its polarity and lower bond dissociation energy (92 kcal mol^{−1} in SiH₄ vs. 104 kcal mol^{−1} in H₂).² 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.³ Importantly, in 1981, Hirai *et al.* extended hydrosilylation strategies to reduce CO₂ using RuCl₂(PPh₃)₃ as a catalyst,⁴ and a variety of organic and organometallic catalysts have been shown to promote the direct hydrosilylation of CO₂ since then.⁵ CO₂ 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, CO₂ 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 CO₂ to carboxylic acids, formamides and

methylamines (Scheme 1).⁶ These new advances have motivated the search for novel efficient catalysts able to facilitate the hydrosilylation of CO₂.^{5b–e,g,i,j,7} From another standpoint, remarkable efforts have recently demonstrated the potential of iron complexes as earth abundant and cost efficient metal catalysts in hydrosilylation reactions.⁸ For example, Sortais, Darcel *et al.* have utilized well-defined iron carbene complexes for the chemoselective reduction of esters to aldehydes.⁹ 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.¹⁰ Recently, our group reported the first examples of urea reduction to formamidines, using iron complexes as hydrosilylation catalysts.^{3k} Yet, so far, iron catalysts have never been utilized in CO₂ hydrosilylation reactions and, herein, we describe the first iron complexes able to promote the reductive functionalization of CO₂ using hydrosilanes. In this contribution, Fe^{II} salts supported by phosphine donors are shown to catalyze the conversion of CO₂ to formamide and methylamine derivatives under mild reaction conditions.

Using CO₂ and hydrosilanes for the formylation of amines affords an attractive route to formamides and this transformation was unveiled for the first time in 2012 in our

Scheme 1 Reductive functionalization of CO₂ to α,β-unsaturated carboxylic acids, formamides and methylamines using hydrosilane reductants.

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laboratories (eqn (2) in Scheme 1).^{6b,d} 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 PhSiH₃, Ph₂SiH₂, (EtO)₃SiH 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.⁷ As such, the formylation of *N*-methylaniline (**1a**) with CO₂ and phenylsilane was selected as a benchmark reaction to test the catalytic activity of a variety of iron complexes in CO₂ hydrosilylation. In the presence of a catalytic amount of FeCl₂, FeCl₃, Fe(SO₄)·7H₂O, Fe(acac)₂ or Fe(acac)₃ (5.0 mol%), addition of 1 equiv. of PhSiH₃ to a THF solution of **1a** under an atmosphere of CO₂ (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 CO₂ molecule to formate derivatives¹¹ and we have found recently that Fe(acac)₂ in combination with tris[2-(diphenylphosphino)ethyl]phosphine (PP₃) can catalyze the hydrosilylation of organic ureas to formamidines.^{3k} Supporting phosphine ligands were therefore screened so as to form complexes with Fe(acac)₂ and generate active catalysts in the formylation of **1a** (entries 1–6, Table 1

and ESI†). While PPh₃, 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)₂, an equimolar mixture of PP₃ (5.0 mol%) and Fe(acac)₂ 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)₂ and the supporting ligand is necessary to obtain catalytic activity in the conversion of **1a** to **2a** (entries 2 and 3). Replacing Fe(acac)₂ with Fe(BF₄)₂·6H₂O lowers the conversion yield of **2a** to 13% (entry 7, Table 1).

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 ϵ_0 greater than 7.5 (THF, CH₂Cl₂, and CH₃CN) lead to the quantitative formation of **2a** (entries 1, 8–11 in Table 1). CO₂ reductive functionalization to **2a** also depends on the nature of the reductant and less reactive hydrosilanes, such as Et₃SiH, 1,1,4,4-tetramethyldisiloxane (TMDS) and PMHS, are unreactive in eqn (4), even at 70 °C (entries 12–14, Table 1). As a result, Fe(acac)₂ + PP₃ 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. of PhSiH₃.^{6b} For comparison, low catalyst loadings of Cu(OAc)₂ + 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 which are able to promote the formylation of N–H bonds of amines, anilines, hydrazines and hydrazones at room temperature.^{6d}

The scope of active amine substrates in the iron(II) catalyzed formylation reaction was then explored (eqn (5) and Table 2). Using 5.0 mol% of Fe(acac)₂ + PP₃ with PhSiH₃, 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 CO₂ (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 bond 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 good conversion (79%) from aniline **1i** (entry 8, Table 2). Despite the presence of two iso-propyl substituents at the α -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

Table 1 Iron-catalyzed formylation of **1a** using CO₂

Entry ^a	Catalyst ^a	Solvent	R ₃ SiH (n)	Yield ^b (%)
1	Fe(acac) ₂ + PP ₃ (1 : 1)	THF	PhSiH ₃ (1)	>95 (92) ^c
2	Fe(acac) ₂	THF	PhSiH ₃ (1)	<1
3	PP ₃	THF	PhSiH ₃ (1)	<1
4	Fe(acac) ₂ + PPh ₃ (1 : 4)	THF	PhSiH ₃ (1)	<1
5	Fe(acac) ₂ + dppp (1 : 2)	THF	PhSiH ₃ (1)	<1
6	Fe(acac) ₂ + dppBz (1 : 2)	THF	PhSiH ₃ (1)	<1
7	Fe(BF ₄) ₂ ·6H ₂ O + PP ₃ (1 : 1)	THF	PhSiH ₃ (1)	13
8	Fe(acac) ₂ + PP ₃ (1 : 1)	CH ₃ CN	PhSiH ₃ (1)	>95
9	Fe(acac) ₂ + PP ₃ (1 : 1)	CH ₂ Cl ₂	PhSiH ₃ (1)	>95
10	Fe(acac) ₂ + PP ₃ (1 : 1)	Toluene	PhSiH ₃ (1)	63
11	Fe(acac) ₂ + PP ₃ (1 : 1)	1,4-Dioxane	PhSiH ₃ (1)	48
12	Fe(acac) ₂ + PP ₃ (1 : 1)	THF	Et ₃ SiH (3)	<1
13	Fe(acac) ₂ + PP ₃ (1 : 1)	THF	TMDS (1.5)	<1
14	Fe(acac) ₂ + PP ₃ (1 : 1)	THF	PMHS (3)	<1 ^d

^a Reaction conditions: *N*-methylaniline (**1a**, 0.250 mmol), hydrosilane R₃SiH (3 eq. Si–H), catalyst (0.0125 mmol, 5.0 mol%), solvent (0.7 mL), CO₂ (1 bar), 18 h, RT. ^b Determined by GC/MS using mesitylene as the internal standard after calibration. ^c Isolated yield. ^d 70 °C.

Table 2 Formylation of various amines with the described system

$ \begin{array}{c} \text{R}_1\text{N}(\text{R}_2)\text{H} + \text{PhSiH}_3 + \text{CO}_2 \xrightarrow[\text{THF, RT, 18 h, -siloxanes}]{\text{Fe(acac)}_2 + \text{PP}_3 (5 \text{ mol}\%)} \text{R}_1\text{N}(\text{R}_2)\text{CHO} \\ \text{1} \quad \quad \quad 1 \text{ eq.} \quad 1 \text{ bar} \quad \quad \quad \text{2} \end{array} \quad (5) $			
Entry ^a	Substrate (1)	Product (2)	Yield ^b (%)
1	1b, Et ₂ N-H	2b,	>95
2	1c, (i-Pr) ₂ N-H	2c,	40
3	1d,	2d,	>95
4	1e,	2e,	>95
5	1f,	2f,	>95
6	1g,	2g,	<1
7	1h,	2h,	>95
8	 1i R ₁ =H, R ₂ =H, R ₃ =H 1j R ₁ =H, R ₂ =iPr, R ₃ =iPr 1k R ₁ =OMe, R ₂ =H, R ₃ =H 1l R ₁ =Cl, R ₂ =H, R ₃ =H	 2i R ₁ =H, R ₂ =H, R ₃ =H 2j R ₁ =H, R ₂ =iPr, R ₃ =iPr 2k R ₁ =OMe, R ₂ =H, R ₃ =H 2l R ₁ =Cl, R ₂ =H, R ₃ =H	79 38 34 62
9	1m,	2m, 2m',	76/17
10	1n,	2n,	70
11	1o,	2o, 2o',	45/25
12	1p,	2p,	<1

Table 2 (continued)

$ \begin{array}{c} \text{R}_1\text{N}(\text{R}_2)\text{H} + \text{PhSiH}_3 + \text{CO}_2 \xrightarrow[\text{THF, RT, 18 h, -siloxanes}]{\text{Fe(acac)}_2 + \text{PP}_3 (5 \text{ mol}\%)} \text{R}_1\text{N}(\text{R}_2)\text{CHO} \\ \text{1} \quad \quad \quad 1 \text{ eq.} \quad 1 \text{ bar} \quad \quad \quad \text{2} \end{array} \quad (5) $			
Entry ^a	Substrate (1)	Product (2)	Yield ^b (%)
13	1q,	2q,	<1
14	1r,	2r,	24
15	1s,	2s,	8
16	1t,	2t,	26
17	1u,	2u,	65
18	1v,	2v,	58
19	1w,	2w,	<1

^a Reaction conditions: amine (0.250 mmol), PhSiH₃ (0.250 mmol), catalyst (0.0125 mmol), solvent (0.7 mL), CO₂ (1 bar), 18 h, RT. ^b Determined by GC/MS using mesitylene as the internal standard after calibration.

to the results obtained with NHCs, the bis-formylated products are not observed when aniline derivatives are reacted with PhSiH₃ and CO₂ in the presence of Fe(acac)₂ + PP₃.^{6d} Yet, starting with aliphatic primary amines, a competition between mono- and bis-formylation appears and, although the monoformamides **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 and 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 products were 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 resistant 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 from 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 into 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).

In 2013, we designed a novel catalytic reaction to utilize CO₂ as a C₁-building block in the methylation of amines.^{6c} Using zinc catalysts and hydrosilanes as reductants, CO₂ was shown to undergo a complete deoxygenation *via* a 6-electron reduction pathway coupled to the formation of a C–N bond (eqn (3) in Scheme 1). Shortly afterwards, Beller *et al.* reported an efficient ruthenium phosphine catalyst for this transformation.¹² Both the Zn and Ru catalytic systems operate at 100 °C with PhSiH₃. 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)₂ + PP₃ in the catalytic methylation of amines with CO₂, the reduction of formamide **2a** was first tested in the presence of a stoichiometric amount of PhSiH₃. As depicted in eqn (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 CO₂. In fact, using 1 bar CO₂ and 4 equiv. of PhSiH₃, Fe(acac)₂ + PP₃ (5.0 mol%) is able to convert

directly **1a** to *N,N*-dimethylaniline (**3a**) in 23% yield after 18 h (eqn (7), Scheme 2). As such, the iron catalyst exhibits a somewhat lower activity than the zinc carbene or ruthenium phosphine complexes utilized previously by Cantat *et al.* and Beller *et al.*, respectively.^{6c,12} 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 conversion to methylamines and **3a**, **3x** and **3y** are obtained in good yields, ranging from 51 to 84%, from **1a**, **1x** and **1y**, respectively (eqn (7), Scheme 2). Under the same conditions, the aliphatic dibenzylamine (**1h**) yields selectively formamide **2h**. Although modest, the catalytic activity of Fe(acac)₂ + PP₃ in the methylation of amines establishes the potential of iron complexes to promote the 6-electron reduction of CO₂ 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 CO₂, we have reported herein the first examples of iron catalysts able to promote the hydrosilylation of CO₂. Iron(II) salts supported by a tetraphosphine ligand are able to transform CO₂ to formamides in the presence of amines and PhSiH₃ 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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Scheme 2 Iron-catalyzed reduction of **2a** to **3a** and methylation of *N*-methylanilines.

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