

Iron Catalyzed CO₂ Activation with Organosilanes

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Abstract

Iron nanoparticles generated in situ from $[Fe_3(CO)_{12}]$ catalyzed CO₂ reduction in the presence of Et₃SiH as a reductant and tetrabutylammonium fluoride as a promoter to yield silvl formate (**1s**) under relatively mild reaction conditions. Additionally, when CO₂ hydrosilvlation was carried out in water, the product of CO₂ reduction was formic acid. Additionally, a similar reaction using $[Fe_3(CO)_{12}]$ as a catalytic precursor, PhSiH₃ as a reductant, and CO₂ in the presence of amines allowed the immediate formation of ureas at room temperature. Here, CO₂ acted as a C1 building block for value-added products.

Graphical Abstract



Keywords Carbon dioxide · Reduction · Silane · Formate · Iron · Nanoparticles · Urea · Catalysis

1 Introduction

Nowadays, one of the most biggest pollution problems related to the greenhouse effect is the increasing concentration of atmospheric CO_2 . This is associated with the global

Dedicated to Professor Peter M. Maitlis on occasion of his 85th birthday.

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demand for energy and, consequently, CO_2 emissions are not yet under control [1]. That is why efforts are focused on the development of new and efficient methods that use CO_2 as a building block for organic molecules, and its hydrogenation to produce formate or methanol is badly needed [2].

Despite many reports using a variety of transition metals acting as catalysts for the activation of CO_2 , the most active systems often require low-abundance, expensive, and toxic metals, such as ruthenium, rhodium, palladium, or iridium [3–7], which are used for the synthesis of the most active catalytic systems. Thus, carrying out the activation of CO_2 at industrial levels is still not profitable.

Sustainable catalysis aims to eliminate the above problems in the field through the development of novel, environmentally benign, cost-effective catalytic pathways. This approach involves the use of metal complexes based on

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inexpensive, earth-abundant, environmentally friendly elements, such as magnesium, iron, copper and zinc [8].

In this context, there are relatively few reports of hydrogenation of CO_2 with iron catalysts [9–16]. It is worth mentioning that reports by Beller in 2010 [13], Milstein in 2011 [15], and Gonsalvi in 2016, produced formates. In all of these cases, the CO_2 reduction was carried out in the presence of hydrogen gas (H₂). Due to the inherent risks related to handling H₂, a safe alternative is to replace this reactive gas with alternative sources of hydrogen such as silanes; however, producing residues from the corresponding silanes. In the area of hydrosilylation of CO_2 , a study using iron was reported by Cantat and colleages [17], in 2014 using [Fe(acac)₂] as a catalyst precursor and PP₃ as ancillary ligand. Recently the photo- and electrocatalytic reduction of CO_2 to produce methane, HCOOH and carbon monoxide, using an iron tetraphenylporphyrin catalyst has been disclosed [18].

In 2013, Feng and colleagues [19] reported the complete reduction of CO_2 to produce methane at 200 °C in 75 h. In 2016, Kang and colleagues [20] reported the complete reduction of CO_2 to produce methane using UV radiation and iron nanoparticles (Fe–NPs) as a catalyst.

Our group recently explored CO_2 activation in the presence of a commercially available catalytic precursor, such as $[Ru_3(CO)_{12}]$ [21]. With the aim to carry out the CO_2 transformation in an efficient way with low costs, we report the catalytic activation of this polluting gas with iron using $[Fe_3(CO)_{12}]$ as a readily available and inexpensive precursor of Fe–NPs.

2 Results and Discussion

Table 1 Promoter screening

The reduction of CO_2 with $[Fe_3(CO)_{12}]$ as a catalytic precursor and Et_3SiH as a reductant was initially assessed with a variety of different promoters (Table 1). Without the use of a

promoter (entry 1) the yield was low and the main reduction product was triethylmethoxysilane (2s) with a 7% yield. The use of tetrabutylammonium fluoride (TBAF) as a reaction promoter (entry 4) allowed a higher conversion and produced silyl formate 1s (17% yield). Compound 1s is a valuable product since it is a precursor of a variety of organic compounds [2, 22, 23].

Considering these results, it was decided to use TBAF as a reaction promoter; therefore, a variety of reaction conditions for CO_2 hydrosilylation were assessed (see Table S1 and 2S). It was found that the optimum reaction conditions were 60 °C and 60 psi after 24 h.

Under these conditions, the amount of reaction promoter (TBAF) was further optimized (Table 2). It was found that the use of 5 mol % of TBAF:Et₃SiH gave the best conversion to produce **1s**. Most likely, TBAF had an important role in the hydrosilylation of CO_2 due to the formation of a very strong Si–F bond, which released a very reactive H⁻.

Likewise, the amount of catalytic precursor $[Fe_3(CO)_{12}]$ amount was then optimized (Table 3), and optimal amount found to be 0.5 mol % versus Et₃SiH.

As shown in Table 2, there was a strong dependence on the amount of TBAF and CO_2 hydrosilylation. Consequently, it was necessary to carry out a control test without the use of the iron precursor (Table 3, entry 4). Only a small yield of product **1s** was observed; therefore, the iron catalytic precursor was necessary for an efficient reaction.

Additionally, a mercury drop test allowed us to identify the decomposition of the used catalytic precursor that formed Fe–NPs [24] (Table 3, entry 5) [25]. The reaction yield decreased significantly from 50 to 10% for CO_2 hydrosilylation.

To confirm the formation of Fe–NPs in the reaction mixture, centrifugation of the mother liquid of the catalytic mixture led to a residue which was characterized by transmission electron microscopy (TEM) (Fig. 1). As observed in Fig. 1,

	Et ₃ SiH + CO ₂ $\frac{[Fe_3(CO)_{12}] \text{ 1 mol\%}}{50^{\circ}\text{C} / 48 \text{ h}}$	→ Et ₃ Si–O [∕]	O ∬H + Et₃Si∽ ^O _N	∕le + Et₃Si∽ ^O ∖SiEt	-3
	100psi	1s	2s	3s	
Entry	Promoter (10 mol%)	Yield (%) ^a			
		1 s	2s	3s	Total
1	None	n.d.	7	10	17
2	NaB(Ph) ₄	n.d.	n.d.	n.d.	0
3	Et ₃ B	n.d.	5	8	13
4	TBAF	17	n.d.	77	94

^aAll yields were determined by GC-MS, using Et₃SiOCOH as internal std

Table 2TBAF optimization



Entry	TBAF (mol %)	Yield (%) ^a				
		<u>1s</u>	3 s	4 s	Total	
1	10	33	57	2	92	
2	5	40	43	2	85	
3	2.5	0	37	2	39	
4	0	n.d.	n.d.	n.d.	n.d.	

^aAll yields were determined by GC-MS, using Et₃SiOCOH as internal std

Table 3 [Fe₃(CO)₁₂] amount optimized

	[Fe ₃ (CO) ₁₂] X Et ₃ SiH + CO ₂ 60psi 60 °C / 24 THF	i mol % ll % h → Et ₃ Si	0 −0 H Et₃Si 3	OSiEt₃ Et₃Si–F s 4s	
Entry	[Fe ₃ (CO) ₁₂] (mol %)	Yield (%) ^a			
		<u>1s</u>	3 s	4s	Total
1	1	40	43	2	85
2	0.5	50	47	2	99
3	0.3	13	56	3	72
4	0.0	9	58	4	71
5	0.5 ^b	10	42	4	56

^aAll yields were determined by GC-MS, using Et₃SiOCOH as internal std

^bMercury drop test Hg(0):Fe(0) 5:1

the formation of iron nanoparticles was confirmed in the reaction medium. These nanoparticles had an average size of 5 nm (Graphic 1).

These Fe–NPs could be recycled several times (Graphic 2). However, the conversion to product **1s** substantially decreased after the first recycling, yielding a final TON = 232. This was probably due to agglomeration of the Fe–NPs.

In an effort to substitute the use of a solvent (THF) for a green solvent, the reaction was carried out in water using a type of silane not prone to hydrolysis (Et_3SiH) (Scheme 1). With this method, formic acid was obtained (38% isolated yield).

With the aim of using CO_2 as a building block for organic molecules [26–28], the reactivity of CO_2 in the presence of benzylamine was studied. Here, $[Fe_3(CO)_{12}]$ was used as a catalytic precursor, along with two different silanes as a reducing agent (Table 4). With this methodology, 1,3-bis(benzyl)urea (**1a**) was obtained as the main product. The best conversion was obtained using $PhSiH_3$ (entry 2). A control experiment (entry 3) demonstrated that the reaction requires the use of the corresponding reducing agent.

This reaction was optimized in a variety of reaction conditions (see SI, Tables S3 and S4). The best yields were obtained at 60 °C and 20 mol % of PhSiH₃ at atmospheric pressure (Scheme 2) with a urea yield of 46%.

Considering the previous results, we explored the same reaction without a solvent (THF) (i.e., under neat conditions) (Table 5). A good conversion was obtained in entry 1 for the preparation of **1a**. However, we noticed the immediate formation of a white solid soon after all reagents mixed (entry 2), resulting in the immediate formation of **1a** at room temperature at a 46% yield. In entry 3, the reaction was performed without the use of



Fig. 1 TEM of final reaction mix





Graphic 2 Recycling of Fe–NPs

Graphic 1 Size distribution of Fe-NPs

 $[Fe_3(CO)_{12}]$, suggesting that the use of such a catalytic precursor is mandatory in order to obtain the corresponding urea.



3 Conclusions

The catalytic reduction of CO_2 was carried out using iron nanoparticles in a catalytic amount of 0.5 mol%. TBAF was a necessary reaction promotor at 5 mol%, and Et₃SiH was a reductant, yielding silyl formate. The CO₂ reduction

was carried out in water to produce formic acid under relatively mild conditions. Additionally, CO_2 was obtained in the presence of benzylamine, generating 1,3-bis(benzyl) urea and PhSiH₃ using the same catalytic precursor at room temperature.

Table 4 CO_2 activation to yield ureas



Епиу	к ₃ 5іп					
		1 a	2a	3 a	Total	
1	Et ₃ SiH	0	n.d.	n.d.	0	
2	PhSiH ₃	78	6	4	88	
3	None	0	n.d.	n.d.	0	

^aAll yields were determined by GC-MS, using N-benzylmethylamine as internal std



Scheme 2 CO_2 activation to produce urea

Table 5 Urea preparation using neat conditions



Entry	Conditions	Yield (%) ^a			
		1 a	2a	Total	
1	17 h/60 °C	76	3	79	
2	T = 0/R.T.	46	n.d.	46	
3	T = 0/R.T.	n.d.	n.d.	0	

^aAll yields were determined by GC-MS, using N-benzylmethylamine as internal std

4 Experimental Section

4.1 General Considerations

Unless otherwise stated, all processes were performed using an MBraun glovebox (<1 ppm H_2O and O_2) under

an argon atmosphere (Praxair 99.998) or by using highvacuum and standard Schlenk techniques under an argon atmosphere. Triethylsilane (99% purity, Aldrich), carbon dioxide (99.998% purity, supplied by Praxair), phenylsilane (97% purity, Aldrich), triethylborane (95% purity, Aldrich), triiron dodecacarbonyl (99% Aldrich), TBAF (98% Aldrich), benzylamine (80% Aldrich), THF (J. T. Baker, reagent grade) were dried and distilled from sodium/benzophenone. All reagents for the catalytic reactions were loaded in the glove box. The GC-MS determinations were made using an Agilent 5975C system equipped with a 30 m DB-5MS capillary column (0.25 mm i.d.; 0.25 μ m).

4.2 Reactivity of CO₂ with Et₃SiH Catalyzed by [Fe₃(CO)₁₂] in Presence of Different Promoters

All reactions were performed in a 100 mL stainless steel Parr autoclave. The reactor was loaded with 8.6 mg (0.017 mmol) of $[Fe_3(CO)_{12}]$, 200.0 mg (1.724 mmol) of Et_3SiH , and 0.172 mmol (16.8 mg) of Et_3B , 58 mg of Na(BPh)₄, 44.9 mg of TBAF, and 10 mL of THF. This sample was then pressurized with CO₂. All the reagents were loaded in a glove box except CO₂. CO₂ was added by using a transfer hose at 100 psi. The mixture was heated at 80 °C in a silicon oil bath for 48 h. The final reaction mixtures were analyzed by GC/MS.

4.3 Optimized Reaction Conditions

Using a 100 mL stainless steel Parr autoclave, the reactor was loaded with 8.6 mg (0.017 mmol) of $[Fe_3(CO)_{12}]$, 200 mg (1.724 mmol) of Et₃SiH, 44.9 mg (0.172 mmol) of TBAF, 10 mL of THF, and CO₂ at a desired pressure. The reactor was heated at different temperatures and reaction times. After this, the reactor was cooled to room temperature and depressurized in a hood. The final reaction mixture was analyzed by GC/MS.

4.4 Load of TBAF

All reactions were performed in a 100 mL stainless steel Parr autoclave. The reactor was loaded with 8.6 mg (0.017 mmol) of $[Fe_3(CO)_{12}]$, 200 mg (1.724 mmol) of Et₃SiH, and 44.9, 22.5, and 11.2 mg (0.172, 0.086, 0.043 mmol, respectively) of TBAF. This represented a catalysis load of 10, 5, and 2.5 mol%, respectively, in 10 mL of THF. All reactions were heated at 60 °C for 24 h at 60 psi of CO₂. The reaction mixtures were analyzed by GC/MS.

4.5 Load of [Fe₃(CO)₁₂]

All reactions were performed in a 100 mL stainless steel Parr autoclave. The reactor was loaded with 22.5 mg (0.86 mmol) of TBAF, 200 mg (1.724 mmol) of Et₃SiH, and 8.6, 4.3, and 2.5 mg (0.0172, 0.0086, 0.0051 mmol, respectively) of $[Fe_3(CO)_{12}]$. This represented a catalysis load of 1, 0.5, and 0.3 mol%, respectively, in 10 mL of THF. All reactions were

heated at 60 °C for 24 h at 60 psi of CO_2 , and the reaction mixtures were analyzed by GC/MS.

4.6 Hg Drop Test

This reaction was performed as in the previously described reaction, but an additional 25.8 mg (0.129 mmol) of Hg and CO_2 at 60 psi was used. This was then heated at 60 °C for 24 h. The reaction mixture was filtered on Celite and analyzed by GC/MS.

4.7 Nanoparticles Isolation and Characterization

This was carried out in a reaction under optimized conditions (60 °C, 60 psi of CO₂, 24 h, 200 mg of Et₃SiH, 22.5 mg of TBAF, 4.3 mg of [Fe₃(CO)₁₂], and 10 mL of THF). After the reaction time, the autoclave was opened under an argon atmosphere, and all reactions mixtures were transferred to a 50 mL Schlenk flask equipped with a Rotaflo valve. Then, the reaction mixture was evaporated to dryness using a high vacuum for 4 h. TEM was used for further characterization.

4.8 Iron Nanoparticles Recycling

This reaction was carried out under optimized conditions (60 °C, 60 psi of CO₂, 24 h, 200 mg of Et₃SiH, 22.5 mg of TBAF, 4.3 mg of $[Fe_3(CO)_{12}]$, and 10 mL of THF). After the reaction, the autoclave was opened under an argon atmosphere. The reaction mixtures were analyzed by GC/MS, and all reaction mixtures were transferred to a 50 mL Schlenk flask equipped with a Rotaflo valve. Then, the reaction mixture was evaporated to dryness using a high vacuum for 4 h. After that, the dirty nanoparticles were used in the next reaction (cycle 1) with 200 mg of Et₃SiH and 22.5 mg of TBAF. The reaction mixture was analyzed by GC/MS. This procedure was repeated two more times (for second and thirty cycle).

4.9 CO₂ Reduction Using Water as a Solvent

This was performed using optimized conditions (60 °C, 60 psi of CO₂, 24 h, 200 mg of Et₃SiH, 22.5 mg of TBAF, 4.3 mg of [Fe₃(CO)₁₂], and 10 mL of H₂O). After the reaction time, KOH was added to the reaction mixture to obtain potassium formate.

4.10 Reactivity of CO₂ with Benzylamine

This was catalyzed by $[Fe_3(CO)_{12}]$ in the presence of different reductants. All reactions were performed in a 100 mL

stainless steel Parr autoclave, and the reactor was loaded with 2.3 mg (0.0045 mmol) of $[Fe_3(CO)_{12}]$, 0.9259 mmol of (100.0 and 107 mg) of PhSiH₃ and Et₃SiH, respectively, 100 mg (0.9259 mmol) of benzylamine, and 10 mL of THF. The mixture was then pressurized with 60 psi of CO₂. All the reagents were loaded in a glove box except CO₂. CO₂ was added using a transfer hose. The mixture was heated at 60 °C in a silicon oil bath for 24 h. The final reaction mixtures were analyzed by GC/MS.

4.11 Synthesis of Ureas at Atmospheric Pressure

This reaction was carried out in a 50 mL Schlenk flask equipped with a Rotaflo valve and a magnetic stirring bar loaded with 1.0 mg (0.0024 mmol) of $[Fe_3(CO)_{12}]$, 10.6 mg (0. 0987 mmol) of PhSiH₃, 52.8 mg (0.4938 mmol) of benzylamine, 5 mL of THF, and a CO₂ atmosphere. All reagents were loaded in a glove box, except for CO₂. CO₂ was added using a double-manifold gas/vacuum, and the reaction was heated at 60 °C for 24 h. The final reaction mixture was analyzed by GC/MS.

4.12 Synthesis of Urea at Atmospheric Pressure and Neat Conditions

This was carried out using benzylamine as a reagent and solvent (neat) in a 50 mL Schlenk flask equipped with a Rotaflo valve and a magnetic stirring bar. It was loaded with 1.0 mg (0.0024 mmol) of $[Fe_3(CO)_{12}]$, 10.6 mg (0.0987 mmol) of PhSiH₃, 52.8 mg (0.4938 mmol) of benzylamine, and a CO₂ atmosphere. All reagents were loaded in a glove box except for CO₂. CO₂ was added using a double-manifold gas/vacuum. The reaction was heated at 60 °C for 17 h. The final reaction mixture was solubilized with 5 mL of THF and analyzed by GC/MS.

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