

Functionalization of CO₂ with Amines and Hydrosilanes Catalyzed by a Zwitterionic Iridium Carboxylate-Functionalized Bis-NHC Catalyst

Ana I. Ojeda-Amador,^a Julen Munarriz,^b Pablo Alamán,^a Víctor Polo,^b Raquel Puerta-Oteo,^a M. Victoria Jiménez,^a Francisco J. Fernández-Alvarez^{*a} and Jesús J. Pérez-Torrente^{*a}

(a) Departamento de Química Inorgánica – Instituto de Síntesis Química y Catálisis Homogénea (ISQCH). Universidad de Zaragoza. Facultad de Ciencias 50009, Zaragoza – Spain, e-mail: paco@unizar.es, perez@unizar.es; (b) Departamento de Química Física – Instituto de Biocomputación y Física de Sistemas complejos (BIFI) – Universidad de Zaragoza. Facultad de Ciencias 50009, Zaragoza – Spain.

ABSTRACT: The zwitterionic iridium complex [Cp*IrCl{(MeIm)₂CHCOO}] (**1**) efficiently catalyzes the selective hydrosilylation of CO₂ with HSiMe₂Ph, HSiMePh₂, HSiEt₃, HSiMe(OSiMe₃)₂ and 1,4-bis(dimethylsilyl)benzene to afford the corresponding silylformate derivatives. The best reaction performance has been achieved in acetonitrile at 348 K using HSiMe₂Ph as hydrosilane. The **1**-catalyzed reaction of pyrrolidine with CO₂ and HSiMe₂Ph strongly depends on the CO₂ pressure. In particular, at low concentration of CO₂ (1 bar) the formation of the corresponding silylcarbamate, by insertion of CO₂ into the Si–N bond of the in situ generated silylamine was observed, while at higher pressure (3 bar) the corresponding formamide derivative was obtained although in a non-selective way. In addition, a mechanism for the **1**-catalyzed reaction of CO₂ with hydrosilanes, in the presence and in the absence of amines, based on theoretical calculations has been proposed. Moreover, reductive functionalization studies of CO₂ with pyrrolidine and HSiMe₂Ph have shown the formation of the pyrrolidin-1-ium formate salt under reaction conditions. The role of this salt in the formation of 1-formylpyrrolidine has been rationalized. The catalyst-free reaction of silylformate with pyrrolidine afforded an equimolar mixture of 1-formylpyrrolidine and the pyrrolidin-1-ium formate salt which reacts with excess of hydrosilane to give 1-formylpyrrolidine and O(SiMe₂Ph)₂ with hydrogen evolution.

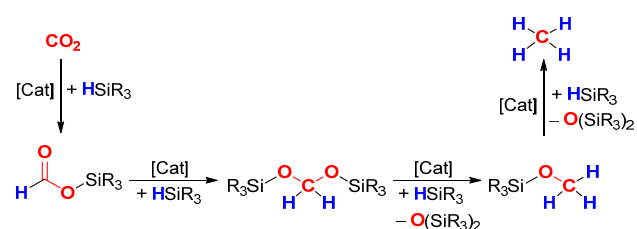
INTRODUCTION

Nowadays, there is an increasing interest in developing chemical processes that allow using carbon dioxide as a C1 carbon source for the industrial preparation of value-added chemicals.¹ The reasons, beyond the well-known problem of the increase in the concentration of CO₂ in the Earth atmosphere, are related to its low toxicity, abundance and availability. However, the high thermodynamic and kinetic stability of CO₂ hinders its chemical transformation.^{1a,1b}

The catalytic reaction of CO₂ with hydrosilanes has emerged as a thermodynamically favoured procedure that allows for the reduction of CO₂ under mild reaction conditions.² Nonetheless, this methodology still faces lack of selectivity, as silylformates are usually obtained among other products, such as bis(silyl)acetals, methoxysilanes and methane, in variable relative amounts (Scheme 1).³ In this sense, it should be noted that during the last few years, several examples of effective catalytic systems for the selective reduction of CO₂ with hydrosilanes to give silylformates^{4,5,6,7,8,9,10} bis(silyl)acetals,¹¹ methoxysilanes¹² or methane¹³ have been reported. Moreover, some catalysts have also been employed for the formylation and/or subsequent methylation of N–H amine bonds by reaction with CO₂ and hydrosilanes.¹⁴ This methodology has also been recently employed to prepare unsymmetrical amins¹⁵ and spiroindolepyrrolidines.¹⁶

N-heterocyclic carbenes (NHCs) are now ubiquitous in organometallic chemistry and catalysis because of their strong coordination ability and tunable character, which facilitates the control of the steric and electronic properties at the metal center.^{17,18} The chelate effect derived from coordination of bis-NHC lig-

ands results in a stable metal-ligand platform with easily moldable properties.¹⁹ In this context, it is worth noting that iridium(III) bis-NHC complexes have been reported as active and selective catalysts for the hydrosilylation of alkynes^{20,21} However, it draws attention that examples of CO₂ hydrosilylation catalysts based on iridium(III) bis-NHC species have not been so far reported.



Scheme 1. Stepwise reduction of CO₂ to methane with hydrosilanes.

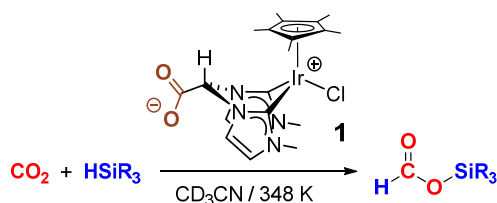
We have recently focused our attention on the potential of a carboxylate-functionalized methylene-bridged bis-NHC ligand for the construction of a versatile metal-ligand platform with application in catalysis.²² In this regard, we have shown that the carboxylate group at the linker provides hemilabile properties to the ligand, allowing for the stabilization of catalytic intermediates through the κ^3 -C,C',O-tridentate coordination mode.²³ However, in most complexes the bis-NHC ligand exhibits a κ^2 -C,C bidentate coordination mode with an uncoordinated functional group in the skeleton that has shown to be a reactive site.²²

As a continuation of our studies on the catalytic applications of zwitterionic bis-NHC metal complexes, we have found that the zwitterionic iridium(III) complex, [Cp*IrCl{(MeIm)₂-

CHCOO}] (MeIm = 3-methylimidazol-2-yliden-1-yl),²² which features a carboxylate bridge-functionalized bis-NHC ligand efficiently catalyzes the reduction of CO₂ with hydrosilanes to selectively afford the corresponding silylformates. Besides, the investigation of the reaction mechanism has disclosed the key role of the uncoordinated carboxylate fragment on the catalytic activity. In addition, the catalytic activity in the reductive functionalization of CO₂ with amines and hydrosilanes, which combines both reduction of CO₂ and C–N bond formation, has been also investigated. Moreover, the reaction mechanism for the reduction of CO₂ with hydrosilanes, both in the presence and in the absence of amines, has been studied by theoretical calculations.

RESULTS AND DISCUSSION

Catalytic hydrosilylation of carbon dioxide. The zwitterionic iridium complex [Cp*IrCl{(MeIm)₂CHCOO}]²² (**1**) (Scheme 2) has proved to be an active catalyst precursor for the selective reduction of CO₂ with hydrosilanes to afford the corresponding silylformate. The **1**-catalyzed reaction of CO₂ (3 bar) with HSiEt₃ was investigated as a test bench to explore the viability of using **1** as a catalyst for the hydrosilylation of CO₂. A preliminary study of the catalytic activity of **1** was performed in different deuterated solvents. Acetonitrile-*d*₃ was found to be the most suitable solvent for the hydrosilylation of CO₂ using catalyst **1**, this addressing solubility of the catalyst and inhibition of competitive reactions. Conversely, benzene-*d*₆ and chlorinated solvents such as dichloromethane-*d*₂ and chloroform-*d*₁ did not show to be a good option for different reasons. In the case of benzene-*d*₆, the poor solubility of the catalyst precursor prevented its use, while chlorinated solvents yielded mixtures of reaction products, including ClSiEt₃, as confirmed by NMR studies. Next, a temperature screening was performed for experiments containing **1** (5 mol% with respect to the hydrosilane) in acetonitrile-*d*₃, along with HSiEt₃, CO₂ (3 bar) and hexamethylbenzene as internal standard. The reactions were monitored by ¹H NMR at 298 K and 348 K, showing the best catalytic performance in acetonitrile-*d*₃ at 348 K. ¹H NMR measurements revealed the formation of the respective silylformate, HC(O)OSiEt₃ (**2a**), reaching almost full HSiEt₃ conversion (95 %) within 7.5 h at 348 K. This result was evidenced by a resonance observed at δ 8.12 ppm at the time that the signal at δ 3.63 ppm corresponding to the Si–H proton of the hydrosilane disappears in the ¹H NMR spectrum. Moreover, the influence of the catalyst loading on the activity of this catalytic system was also investigated. These studies revealed that when using catalyst loadings of 1.0 and 2.0 mol% under the same conditions, full HSiEt₃ conversion required 72 h and 16 h, respectively.



Scheme 2. CO₂ hydrosilylation catalyzed by the zwitterionic iridium(III) compound [Cp*IrCl{(MeIm)₂CHCOO}] (**1**) (SiR₃ = SiEt₃, **2a**; SiMe₂Ph, **2b**; SiMePh₂, **2c**; SiMe(OSiMe₃)₂, **2d**).

The success of this reaction prompted us to explore its generality. In this sense, the influence of the silicon-hydride nature on the activity of **1** as a CO₂ hydrosilylation catalyst was analyzed using the same synthetic methodology. Thus, the **1**-catalyzed (1.0 mol%) reactions of CO₂ (3 bar) with HSiEt₃, HSiMe₂Ph, HSiMePh₂ and HSiMe(OSiMe₃)₂ in acetonitrile-*d*₃ at 348 K with hexamethylbenzene as internal standard were monitored by ¹H NMR spectroscopy (Scheme 2). The results of these experiments are summarized in Table 1 and the reaction profiles shown in Figure 1. A first view of the figure shows a relevant influence of the hydrosilane nature on the catalytic activity. Using HSiMe₂Ph, full conversion of the starting hydrosilane to selectively afford the corresponding silylformate, HC(O)OSiMe₂Ph (**2b**), was accomplished in less than two hours. However, when HSiMePh₂ was used as the reducing agent, a clear activity decrease was observed, probably due to the hindrance around the Si–H bond. Indeed, under the same reaction conditions, more than 8 hours were required to fulfill the conversion of HSiMePh₂ into HC(O)OSiMePh₂ (**2c**). In contrast, HSiEt₃ was comparatively much less reactive reaching a 24% conversion in 10 h. The **1**-catalyzed reactions of CO₂ with HSiMe₂Ph and HSiMePh₂ were highly selective to the formation of the corresponding silylformate. Conversely, in the case of HSiEt₃ both parameters activity and selectivity decreased, and the resulting **2a** (> 88%) was always accompanied by CH₃OSiEt₃ and O(SiEt₃)₂, which were identified by ¹H and ²⁹Si{¹H} NMR spectroscopy. On the other hand, when HSiMe(OSiMe₃)₂ was used as the reductant, no reaction was observed during the first 24 hours, and only 12% of the corresponding silylformate HC(O)OSiMe(OSiMe₃)₂ (**2d**) was produced after 40 hours.

Table 1. [Cp*IrCl{(MeIm)₂CHCOO}] (**1**) catalyzed hydrosilylation of CO₂ with different hydrosilanes.^[a]

Entry	1 (mol %) ^[b]	Hydrosilane	t (h)	Conv. (%) ^[c]
1	5	HSiEt ₃	7.5	95
2	1	HSiEt ₃	10	24
3	1	HSiMe ₂ Ph	2	95
4	1	HSiMePh ₂	8	95
5	1	HSiMe(OSiMe ₃) ₂	10	-

[a] Reaction conditions: hydrosilane (0.153 mmol), CO₂ (3 bar), acetonitrile-*d*₃ (0.50 mL), 348 K; [b] 1.0 mol% or 5.0 mol% with respect to the hydrosilane; [c] Determined by ¹H NMR integration using hexamethylbenzene as internal standard.

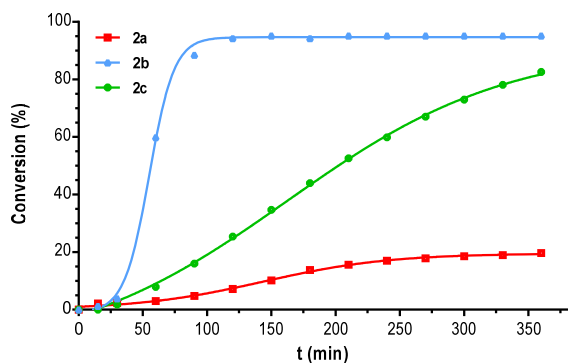
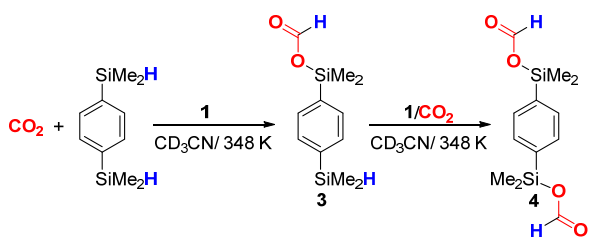


Figure 1. Hydrosilane conversion versus time for the **1**-catalyzed (1.0 mol%) reaction of CO₂ (3 bar) with HSiEt₃ (**2a**), HSiMe₂Ph (**2b**) and HSiMePh₂ (**2c**) monitored by ¹H NMR in acetonitrile-*d*₃ at 348 K.

Moreover, the **1**-catalyzed (1.0 mol%) reaction of 1,4-bis(dimethylsilyl)benzene with CO₂ (3 bar) in acetonitrile-*d*₃ at 348 K has been studied. The results show the formation of 1-(dimethylsilylformate)-4-(dimethylsilyl)benzene (**3**) and 1,4-bis(dimethylsilylformate)benzene (**4**) (Scheme 3). At the early stage of the reaction, a continuous growth of the resonances corresponding to compounds **3** and **4** was observed. However, after 40 minutes the concentration of **4** increased to detriment of that of 1,4-bis(dimethylsilyl)benzene and the mono-silylformate derivative **3** (Figure 2). Notice that a 98% conversion was attained after 90 minutes to give a mixture of **4** (72%) and **3** (26%).



Scheme 3. Reaction of CO₂ with 1,4-bis(dimethylsilyl)benzene in acetonitrile-*d*₃ at 348 K catalyzed by the zwitterionic iridium species [Cp*IrCl{(MeIm)₂CHCOO}] (**1**) (1.0 mol%).

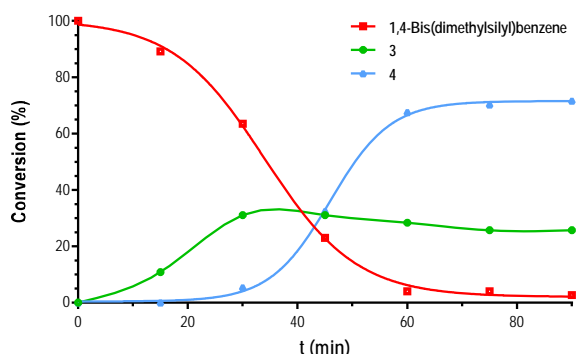


Figure 2. Time dependence of the hydrosilylation of CO₂ (3 bar) with 1,4-bis(dimethylsilyl)benzene catalyzed by **1** (1.0 mol%) monitored by ¹H NMR in acetonitrile-*d*₃ at 348 K.

In order to ascertain the role of the uncoordinated carboxylate fragment on the catalytic activity of **1**, the performance of the

related iridium(III) species [Cp*IrCl{(MeIm)₂CH₂}][PF₆] (**5**)²⁴ as catalyst for the hydrosilylation of CO₂ (3 bar) with HSiMe₂Ph has also been investigated. This experiment evidenced that **5** also promotes the formation of the silylformate **2b** but showed to be a less active catalyst precursor than **1** (Figure 3). Indeed, under the same reaction conditions but using **5** (1.0 mol%) as precatalyst only 39% of **2b** was produced after 6 hours (Figure 3). This result demonstrates that the uncoordinated carboxylate moiety at the linker of the bis-NHC ligand in **1** plays a key role on the mechanism, speeding up the CO₂ hydrosilylation process.

The activity of the catalytic system **1**/HSiMe₂Ph/NCMe as CO₂ hydrosilylation catalyst compares with the reported activity of other iridium catalyst recently reported.^{12d,25}

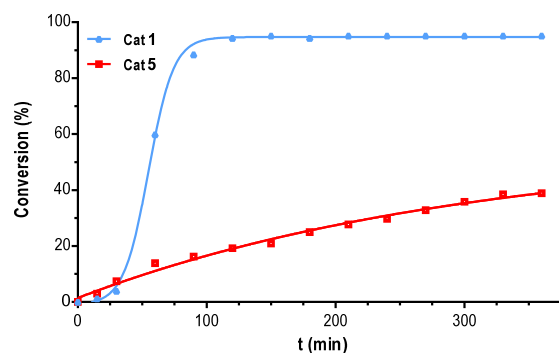


Figure 3. Hydrosilylation of CO₂ (3 bar) with HSiMe₂Ph to HC(O)OSiMe₂Ph (**2b**) catalyzed by [Cp*IrCl{(MeIm)₂CHCOO}] (**1**) and [Cp*IrCl{(MeIm)₂CH₂}][PF₆] (**5**) (1.0 mol%) monitored by ¹H NMR in acetonitrile-*d*₃ at 348 K.

Theoretical calculations on the **1-catalyzed CO₂ hydrosilylation.** To gain insight into the operating mechanism in the hydrosilylation of CO₂ catalyzed by **1**, a computational study using Density Functional Theory (DFT) at the B3LYP-D3BJ/def2-TZVP//def2-SVP (PCM, acetonitrile) level of theory was performed as explained in the Experimental section. Within the calculations, we have considered the full structure of precatalyst **1**, as the use of model catalyst systems for this type of processes where the metallic center bears non-innocent ligands has been severely discouraged.²⁶ The most active reductant, HSiMe₂Ph, was used as a model for the hydrosilane. For the sake of clarity, the different reaction intermediates and transition structures will be referred to by capital letters, starting by precatalyst **1**, which corresponds to structure A. The proposed reaction mechanism is provided in Figure 4.

The theoretical calculations revealed the presence of a pre-activation step (see left part of Figure 4) that is required to form the catalytic active species (C). First, a ligand exchange between the chlorido ligand and a hydrosilane takes place, *via* TSAB. Notice that within the transition structure, the Cp* ligand changes its coordination mode from η⁵ to η¹, which is possible thanks to its coordination modes flexibility.^{27,28} The change in Cp* hapticity has also been proposed by other authors in similar catalytic processes.²⁹ This step requires to surmount an energy barrier of 25.4 kcal·mol⁻¹, which is affordable under the reaction conditions. As a result, the chlorido ligand is released, upon

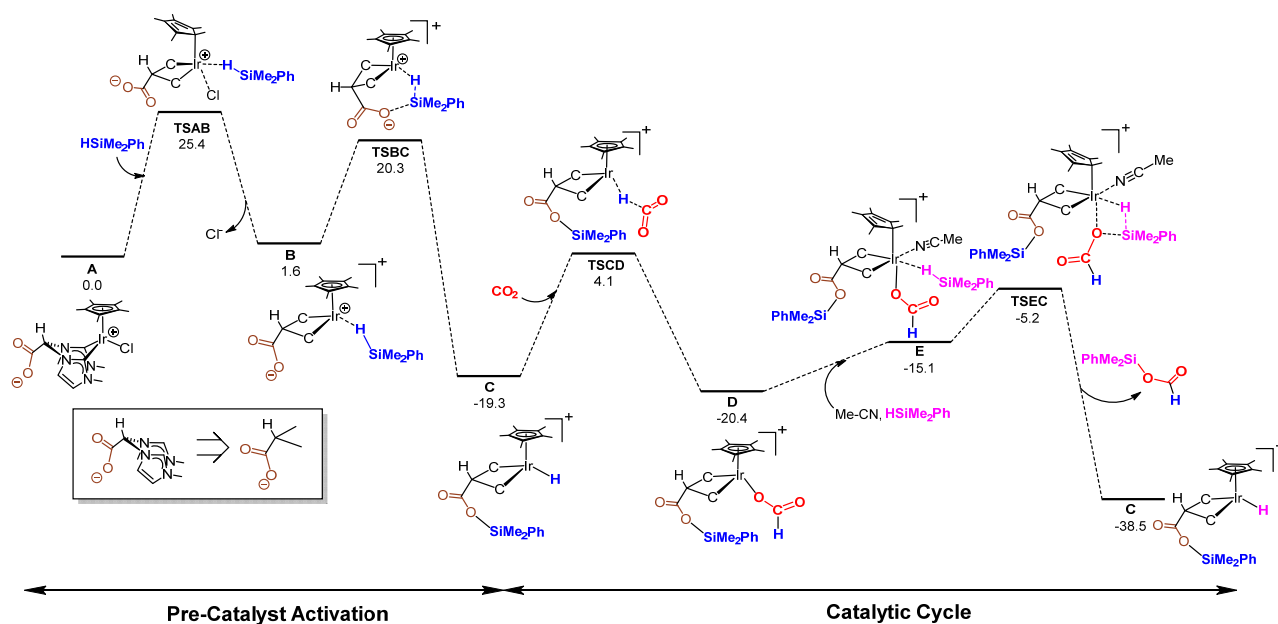


Figure 4. DFT calculated Gibbs free energy profile at 348 K (in kcal·mol⁻¹) relative to A and the isolated molecules.

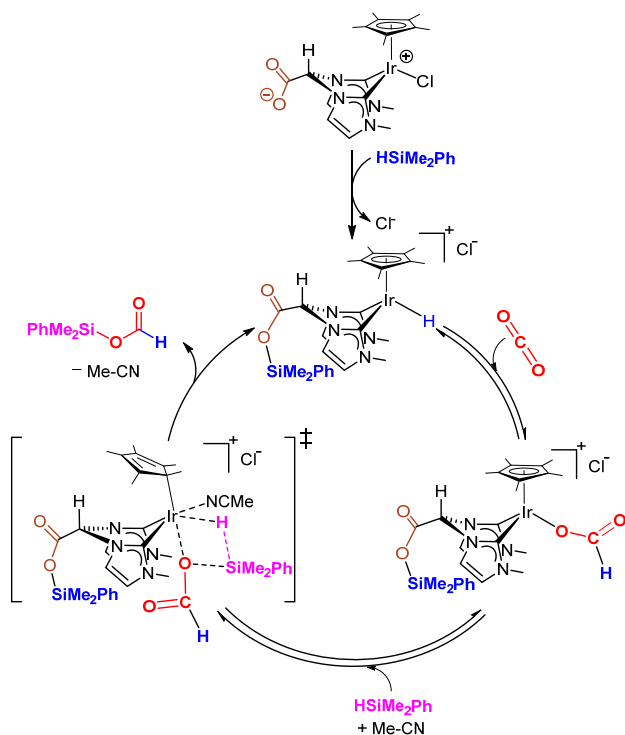
formation of intermediate **B**. This species is only 1.6 kcal·mol⁻¹ less stable than the starting structure (**A**).

The next step involves the activation of a hydrosilane molecule by means of a ligand assisted Si–H bond cleavage.²⁵ This process is possible because of the high oxophilicity of silicon atoms in conjunction with the presence of an available oxygen atom in the uncoordinated carboxylate group at the bis-NHC ligand linker. For this step to proceed, an energy barrier of 18.7 kcal·mol⁻¹ must be overcome, dictated by transition structure **TSBC**. Therefore, a hydride species, intermediate **C**, is produced with concomitant formation of a silyl-carboxylate moiety at the linker of the bis-NHC ligand. Notice that this step is very favorable from a thermodynamic point of view, as **C** has a relative energy of -19.3 kcal·mol⁻¹. Moreover, this step is kinetically irreversible, as the opposite process (the recovering of **B**) would require surmounting an energy barrier of 39.6 kcal·mol⁻¹, which is not at all attainable at the reaction temperature (348 K). The result of the activation step is **C**, which constitutes the active species for the subsequent catalytic cycles. On balance, the effective energy span for the catalyst activation is 25.4 kcal·mol⁻¹, according to the model proposed by Kozuch *et al.*,³⁰ which corresponds to the ligand exchange between the hydrosilane and the chlorido ligand.

The computed reaction profile for the catalytic cycle is presented in the right part of Figure 4. The first reaction step consists on the carbon dioxide activation by means of the hydride migration from the metallic center to the CO₂ molecule.³¹ The process requires to surmount an energy barrier of 23.4 kcal·mol⁻¹, dictated by transition structure **TSCD**. As a result, the CO₂ molecule transforms into a formate ligand, which is κ^1 -O-coordinated to the iridium center, yielding intermediate **D**. Then, the silylformate product is generated by means of a σ -complex assisted metathesis (σ -CAM) between the Ir–O bond of the metallic complex and the Si–H bond of the hydrosilane, as previously proposed for other processes of hydrosilanes activation

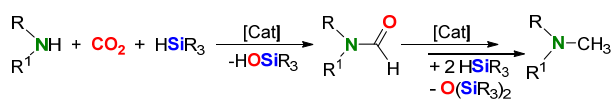
by related complexes.^{32,33,34} Interestingly, within the transition state, the Cp* ligand coordinates in a η^1 manner, leaving a coordination vacancy. Consequently, the presence of a coordinating solvent, such as acetonitrile, able to stabilize the compound is essential for the reaction to proceed. Then, upon acetonitrile coordination, intermediate **E** is produced, which can undertake the σ -CAM process *via* **TSEC**. Remarkably, the effective energy barrier for this process is only 15.2 kcal·mol⁻¹, being determined by the energy difference between transition structure **TSEC** and intermediate **D**. As a result, the final reaction product is yielded, and the catalytic active species **C** is regenerated. Notice that, contrarily to the previous reaction steps, this one is kinetically irreversible, as the inverse process would have to overcome an energy barrier of 33.3 kcal·mol⁻¹ to take place, which is not affordable under the experimental reaction conditions (348 K).

Overall, the thermodynamics for the catalytic cycle is highly favorable, with ΔG equals -19.2 kcal·mol⁻¹ (energy difference between **C** and **C** + products). The effective activation energy is 23.4 kcal·mol⁻¹ and corresponds to the CO₂ fixation step. This value agrees with the experimental observations, as the reaction proceeds in good yields at a temperature of 348 K. On the other hand, the effect of the solvent is crucial as contributes to the stabilization of the transition state involved in the σ -CAM process. Based on the theoretical calculations, the catalytic cycle depicted in Scheme 4 is proposed.



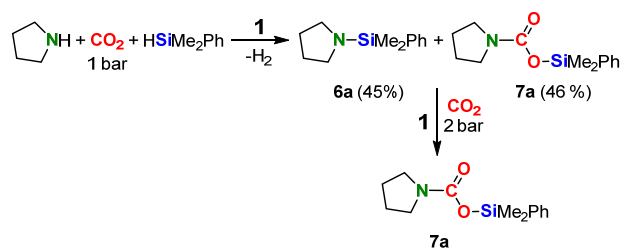
Scheme 4. Proposed mechanism for the **1**-catalyzed hydrosilylation of CO₂.

1-Catalyzed reaction of secondary amines with carbon dioxide and HSiMe₂Ph: Synthesis of silylcarbamates. The catalytic reaction of secondary and primary amines with CO₂ using hydrosilanes as reductants has emerged as a useful methodology for the preparation of formamides, which in conjunction with proper catalysts could be further reduced to the corresponding methylamines (Scheme 5).^{14,34} In view of the catalytic activity of **1** as CO₂ hydrosilylation catalyst, we decided to explore its potential as a catalyst for the reductive functionalization of CO₂ with secondary amines using HSiMe₂Ph as reductant.



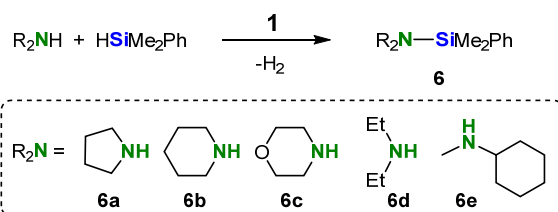
Scheme 5. Catalytic N-formylation and N-methylation of amines with CO₂ and hydrosilanes.

Preliminary studies of the **1**-catalyzed reaction of pyrrolidine, *c*-H(NC₄H₈), with CO₂ (1 bar) and one equivalent of HSiMe₂Ph in acetonitrile-*d*₃ (0.5 mL) at 348 K showed the consumption of the starting amine to yield roughly an equimolar mixture of the corresponding silylamine, Me₂PhSi(NC₄H₈) (**6a**), and silylcarbamate, Me₂PhSiOC(O)(NC₄H₈) (**7a**) (Table 2, entry 1). Further addition of CO₂ (up to 3 bar) to this mixture (Figures SI61 and SI62) resulted in the full transformation of silylamine **6a** into the corresponding silylcarbamate **7a**, which was quantitatively obtained under this reaction conditions (Scheme 6). This outcome suggests that the **1**-catalyzed dehydrogenative silylation of pyrrolidine could be the driving force behind the formation of silylcarbamate **7a**.³⁵



Scheme 6. Functionalization of CO₂ with pyrrolidine and HSiMe₂Ph catalyzed by **1** (1.0 mol%).

Prompted by these promising results, we decided to study the **1**-catalyzed (1.0 mol%) reactions of HSiMe₂Ph with various secondary amines, HNR₂ (NR₂ = *c*-(NC₄H₈), *c*-(NC₅H₁₀), *c*-(NC₄H₈O), NEt₂, NMe(*c*-hex) and NⁱPr₂) in acetonitrile-*d*₃ at 348 K. All of them, except HNⁱPr₂, were quantitatively transformed into the corresponding silylamine (Scheme 7). The reaction profiles, determined by ¹H NMR, displaying the hydrosilane conversion versus time are shown in Figure 5.



Scheme 7. Dehydrogenative silylation of amines with HSiMe₂Ph catalyzed by **1** (1.0 mol%).

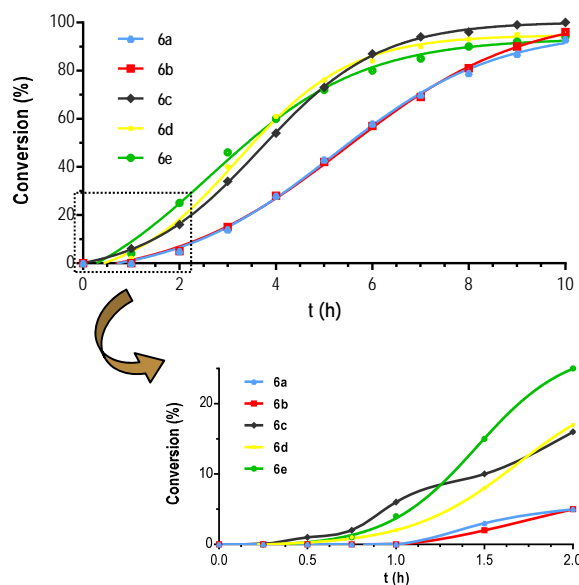


Figure 5. Hydrosilane conversion versus time for the **1**-catalyzed (1.0 mol%) reaction of HSiMe₂Ph with HNR₂ (NR₂ = *c*-(NC₄H₈), *c*-(NC₅H₁₀), *c*-(NC₄H₈O), NEt₂ and NMe(*c*-hex)) monitored by ¹H NMR in acetonitrile-*d*₃ at 348 K. Enlarged plots of the boxed region show the reaction profile at 2 h reaction time.

A first view of Figure 5 shows that amines of similar nature exhibit comparable profiles. The use of secondary amines containing cyclic or acyclic aliphatic substituents such as *c*-H(NC₄H₈), *c*-H(NC₅H₁₀), *c*-H(NC₄H₈O), HNEt₂ and HNMe(*c*-hex), give conversions close to 95% into the corresponding silylamines Me₂PhSiNR₂ (**6a-6e**) within 10 hours of reaction. However, there are some significant differences between them (Figure 5, bottom). The cyclic amines *c*-H(NC₄H₈) and *c*-H(NC₅H₁₀) require a preactivation step (induction time) of around 1 hour, whilst the reaction with *c*-H(NC₄H₈O) starts immediately. In this sense, a 73% conversion was attained for *c*-H(NC₄H₈O) in 5 hours whereas *c*-H(NC₄H₈) and *c*-H(NC₅H₁₀) afforded only 42% conversion at the same reaction time. HNEt₂, HNMe(*c*-hex) and *c*-H(NC₄H₈O) present a similar profile being the most active among the studied derivatives. No reaction was observed with bulkier amines such as HN^{*i*}Pr₂ after 10 h under the same conditions. The silylamines **6a-6e** were characterized by multinuclear NMR spectroscopy (see Experimental Section and Supporting Information).

To explore the influence of the uncoordinated carboxylate moiety in **1** on the catalytic dehydrogenative silylation of amines, the reaction of pyrrolidine with HSiMe₂Ph in presence of **5**, lacking a carboxylate group, was monitored by ¹H NMR spectroscopy. These experiments revealed that both catalysts are active for the dehydrogenative silylation of pyrrolidine (Figure 6). However, at the first stage of the reaction catalyst **5** is more active than **1**. In addition, the dissimilar reaction profiles suggest that both catalysts could operate through different reaction mechanisms (Figure 6).

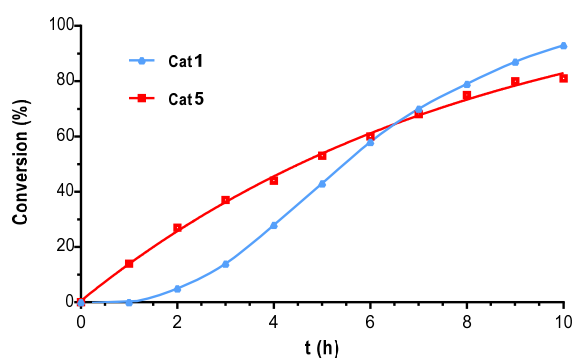
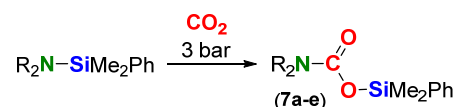


Figure 6. Hydrosilane conversion versus time for the **1**- and **5**-catalyzed (1.0 mol%) reaction of HSiMe₂Ph with pyrrolidine in acetonitrile-*d*₃ at 348 K.

In agreement with our previous observations, the addition of CO₂ (3 bar) to the solutions containing the freshly prepared silylamines Me₂PhSiNR₂ (**6a-6e**) at 298 K allows for the quantitative formation of the corresponding silylcarbamates Me₂PhSiOC(O)NR₂ (**7a-7e**) (Scheme 8). These products, **7a-7e**, were fully characterized by ¹H, ²⁹Si and ¹³C{¹H} NMR spectroscopy, presenting distinctive signals that demonstrate the formation of silylcarbamates. Specifically, ¹H NMR spectra of the species Me₂PhSiOC(O)NR₂ show a signal at δ 0.55 ppm for the methyl groups of the silyl moiety, which appears down-field shifted with respect to the parent silylamines (δ 0.30-0.36 ppm). Moreover, ¹³C{¹H} NMR spectra exhibit the typical signal for the CO₂ insertion products at around δ 155 ppm. In addition, the ²⁹Si{¹H} NMR spectra has a resonance around δ 10.0-11.4 ppm

also down-field shifted compared to that of the corresponding silylamines.



Scheme 8. Synthesis of silylcarbamates by insertion of CO₂ into the Si-N bond of silylamines.

N-formylation of amines: influence of the CO₂ pressure and amine concentration. The catalytic *N*-formylation of amines by their reaction with CO₂ and hydrosilanes has been the subject of several studies during the recent years.^{36,37,38,39} The reaction proceeds by a series of fast and complex chemical equilibria, involving carbamate salts,³⁷ silylformates^{38a-38e} or silylcarbamates³⁹ as intermediates.

For the case of the **1**-catalyzed reaction of pyrrolidine with CO₂ and HSiMe₂Ph, it has been observed that the CO₂ pressure and amine concentration strongly influence the reaction products (Tables 2 and 3). In order to shed light on the reasons behind this behavior a series of experiments were carried out.

As we have just commented, ¹H NMR evidenced that under low CO₂ pressure (1 bar), silylamine, Me₂PhSi(NC₄H₈) (**6a**) (45%), and silylcarbamate, Me₂PhSiOC(O)(NC₄H₈) (**7a**) (46%), are obtained as products (Table 2, entry 1). Under similar reaction conditions, catalyst **5** showed a comparable product selectivity to that of **1** (Table 2, entry 2).

Table 2. Effect of the CO₂ pressure in the reaction of pyrrolidine with CO₂ and HSiMe₂Ph.^{[a],[b]}

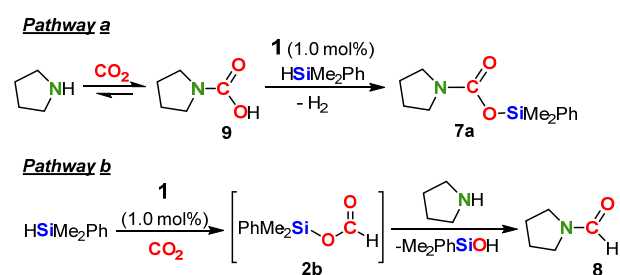
Entry	Cat.	CO ₂ (bar)	Selectivity ^[c]				
			6a (%)	7a (%)	8 (%)	9 / fa (%) ^[d]	
1	1	1	45	46	-	-	9
2	5	1	54	36	-	-	10
3	1	1.5	13	53	13	-	21
4	1	2	-	61	24	15	-
5	1	3	-	52	30	18	-
6	5	3	-	37	41	22	-

[a] Reaction conditions: HSiMe₂Ph (0.5 mmol), *c*-H(NC₄H₈) (0.5 mmol) in acetonitrile-*d*₃ (0.50 mL) at 348 K for 15 h. [b] 1.0 mol% of **1** or **5** with respect to the hydrosilane. [c] Determined by ¹H NMR integration using hexamethylbenzene as internal standard. [d] fa = free amine.

As the pressure of CO₂ is increased to 1.5 bar, a mixture of products, silylamine **6a**, silylcarbamate **7a**, formamide HC(O)(NC₄H₈) (**8**) and free amine was obtained (Figure SI63 and Table 2, entry 3). When the pressure of CO₂ was successively increased to 2 and 3 bar, silylcarbamate **7a** and formamide **8** along with carbamic acid derivative HOC(O)(NC₄H₈)

(9),⁴⁰ were observed (Table 2, entries 4 and 5). It should be noted that catalyst **5** shows a parallel result to that obtained by **1** under high pressure of CO₂ (3 bar) (Table 2, entry 6).

The decrease in the amount of silylamine **6a** and the increase in that of silylcarbamate **7a** at 1.5 bar of CO₂ agrees with the reactivity studies of Schemes 6 and 7 that have shown that **7a** is formed by CO₂ insertion into **6a** (Table 2, entry 3). In this context, it is necessary to consider that an equilibrium between free amine and carbamic acid is established under reaction conditions (see Figures SI65, SI66).⁴¹ Thus, formation of silylcarbamate **7a** could also result from the reaction of carbamic acid with HSiMe₂Ph (*pathway a*, Scheme 9). In agreement with this possibility, it is worth mentioning that it has been proven that, as other iridium complexes,⁴² **1** catalyzes the dehydrogenative silylation of formic acid with HSiMe₂Ph to give the silylformate **2b** and H₂ (Figure SI64). On the other hand, the equilibrium between free amine and carbamic acid is displaced to the formation of **9** as the CO₂ pressure is increased (Figure SI65) which agrees with the presence of carbamic acid **9** in the reaction medium (Table 2, entries 4 and 5).



Scheme 9. Proposed mechanistic pathways for the **1**-catalyzed dehydrogenative silylation of pyrrolidine-1-carboxylic acid versus **1**-catalyzed *N*-formylation of pyrrolidine with CO₂ and HSiMe₂Ph.

Under 3 bar of CO₂ the selectivity in formamide product of the **1**-catalyzed reaction of pyrrolidine with the stoichiometric amount of HSiMe₂Ph is surprisingly low, reaching a maximum of 30% with silylcarbamate as the major reaction product (Table 2, entry 5). In this regard, it is worth mentioning that no reaction of silylcarbamate **7a** with HSiMe₂Ph has been observed at 348 K. Therefore, it is reasonable to propose that in this case formamide **8** should exclusively be generated by reaction of silylformate **2b** intermediate (not observed) with pyrrolidine (*pathway b*, Scheme 9).

In order to unravel the reasons behind the low selectivity in the formamide product, we have carried out a study of the influence of the relative hydrosilane and amine concentration. Experiments performed at constant CO₂ pressure (3 bar) evidenced that the reaction outcome is strongly dependent on the relative concentration of the amine and the silane (Table 3). Thus, reducing the amine and hydrosilane concentration from 0.50 mmol to 0.15 mmol resulted in the formation of formamide **8** (74%) and a 20% of the formate salt, [H₂(NC₄H₈)] [HCO₂] (**10**) (Table 3, entry 2).⁴³ The formation of **10** could only be explained by reaction of formic acid with pyrrolidine (Figure SI67). In this regard, although the presence of silanol was not detected, it is known that silanols react with silylformate in presence of amine to generate formic acid and siloxane.^{36b} The decrease in the amine concentration results in a decrease in the amount of carbamic acid **9**, as a consequence of the shift of the

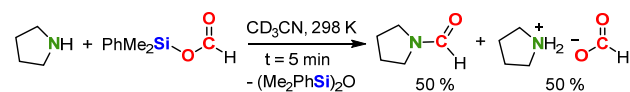
amine/carbamic acid equilibrium, and in turn of that of the silylcarbamate **7a** (6%). This outcome supports the participation of silylformate **2b** as a reaction intermediate, which further reacts with pyrrolidine through *pathway b* (Scheme 9) to give formamide **8** and silanol. Thus, under this reaction conditions, CO₂ hydrosilylation to silylformate **2b** is favored over silylative dehydrogenation of carbamic acid to **7a**. As a consequence, a significant increase on the amount of produced formamide is observed.

Table 3. Effect of the concentration of amine and hydrosilane in the **1**-catalyzed reaction of pyrrolidine with CO₂ and HSiMe₂Ph.^{[a],[b]}

Entry	Pyrrolidine ^[c]	HSiMe ₂ Ph ^[c]	Selectivity ^[d]			
			7a (%)	8 (%)	9 (%)	10 (%)
1	0.50	0.50	52	30	18	-
2	0.15	0.15	6	74	-	20
3 ^[e]	0.15	0.3	29	68	-	-
4	0.30	0.15	30	20	50	-

[a] Reaction conditions: CO₂ (3 bar), in acetonitrile-*d*₃ (0.50 mL) at 348 K for 15 h. [b] 1.0 mol% of **1** with respect to the reagent in lower concentration. [c] mmol. [d] Determined by ¹H NMR integration using hexamethylbenzene as internal standard. [e] 3% of unidentified products.

Interestingly, the catalyst-free reaction of freshly prepared silylformate **2b**, which was synthesized according to a catalyst-free methodology,⁴⁴ with one equivalent of pyrrolidine quantitatively yielded a 1:1 mixture of formamide **8** and the formate salt **10** (Scheme 10). This result further supports that at least a 20% of the formamide obtained from the **1**-catalyzed reaction of pyrrolidine with CO₂ (3 bar) and HSiMe₂Ph is formed via *pathway b* of Scheme 9 (Table 3, entry 2).

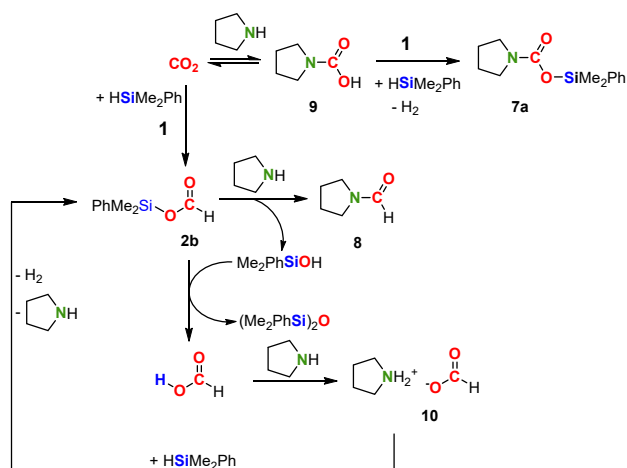


Scheme 10. Reaction of pyrrolidine with HC(O)OSiMe₂Ph (**2b**).

The increase of the relative hydrosilane concentration resulted in a significant decrease of the amount of the formate salt **10** (3%) and an increase of that of silylcarbamate **7a** (29%) (Table 3, entry 3). This result suggests that **10** further reacts with HSiMe₂Ph to give silylformate **2b** and H₂. In addition, we have found that the reaction of the formate salt **10** (independently prepared) with HSiMe₂Ph in acetonitrile-*d*₃ at 298 K affords 1-formylpyrrolidine **8** and O(SiMe₂Ph)₂ with hydrogen evolution (NMR evidence, Figure SI68). On the other hand, the shift of the amine/carbamic acid equilibrium when increasing the relative pyrrolidine concentration affords a large amount of carbamic acid **9** (50%) and silylcarbamate **7a** (30%) and, therefore, a significant decrease of formamide **8** (20%) (Table 3, entry 4). Interestingly, although the formate salt is not observed at the end of the reaction, formation of **10** has been detected by ¹H NMR spectroscopy along the reaction. This result indicates that

under the reaction conditions *pathway b* (Scheme 9) is also an active route for the formation of **8** (Figure SI69).

The set of reactions that take place in the hydrosilylation of CO₂ with HSiMe₂Ph in the presence of pyrrolidine are shown in Scheme 11. In particular, silylformate **2b** reacts with pyrrolidine to give 1-formylpyrrolidine **8** and silanol, HOSiMe₂Ph. The latter reacts with **2b** to afford formic acid and siloxane O(SiMe₂Ph)₂. In presence of pyrrolidine formic acid is neutralized to yield the pyrrolidin-1-ium formate salt **10**. Salt **10** reacts with HSiMe₂Ph to produce hydrogen, **2b** and pyrrolidine. Under these conditions, **2b** and pyrrolidine reacts to produce 1-formylpyrrolidine and silanol, restarting the cycle (Scheme 11).



Scheme 11. Reactions involved in the **1**-catalyzed hydrosilylation of CO₂ with HSiMe₂Ph in the presence of pyrrolidine.

Proposed mechanistic pathways for the 1-catalyzed reactions of pyrrolidine with CO₂ and hydrosilanes.

To further understand the reaction mechanism that operates on the amine silylation process, a computational study at the same level of theory as in the formylation process was performed. We have compared the energy profile for the carboxylate silylation (catalyst **1** preactivation, steps **B** to **C** in Figure 4) with the **1**-catalyzed dehydrogenative amine silylation (**B** to **C'** in Figure 7). In particular, we have explored the direct amine silylation through a concerted process (*via* **TSBC'**), as previously proposed for similar processes.³⁵ As is shown in Figure 7, the amine silylation is more energetically favorable than the carboxylate silylation process with transition structure **TSBC'** being 21.6 kcal·mol⁻¹ lower in energy than **TSBC**.

From **C'** there are two possible pathways: the first one consists in the CO₂ insertion into the Ir–H bond to generate a formate intermediate **D'**; which would result into the silylformate accordingly with Figure 4. This process requires to surmount an energy barrier of 24.6 kcal·mol⁻¹, dictated by **TSCD'**. The second pathway involves the elimination of the silylamine and formation of an iridium-dihydrogen intermediate **F**, the energy barrier for this step is **TSC'F** (15.9 kcal mol⁻¹). This outcome also explains why catalysts **1** and **5** have comparable catalytic activity (Figure 6) as the uncoordinated carboxylate fragment of **1** is not involved in this reaction pathway. These findings allow to rationalize the reaction selectivity. At the reaction temperature (348 K) and lower CO₂ pressure, the energy barrier for the formylation process is too high to be overcome, and thus the CO₂ insertion in the silylamine, the dehydrogenative silylation product, takes place. It should be mentioned that the insertion of CO₂ into the Si–N of silylamines is a thermodynamically and kinetically favored process.^{35,45} Therefore, accordingly with the experimental observations, under low CO₂ pressure silylamine and silylcarbamate should be the only expected reaction products (Table 2, entry 1). However, increasing the CO₂ pressure should favor the CO₂ activation pathway via **TSCD'** (Figure 7), enabling the formation of silylformate, which evolves according to Scheme 10. Therefore, the observed change in selectivity when increasing the CO₂ pressure (Table 2) is a consequence of

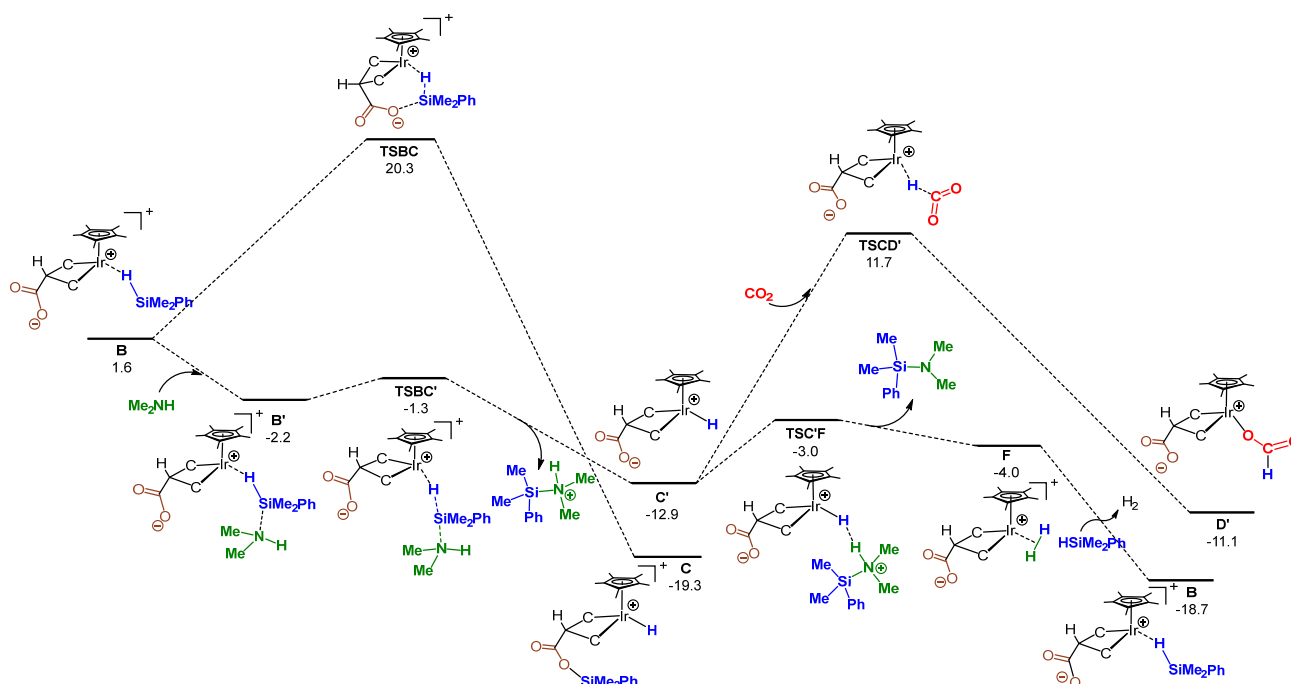


Figure 7. DFT calculated Gibbs free energy profile at 348 K (in kcal·mol⁻¹) relative to **A** and the isolated molecules for the amine silylation and posterior CO₂ activation.

the direct involvement of CO₂ in the formation of the transition state TSCD'.

CONCLUSIONS

The zwitterionic complex [Cp*IrCl{(MeIm)₂CHCOO}] (**1**) catalyzes the selective hydrosilylation of CO₂ with HSiMe₂Ph, HSiMePh₂, HSiEt₃, HSiMe(OSiMe₃)₂ and 1,4-bis(dimethylsilyl)benzene to the corresponding silylformate derivatives. The best reaction performance has been achieved in acetonitrile at 348 K using HSiMe₂Ph as reductant. It has been proven that the carboxylate moiety at the bis-NHC ligand in **1** plays a relevant role on the catalytic mechanism. Indeed, the related carboxylate-free iridium cationic species [Cp*IrCl{(MeIm)₂CH₂}]⁺ (**5**) shows a poor activity as CO₂ hydrosilylation catalyst compared to **1**. In agreement with this experimental finding, theoretical calculations have revealed that the carboxylate moiety is involved in the pre-catalyst activation step leading to the formation of an iridium(III) hydrido active species having a silyl-carboxylate moiety at the bis-NHC linker.

Complex **1** promotes the reaction of pyrrolidine with CO₂ in the presence of HSiMe₂Ph as reductant although in a non-selective way. The catalyst performance has proven to be highly dependent on both the CO₂ pressure and the relative concentration of pyrrolidine and HSiMe₂Ph. Thus, under a pressure of CO₂ of 3 bar and both reagents in low concentration the corresponding formamide was obtained as the major product, while at lower CO₂ pressure (1 bar) a mixture of silylamine and silylcarbamate was formed. Moreover, the **1**-catalyzed dehydrogenative silylation of *in situ* generated carbamic acid leading to silylcarbamate is also operative when increasing the pressure of CO₂. In full agreement with these observations, compound **1** efficiently catalyzes the dehydrogenative silylation of a range of secondary amines with HSiMe₂Ph to afford the corresponding silylamine derivatives which further react with CO₂ (3 bar) to quantitatively afford the corresponding silylcarbamates, formed by CO₂ insertion into the Si-N bond. Theoretical calculations confirm that the dehydrogenative silylation of amines is preferred to the CO₂ hydrosilylation at low CO₂ pressure. However, increasing the CO₂ concentration favors the CO₂ hydrosilylation and therefore the formation of formamide. Interestingly, an amine-promoted pre-activation pathway leading to an iridium(III) hydrido active species, without the participation of carboxylate moiety at the bis-NHC linker, has been identified. In full agreement with this finding, complexes **1** and **5** exhibited a similar catalytic performance in presence of pyrrolidine.

Reductive functionalization studies have shown that the formation of 1-formylpyrrolidine from silylformate and pyrrolidine might not be as simple as it had previously been reported. In fact, the catalyst-free reaction of silylformate with pyrrolidine in acetonitrile afforded an equimolar mixture of 1-formylpyrrolidine and the pyrrolidin-1-ium formate salt **10**. This salt is presumably formed from the formic acid generated by reaction of the produced silanol with silylformate in presence of pyrrolidine. Interestingly, the pyrrolidin-1-ium formate salt reacts with excess of hydrosilane to give 1-formylpyrrolidine and O(SiMe₂Ph)₂ with hydrogen evolution.

EXPERIMENTAL SECTION

General procedures. All reactions and manipulations were performed under an argon atmosphere using Schlenk-type techniques or in a glovebox (MBraun UNILab). Organic solvents were dried by standard procedures and distilled under an argon

atmosphere prior to use or obtained oxygen- and water-free from a solvent purification system (Innovative Technologies). Acetonitrile-*d*₃ was dried with CaH₂ and degassed under argon prior to use. ¹H NMR, ¹³C-APT NMR, and ²⁹Si NMR spectra were recorded on a Bruker AV-300 and AV-400 spectrometer using hexamethylbenzene as internal reference. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) are reported in Hz and refer to apparent peak multiplicities. ¹H/¹³C-HSQC, ¹H/¹³C-HMBC and ¹H/²⁹Si-HMBC sequences were used to assign the ¹H and ¹³C{¹H} spectra. The zwitterionic iridium compound [Cp*IrCl{(MeIm)₂CHCOO}] (**1**) was prepared following the procedure recently described by us.²⁰ Amine (pyrrolidine, piperidine, morpholine, Et₂NH, Me(*c*-hexyl)NH, ¹Pr₂NH) and silane reagents (HSiMe₂Ph, HSiMePh₂, HSiEt₃, and 1,4-(HMe₂Si)₂(C₆H₄)) used in the catalytic experiments were purchased from commercial sources and dried over 4 Å molecular sieves prior to use.

General procedure for the NMR studies of the 1-catalyzed reactions of CO₂ with HSiR₃. A Young NMR tube was charged with 0.153 mmol of the corresponding HSiR₃ (SiR₃ = SiMe₂Ph, SiMePh₂ or SiEt₃, complex **1** (0.89 mg, 0.00153 mmol, 1 mol%; for experiment with 5 mol %, 4.45 mg, 0.00765 mmol), CD₃CN (0.5 mL) and hexamethylbenzene (0.016 mmol, as internal standard). The tube was pressurized with CO₂ (3 bar) and the reaction was monitored by ¹H NMR at 348 K.

Data for HC(O)OSiEt₃ (**2a**). ¹H NMR (300 MHz, CD₃CN, 348 K): δ 8.14 (s, 1H, HC(O)O), 1.02 (t, 9H, CH₃), 0.84 (q, 6H, CH₂). ¹H NMR (300 MHz, CD₃CN, 298 K): δ 8.12 (s, 1H, HC(O)O), 0.99 (t, 3H, -CH₃), 0.80 (m, 2H, -CH₂-). ¹H-²⁹Si HMBC (80 MHz, CD₃CN, 298 K): δ 26.64 (s).

Data for HC(O)OSiMe₂Ph (**2b**). ¹H NMR (300 MHz, CD₃CN, 348 K): δ 8.15 (s, 1H, HC(O)O), 7.67 (m, 2H, *o*-Ph), 7.46 (m, 3H, *m*, *p*-Ph), 0.60 (s, 6H, SiMe₂). ¹H NMR (300 MHz, CD₃CN, 298 K): δ 8.13 (s, 1H, HC(O)O), 7.67 (m, 2H, *o*-Ph), 7.45 (m, 3H, *m*, *p*-Ph), 0.58 (s, 6H, Me). ¹H-²⁹Si HMBC (80 MHz, CD₃CN, 298 K): δ 13.78 (s).

Data for HC(O)OSiMePh₂ (**2c**). ¹H NMR (300 MHz, CD₃CN, 348 K): δ 8.25 (s, 1H, HC(O)O), 7.68 (m, 4H, *o*-Ph), 7.46 (m, 6H, *m*, *p*-Ph), 0.90 (s, 6H, SiMe₂). ¹H NMR (300 MHz, CD₃CN, 298 K): δ 8.23 (s, 1H, HC(O)O), 7.66 (m, 4H, *o*-Ph), 7.45 (m, 6H, *m*, *p*-Ph), 0.89 (s, 6H, Me). ²⁹Si{¹H} NMR (80 MHz, CD₃CN, 298 K): δ 1.68 (s).

1-Catalyzed reaction of CO₂ with 1,4-bis(dimethylsilyl)benzene. A Young NMR tube was charged with 0.0765 mmol of 1,4-bis(dimethylsilyl)benzene, complex **1** (0.89 mg, 0.00153 mmol), CD₃CN (0.5 mL) and hexamethylbenzene (0.016 mmol, as internal standard). The tube was pressurized with CO₂ (3 bar) and the reaction was monitored by ¹H NMR at 348 K.

Data for {HC(O)OSiMe₂}(C₆H₄)(SiHMe₂) (**3**). ¹H NMR (300 MHz, CD₃CN, 348 K): δ 8.14 (s, 1H, HC(O)O), 7.65 (d, 2H, *o*-Ph), 7.57 (d, 2H, *m*-Ph), 4.42 (m, 1H, Si-H), 0.36 (d, 6H, SiMe₂), 0.59 (s, 6H, SiMe₂). ²⁹Si{¹H} NMR plus ¹H-²⁹Si HMBC (80 MHz, CD₃CN, 298 K): δ 13.71 (s, HCO₂Si), -0.79 (s, Si-H).

Data for {HC(O)OSiMe₂}₂(C₆H₄) (**4**). ¹H NMR (300 MHz, CD₃CN, 348 K): δ 8.14 (s, 2H, HC(O)O), 7.72 (s, 4H, *o*-, *m*-Ph), 0.60 (s, 12H, SiMe₂). ¹H NMR plus HSQC (300 MHz, CD₃CN, 298 K): δ 8.12 (s, 2H, HC(O)O), 7.70 (d, 4H, *m*-, *p*-Ph), 0.58 (s, 12H, SiMe₂). ²⁹Si{¹H} NMR plus ¹H-²⁹Si HMBC (80 MHz, CD₃CN, 298 K): δ 13.71 (s).

General procedure for the NMR studies of the 1-catalyzed reaction of secondary amines with HSiMe₂Ph. A Young

NMR tube was charged with 0.5 mmol of HSiMe₂Ph, 0.5 mmol of the corresponding secondary amine HNR₂ (NR₂ = *c*-(NC₄H₈), *c*-(NC₃H₁₀), *c*-(NC₄H₈O), NEt₂, NMe(*c*-hexyl), NⁱPr₂), complex **1** (2.9 mg, 0.005 mmol, 1 mol%), CD₃CN (0.5 mL) and hexamethylbenzene (0.016 mmol, as internal standard) and the reaction monitored by ¹H NMR at 348 K.

Data for Me₂PhSi(NC₄H₈) (**6a**). ¹H NMR (300 MHz, CD₃CN, 298 K): δ 7.55 (m, 2H, *o*-Ph), 7.36 (m, 3H, *m,p*-Ph), 2.98 (t, 4H, N-CH₂-), 1.71 (q, 4H, -CH₂-), 0.33 (s, 6H, -CH₃). ¹H-²⁹Si HMBC NMR (80 MHz, CD₃CN, 298 K): δ -4.68 (s). ¹³C{¹H} NMR (100.6 MHz, CD₃CN, 298 K): δ 139.8 (Ph C_{ipso}), 133.6 (Ph C_o), 128.9 (Ph C_p), 127.7 (Ph C_m), 46.8 (N-CH₂-), 26.7 (-CH₂-), 3.1 (-CH₃).

Data for Me₂PhSi(NC₃H₁₀) (**6b**). ¹H NMR (300 MHz, CD₃CN, 298 K): δ 7.57 (m, 2H, *o*-Ph), 7.36 (m, 3H, *m,p*-Ph), 2.86 (t, 4H, N-CH₂-), 1.58 (q, 2H, -CH₂-), 1.39 (q, 4H, -CH₂-), 0.30 (s, 6H, -CH₃). ¹H-²⁹Si HMBC NMR (80 MHz, CD₃CN, 298 K): δ -2.84 (s). ¹³C{¹H} NMR (100.6 MHz, CD₃CN, 298 K): δ 140.0 (Ph C_{ipso}), 133.7 (Ph C_o), 128.9 (Ph C_p), 127.8 (Ph C_m), 46.5 (N-CH₂-), 27.7 (-CH₂-), 25.4 (-CH₂-), 2.7 (-CH₃).

Data for Me₂PhSi(NC₄H₈O) (**6c**). ¹H NMR (300 MHz, CD₃CN, 298 K): δ 7.58 (m, 2H, *o*-Ph), 7.38 (m, 3H, *m,p*-Ph), 3.49 (t, 4H, N-CH₂-), 2.86 (t, 2H, OCH₂-), 0.33 (s, 6H, -CH₃). ¹H-²⁹Si HMBC NMR (80 MHz, CD₃CN, 298 K): δ -1.37 (s). ¹³C{¹H} NMR (100.6 MHz, CD₃CN, 298 K): δ 140.0 (Ph C_{ipso}), 134.8 (Ph C_o), 130.1 (Ph C_p), 128.8 (Ph C_m), 69.1 (N-CH₂-), 46.6 (-OCH₂-), -2.2 (-CH₃). Data for Me₂PhSiNEt₂ (**6d**). ¹H NMR (300 MHz, CD₃CN, 298 K): δ 7.59 (m, 2H, *o*-Ph), 7.36 (m, 3H, *m,p*-Ph), 2.87 (q, 4H, -CH₂-), 1.00 (t, 6H, -CH₃), 0.33 (s, 6H, -CH₃). ¹H-²⁹Si HMBC NMR (80 MHz, CD₃CN, 298 K): δ 2.33 (s). ¹³C{¹H} NMR (100.6 MHz, CD₃CN, 298 K): δ 141.9 (Ph C_{ipso}), 135.0 (Ph C_o), 130.0 (Ph C_p), 128.9 (Ph C_m), 41.5 (N-CH₂-), 16.6 (-CH₃), 0.73 (-CH₃).

Data for Me₂PhSiNMe(*c*-hex) (**6e**). ¹H NMR (300 MHz, CD₃CN, 298 K): δ 7.58 (m, 2H, *o*-Ph), 7.34 (m, 3H, *m,p*-Ph), 2.76 (m, 1H, N-CH-), 2.41 (s, 3H, NMe), 1.71 (m, 2H, -CH₂-), 1.57 (m, 4H, -CH₂-), 1.23 (m, 2H, -CH₂-), 1.04 (m, 2H, -CH₂-), 0.31 (s, 6H, -CH₃). ¹H-²⁹Si HMBC NMR (80 MHz, CD₃CN, 298 K): δ -2.21 (s). ¹³C{¹H} NMR (100.6 MHz, CD₃CN, 298 K): δ 142.0 (Ph C_{ipso}), 134.9 (Ph C_o), 130.0 (Ph C_p), 128.8 (Ph C_m), 57.2 (NMe), 33.2 (-CH₂-), 29.2 (-CH-), 27.5 (-CH₂-), 27.0 (-CH₂-), 0.9 (-CH₃).

General procedure for the NMR studies of the 1-catalyzed reaction of silylamines with CO₂ (3 bar). A Young NMR tube containing the corresponding silylamine (**6a-6g**; prepared from the reaction of hydrosilane Me₂PhSiH and the corresponding secondary amine HNR₂) was pressurized with CO₂ (2 or 3 bar) and the reaction monitored by ¹H NMR at 298 K.

Data for Me₂PhSiOC(O)(NC₄H₈) (**7a**). ¹H NMR (300 MHz, CD₃CN, 298 K): δ 7.70 (m, 2H, *o*-Ph), 7.42 (m, 3H, *m,p*-Ph), 3.36 (m, 2H, N-CH₂-), 3.27 (m, 2H, N-CH₂-), 1.83 (m, 4H, -CH₂-), 0.55 (s, 6H, -CH₃). ¹H-²⁹Si HMBC NMR (80 MHz, CD₃CN, 298 K): δ 9.74 (s). ¹³C{¹H} NMR (100.6 MHz, CD₃CN, 298 K): δ 154.3 (-CO₂-), 137.9 (Ph C_{ipso}), 134.5 (Ph C_o), 130.9 (Ph C_p), 128.8 (Ph C_m), 47.4, 46.7 (N-CH₂-), 26.4, 25.9 (-CH₂-), -0.9 (-CH₃).

Data for Me₂PhSiOC(O)(NC₅H₁₀) (**7b**). ¹H NMR (300 MHz, CD₃CN, 298 K): δ 7.69 (m, 2H, *o*-Ph), 7.43 (m, 3H, *m,p*-Ph), 3.40 (m, 4H, N-CH₂-), 1.56 (m, 2H, -CH₂-), 1.51 (m, 4H, -CH₂-), 0.55 (s, 6H, -CH₃). ¹H-²⁹Si HMBC NMR (80 MHz, CD₃CN, 298 K): δ 10.39 (s). ¹³C{¹H} NMR (100.6 MHz, CD₃CN, 298 K): δ 154.63 (-CO₂-), 137.81 (Ph C_{ipso}), 134.5 (Ph C_o), 130.9

(Ph C_p), 128.8 (Ph C_m), 46.5, 45.1 (N-CH₂-), 26.7, 26.4 (-CH₂-), 25.0 (-CH₂-), -0.99 (-CH₃).

Data for Me₂PhSiOC(O)(NC₄H₈O) (**7c**). ¹H NMR (300 MHz, CD₃CN, 298 K): δ 7.69 (m, 2H, *o*-Ph), 7.43 (m, 3H, *m,p*-Ph), 3.58 (t, 4H, O-CH₂-), 3.43 (dt, 4H, N-CH₂-), 0.56 (s, 6H, -CH₃). ¹H-²⁹Si HMBC NMR (80 MHz, CD₃CN, 298 K): δ 11.41 (s). ¹³C{¹H} NMR (100.6 MHz, CD₃CN, 298 K): δ 154.8 (-CO₂-), 137.5 (Ph C_{ipso}), 134.5 (Ph C_o), 131.0 (Ph C_p), 129.0 (Ph C_m), 67.2 (O-CH₂-), 46.0, 44.5 (N-CH₂-), -1.1 (-CH₃).

Data for Me₂PhSiOC(O)NEt₂ (**7d**). ¹H NMR (300 MHz, CD₃CN, 298 K): δ 7.68 (m, 2H, *o*-Ph), 7.43 (m, 3H, *m,p*-Ph), 3.27 (m, 4H, -CH₂-), 1.12 (m, 6H, -CH₃), 0.55 (s, 6H, -CH₃). ¹H-²⁹Si HMBC NMR (80 MHz, CD₃CN, 298 K): δ 10.07 (s). ¹³C{¹H} NMR (100.6 MHz, CD₃CN, 298 K): δ 155.2 (-CO₂-), 137.9 (Ph C_{ipso}), 134.4 (Ph C_o), 130.9 (Ph C_p), 128.8 (Ph C_m), 42.8, 42.2 (-CH₂-), 14.6, 13.8 (-CH₃), -1.0 (-CH₃).

Data for Me₂PhSiOC(O)NMe(*c*-hex) (**7e**). ¹H NMR (300 MHz, CD₃CN, 348 K): δ 7.70 (m, 2H, *o*-Ph), 7.45 (m, 3H, *m,p*-Ph), 3.89 (m, 1H, -CH-), 2.80 (bs, 3H, -NMe), 1.82 (m, 2H, -CH₂-), 1.66 (m, 3H, -CH₂-), 1.41 (m, 4H, -CH₂-), 1.15 (m, 1H, -CH₂-), 0.57 (s, 6H, -CH₃). ¹H-²⁹Si HMBC NMR (80 MHz, CD₃CN, 298 K): δ 10.07 (s). ¹³C{¹H} NMR (100.6 MHz, CD₃CN, 298 K): δ 155.45 (-CO₂-), 137.9 (Ph C_{ipso}), 134.4 (Ph C_o), 130.8 (Ph C_p), 128.8 (Ph C_m), 57.0, 55.6 (NMe), 31.3, 30.7 (-CH₂-), 29.5, 28.9 (-CH-), 26.6 (-CH₂-), 26.2 (-CH₂-), -0.9 (-CH₃).

General procedure for the NMR studies of the 1-catalyzed reaction of secondary amines with CO₂ and HSiMe₂Ph.

Procedure a: A Young NMR tube was charged with 0.5 mmol of HSiMe₂Ph, 0.5 mmol of *c*-H(NC₄H₈), CO₂ (1, 2 or 3 bar), complex **1** (2.9 mg, 0.005 mmol, 1 mol%), CD₃CN (0.5 mL) and hexamethylbenzene (0.016 mmol, internal standard), and the reaction monitored by ¹H NMR at 348 K.

Data for HC(O)(NC₄H₈) (**8**). ¹H NMR (300 MHz, CD₃CN, 348 K): δ 8.19 (s, 1H, HCO), 3.46 (t, 2H, -NCH₂-), 3.32 (t, 2H, -NCH₂-), 1.86 (m, 4H, -CH₂-).

Data for HOC(O)(NC₄H₈) (**9**). ¹H NMR (300 MHz, CD₃CN, 348 K): δ 11.8 (s, 1H, COOH), 3.22 (t, 4H, -NCH₂-), 1.82 (m, 4H, -CH₂-).

Procedure b: A Young NMR tube was charged with 0.153 mmol of HSiMe₂Ph, 0.153 mmol of *c*-H(NC₄H₈), CO₂ (3 bar), complex **1** (0.89 mg, 0.00153 mmol, 1 mol%), CD₃CN (0.5 mL) and hexamethylbenzene (0.016 mmol, as internal standard) and the reaction monitored by ¹H NMR at 348 K.

Data for [H₂(NC₄H₈)] [HCO₂] (**10**). ¹H NMR (300 MHz, CD₃CN, 348 K): δ 11.06 (s, 1H, H₂N⁺-), 8.49 (s, 1H, HCOO⁻), 3.26 (m, 4H, NCH₂-), 1.84 (m, 4H, -CH₂-CH₂-).

Computational Methods. DFT calculations were performed using the Gaussian09 software package, D.01revision.⁴⁶ The B3LYP exchange-correlation functional,⁴⁷ in conjunction with the D3BJ dispersion correction scheme⁴⁸ was applied in energies and gradient calculations, in conjunction with the “*ultrafine*” grid. The df2-SVP basis set was used for all the geometry optimization, and energies were further refined by means of single point calculations using the def2-TZVP basis set.⁴⁹ Solvent corrections were included in all the reported calculations through the PCM model, as implemented in the G09 suite.⁵⁰ The reported Gibbs energies were calculated at 348 K, removing the translational entropy contribution from dissolved species as indicated by Morokuma et al.⁵¹ The nature of the stationary points has been confirmed by analytical frequency analysis, and transition states were characterized by calculation of reaction paths following the intrinsic reaction coordinate.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.xxxxxxxx.

NMR data for the catalytic experiments and synthesized products and DFT energetic data as well as geometrical representations and Cartesian coordinates (xyz in Å) for all DFT optimized structures (PDF)

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AUTHOR INFORMATION

Corresponding Authors.

*E-mail: paco@unizar.es.

*E-mail: perez@unizar.es.

Present Addresses

† Dr. Julen Munarriz: Currently at the Department of Chemistry & Biochemistry, University of California, Los Angeles (UCLA), Los Angeles, California 90095, United States.

ORCID

Francisco J. Fernández-Álvarez: 0000-0002-0497-1969

M. Victoria Jiménez: 0000-0002-0545-9107

Julen Munarriz: 0000-0001-6089-6126

Ana I. Ojeda-Amador: 0000-0001-5204-6236

Victor Polo: 0000-0001-5823-7965

Jesús J. Pérez-Torrente: 0000-0002-3327-09

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