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Mechanistic Insights on the Reduction of CO₂ to Silylformates Catalyzed by Ir-NSiN Species

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Dedication ((optional))

Abstract: The hydrosilylation of CO2 with different silanes such as HSiEt₃, HSiMe₂Ph, HSiMePh₂, HSiMe(OSiMe₃)₂ and HSi(OSiMe₃)₃ in presence of catalytic ammounts of the iridium(III) complex [Ir(H)(CF₃CO₂)(NSiN*)(coe)] (1; NSiN* = fac-bis-(4-methylpyridine-2yloxy); coe = cis-cyclooctene) has been comparatively studied. The activity of the hydrosilylation catalytic system based on 1 depends on the nature of the reducing agent, where HSiMe(OSiMe₃)₂ has proven to be the most active. The aforementioned reactions were found to be highly selective to the formation of the corresponding silvlformate. It has been found that using 1 as catalyst precursor above 328 K there is a decrease in the activity. This has been attributed to consumption of the active species through a thermally competitive mechanistic pathway. Indeed, the reduction of the ancillary trifluoroacetate ligand to give the corresponding silvlether CF₃CH₂OSiR₃ has been observed. Moreover, mechanistic studies for the 1-catalyzed CO₂-hydrosilylation reaction based on experimental and theoretical studies suggest that 1 prefers an inner sphere mechanism for the CO₂ reduction while the closely related [Ir(H)(CF₃SO₃)(NSiN)(coe)] catalyst, having a triflate instead of trifluoroacetate ligand, follows an outer sphere mechanism.

Introduction

The design of new processes that allow the large-scale utilization of CO₂ as chemical feedstock could be considered as one of the challenges for nowadays chemists.^[1,2] In this regard, the catalytic reduction of CO₂ with hydrosilanes has emerged as an useful methodology for the transformation of CO₂ into value-added chemicals under mild reaction conditions.^[3] Conversely, CO₂-hydrosilylation processes are commonly unselective and afford mixtures of reduction products.^[3a] Therefore, the development of active and selective catalytic systems for the

reduction of CO2 with silanes is of great interest. Some examples of catalytic systems that allow the selective reduction of CO₂ with hydrosilanes or hydrosiloxanes to give the silylformate,[4-12] bis-silylacetal,[13] corresponding methoxysilane^[14] methane^[15] are known. Particularly, or silylformates have attracted attention during the last recent years due to their potential as C1 source in organic synthesis. Indeed, silvlformates have been proposed as intermediates in catalytic reactions of CO2 and secondary amines with hydrosilanes to give formamides and methylamines.^[2a,5,9,16] In addition, it has been recently reported that silylformates could also be used as surrogates of hydrosilanes in aldehydes transfer hydrosilylation processes.[17]

In connection with the aforementioned background, our research team has developed a series of iridium(III) complexes with monoanionic tridentate NSiN and NSiN* (NSiN = *fac*-bis-(pyridine-2-yloxy),^[18] NSiN* = *fac*-bis-(4-methylpyridine-2-yloxy)^[19]) ligands, which have proven to be active catalysts for the selective and solvent-free reduction of CO₂ with HSiMe(OSiMe₃)₂ to afford the corresponding silylformate. The iridium(III) species [Ir(H)(CF₃CO₂){*fac*-(κ^3 -S*i*,*N*,*N*)-NSiN*}(coe)] (1) (*coe* = *cis*-cyclooctene) shown in Figure 1 has been found to be the most active and selective of the above mentioned series of Ir-NSiN catalyst precursors, allowing the selective preparation of the silylformate HCO₂SiMe(OSiMe₃)₂ (**2a**) in gram scale after one hour of reaction at 328 K and 8 bar of CO₂ (Scheme 1).^[19]



Figure 1. Representation of the structure of complex 1.

In this work we have expanded the scope of our earlier work on the **1**-catalyzed CO_2 -hydrosilylation with HSiMe(OSiMe₃)₂^[19] to different silanes such as HSiEt₃, HSiMe₂Ph, HSiMePh₂ and HSi(OSiMe₃)₃.

In all the cases the reactions were found to be highly selective to the formation of the corresponding silylformate (Scheme 1). The observed activity strongly depends on the nature of the reducing agent. The reasons behind the decline in activity observed when

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complex **1** was employed at temperatures above 328 K have been unveiled by means of experimental and theoretical studies. These studies show the formation of the silyl ether $CF_3CH_2OSiR_3$ (**3**) by reaction of the trifluoroacetate ancillary ligand with the corresponding hydrosilane. This causes the consumption of the active species, and subsequently a decrease in the activity and selectivity of the catalytic system based on **1**.

Results and Discussion

¹H NMR studies of the 1-catalyzed (10 mol%) reduction of CO₂ (3 bar, 328 K) with HSiEt₃, HSiMe₂Ph, HSiMePh₂, HSiMe(OSiMe₃)₂ and HSi(OSiMe₃)₃ in C₆D₆, using hexamethylbenzene as internal standard have been performed. These studies showed that in all cases the reactions were highly selective to the formation of the corresponding silylformate (Scheme 1). Compounds **2a**, **2c**, **2d** and **2e** were identified by comparison of their ¹H, ¹³C and ²⁹Si NMR spectra with reported data and **2b** was characterized by ¹H, ¹³C(¹H) and ²⁹Si(¹H) NMR spectroscopy (See experimental).



 $\begin{array}{l} \text{SiR}_3 = \text{SiMe}(\text{OSiMe}_3)_2 \ \textbf{(2a)}; \ \text{Si}(\text{OSiMe}_3)_3 \ \textbf{(2b)}; \\ \text{SiMe}_2\text{Ph} \ \textbf{(2c)}; \ \text{SiMePh}_2 \ \textbf{(2d)}; \ \text{SiEt}_3 \ \textbf{(2e)} \end{array}$

Scheme 1. Hydrosilylation of CO_2 (3 bar) with $HSiR_3$ in C_6D_6 using complex 1 (10 mol%) as catalyst precursor.

It is noteworthy that HSiMe(OSiMe₃)₂ has proven to be the most active of the aforementioned reducing agents. Conversely, HSi(OSiMe₃)₃ has showed the poorest activity, being necessary 3 days to achieve the full conversion of the starting siloxane into the corresponding silvlformate 2b. This could be explained taking into account the greater steric hindrance around the Si-H in HSi(OSiMe₃)₃ compared to HSiMe(OSiMe₃)₂. HSiMe₂Ph has found to be slightly less active than HSiMe(OSiMe₃)₂ but more than HSiMePh₂, HSiEt₃ and HSi(OSiMe₃)₃, respectively (Figure 2). These observations suggest that both hindrance and electronic richness of the Si-H bond play an important role in the 1-catalyzed reaction of CO₂ with hydrosilanes and/or hydrosiloxanes. In this context, it should be pointed out that besides its comparatively high reactivity, using HSiMe(OSiMe₃)₂ as reducing agent presents some additional advantages, as for instance, it is relatively cheap and easily available in comparison with organosilanes such as HSiMe₂Ph.





Figure 2. Representation of the concentration (%) of silylformate versus time from the reaction of CO₂ (3 bar, 328 K) with the corresponding hydrosilane in C₆D₆ and using complex 1 (10 mol%) as catalyst precursor. The values were obtained from ¹H NMR integration using hexamethylbenzene (0.016 mmol) as internal standard.

The activity of the catalytic system based on 1 and HSiMe(OSiMe₃)₂ decreases above 328 K. In order to explain that behavior, the reaction of $HSiMe(OSiMe_3)_2$ with CO_2 (3 bar, 348 K) in C₆D₆ and in presence of **1** (10 mol%) was monitored by ¹H NMR spectroscopy. These experiments showed that in consonance with that observed under the solvent-free conditions after 2 hours of reaction all the starting HSiMe(OSiMe₃)₂ has been transformed into a mixture of 2a, O{SiMe(OSiMe₃)₂}₂, CH₃OSiMe(OSiMe₃)₂ together with traces CH₂{OSiMe(OSiMe₃)₂} (Figure S.1.1.). However, what catched our attention from those ¹H NMR spectra was the presence of a quartet resonance at δ 3.82 ppm (${}^{3}J_{H-F}$ = 8.7 Hz). This resonance corresponds to the protons of the CH₂ moiety of the silylether species CF₃CH₂OSiMe(OSiMe₃)₂ (3). This has been corroborated by comparison with NMR spectra of samples of compound 3 (see experimental and Figures S.1.2 to S.1.5). In this regard, it should be pointed out that compound 3 could be easily and quantitatively obtained from the 1-catalyzed dehydrogenative silvlation of CF₃CH₂OH with HSiMe(OSiMe₃)₂ (Scheme 2). Related examples of Ir-catalyzed dehydrogenative silylations of alcohols with silanes have been reported.^[20]

 $CF_{3}CH_{2}OH + HSiR_{3} \xrightarrow{1 (1.0 \text{ mol}\%)} CF_{3}CH_{2}OSiR_{3} + H_{2}$

 $SiR_3 = SiMe(OSiMe_3)_2$

Scheme 2. Dehydrogenative silylation of CF₃CH₂OH with HSiMe(OSiMe₃)₂ in C_6D_6 using complex 1 (1.0 mol%) as catalyst precursor.

Therefore, the formation of the silylether **3** during the **1**-catalyzed reaction of CO₂ with HSiMe(OSiMe₃)₂ at 348 K has been unambiguously demonstrated. This behavior could explain why, in contrast with that observed for the catalytic systems based on the triflate derivatives [Ir(H)(CF₃SO₃)(LSiL)(coe)] (LSiL = NSiN^[18] (**4a**); NSiN^{*[19]} (**4b**)), the activity of **1** decreases with the temperature.

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The reaction of complex 1 with four equivalents of HSiMe(OSiMe₃)₂ and CO₂ (4 bar)^[21] at 328 K was monitored by ¹H NMR with the aim of obtaining information about any reaction intermediate. This study evidenced the slow transformation of 1 into a new highly symmetric species, namely compound 5 in Scheme 3, together with free cyclooctane (see experimental). Accordingly with the symmetric structure proposed for compound 5, its ¹H NMR spectra show a set of three resonances in the aromatic region and one signal due to the methyl substituents of the N-heterocyclic rings of the NSiN ligand (Figure S.1.6.). The presence of two Ir-SiMe(OSiMe₃)₂ moieties in 5 has been corroborated by means of ¹H, ¹³C, and ²⁹Si NMR spectroscopies. Thus, the ¹H NMR spectra of **5** exhibit the resonance due to the 6 protons of the Ir-SiMe moieties of two SiMe(OSiMe₃)₂ groups as a singlet resonance at δ 0.55 ppm. This resonance correlates in the ¹H-²⁹Si Heteronuclear Multiple-Quantum Correlation (HMQC) with a signal at δ -58.6 ppm in the ²⁹Si{¹H} spectra and in the ¹H-¹³C Heteronuclear Single Quantum Correlation (HSQC) with a singlet resonance observed at δ -1.7 ppm in the ¹³C{¹H} NMR spectra. Furthermore, the OSiMe₃ groups appear as singlets at δ 0.10, 1.2 and 12.4 ppm in the ¹H, ¹³C{¹H} and ²⁹Si{¹H} NMR spectra, respectively. even though variable temperature NMR Converselv. experiments were accomplished it was not possible to identify the signal corresponding to Si-H-Si moiety. This could be attributable to a fast exchange between 5a and 5b (Scheme 3).^[22] Interestingly, when four additional equivalents of HSiMe(OSiMe₃)₂ were added to the in situ generated solutions of 5 and 2a and the resulting mixture was pressurized with CO₂ (4 bar) and heated at 328 K the full transformation of the starting siloxane into 2a was observed after two hours. Under these conditions no consumption of compound 5 was observed.



Scheme 3. Reactivity of complexes 1 and 6 with $\mathsf{HSiMe}(\mathsf{OSiMe}_3)_2$ in presence of CO_2 .

It should be mentioned that slight modifications in the ancillary ligand influence the thermal stability of the resulting CO₂-

hydrosilylation catalytic system. Thus, the iridium(III) complex $[Ir(H){CF_3(CF_2)_2CO_2}(NSiN^{*})(coe)]$ (6), with a heptafluorobutyrate ligand instead of trifluoroacetate (Scheme 3 and Figure 3), affords a catalytic system which at 328 K operates similarly to 1 (Table 1 entries 1 and 2). Complex 6 has been prepared by reaction of [Ir(H)(Cl)(NSiN*)(coe)]^[19] with one equivalent of silver heptafluorobutyrate, and fully characterized by elemental analysis and by ¹H, ¹³C{¹H}, ¹⁹F{¹H} and ²⁹Si{¹H} NMR spectroscopy (see experimental). ¹H NMR spectra of 6 show the resonance due to the Ir-H moiety as a singlet at δ -14.12 ppm, slightly low-field shifted compared to the value observed for 1 (δ -14.79 ppm)^[19] (Figure S.1.7.). Furthermore, the solid state structure of 6 has been analyzed by X-ray diffraction studies (Figure 3). Complex 6 exhibits a slightly distorted octahedral metal geometry, with NSiN* ligand facially coordinated to the iridium atom. The pyridine-N atoms are located trans to the hydride and to the n^2 -cyclooctene ligands. As it may be expected stronger structural trans effect of the hydride compared to that of the olefin induces significant differences in Ir-N bond lengths. Accordingly, the Ir-N(2) bond length trans to the hydride has found to be longer than Ir-N(1). This effect has already been in compound 1^[19] observed and in the related (**4a**).^[18a] [Ir(H)(CF₃SO₃)(NSiN)(coe)] In fact. structural parameters in 6 are very close to those of complex 1. No statistically significant differences have been found in the coordination sphere bond lengths and angles of both complexes. Moreover, both Ir-Si-O-C-N metallacycles, with enantiomorphic twisted ${}^{1}T_{2}$ and ${}^{2}T_{1}$ conformations, exhibit, in **6**, ring puckering parameters (Ir-Si-O(1)-C(2)-N(1): q = 0.130(6) Å, $\varphi = 25(4)^{\circ}$; Ir-Si-O(2)-C(8)-N(2): q = 0.146(6) Å, $\varphi = -160(4)^{\circ}$ very close to those reported for compound 1 and similar to those of [Ir(H)(CF₃SO₃)(NSiN)(coe)].^[24] This feature evidences the rigidity of these monoanionic tridentate ligands, which could be a property to take into account when designing Ir(III)-NSiN based catalysts.



Figure 3. Molecular structure of complex 6. Selected bond lengths (Å) and angles (°):Ir-Si, 2.222(3); Ir-O(3), 2.246(7); Ir-N(1), 2.105(9); Ir-N(2), 2.149(8); Ir-Ct, 2.062(12); Ir-H,1.63(2); Si-Ir-O(3), 166.47(18); Si-Ir-N(1), 80.7(3); Si-Ir-N(2), 80.8(2); Si-Ir-Ct, 102.5(3); Si-Ir-H, 89(4); O(3)-Ir-N(1), 91.3(3), O(3)-Ir-N(2), 87.8(3), O(3)-Ir-Ct, 86.7(3), O(3)-Ir-H, 100(4); N(1)-Ir-N(2), 86.2(3); N(1)-Ir-Ct, 172.8(4); N(1)-Ir-H, 81(4); N(2)-Ir-Ct, 100.6(3); N(2)-Ir-H, 165(4); Ct-Ir-H, 92(4). Ct is the centroid of the olefinic C(14)=C(15) bond.

Regarding the catalytic activity it should be mentioned that at 348 K the **6**-catalyzed (1.0 mol%) solvent-free reaction of CO₂ with HSiMe(OSiMe₃)₂ keeps its catalytic performance (Table 1, entry 4) while under the same reaction conditions the activity of the catalytic system based on complex **1** clearly decreases at that temperature (Table 1 entry 3) (see Figures S.2.1 to S.2.3.). In addition, ¹H NMR studies of the **6**-catalyzed (10 mol%) reaction of CO₂ with HSiMe(OSiMe₃)₂ in C₆D₆ did not evidence reduction of the heptafluorobutyrate ligand. Therefore, it is reasonable to propose that the decrease of the activity and selectivity, observed for the **1**-catalyzed CO₂ hydrosilylation with HSiMe(OSiMe₃)₂ at temperatures above 328 K, could be attributable to the partial consumption of the active species during the catalysis (Scheme 2).

| Table 1. Solvent-free Ir-NSiN (1.0 mol%) CO ₂ -hydrosilylation with $HSiMe(OSiMe_3)_2$. | | | | | |
|---|--------------------------|-------|----------|---------------------------|------------------------------|
| Entry | Catalyst | Т (К) | Time (h) | Conversion ^[a] | % of 2 ^[a] |
| 1 | 1 ^[19] | 328 | 1.0 | 99.9 | 98.9 |
| 2 | 6 | 328 | 1.0 | 99.9 | 98.4 |
| 3 | 1 ^[19] | 348 | 4.0 | 88.0 | 72.7 ^[b] |
| 4 | 6 | 348 | 1.0 | 99.9 | 94.6 |
| 5 | 6 | 358 | 2.5 | 97.1 | 71.8 ^[b] |

[a] The yield was determined by GC. [b] GC studies evidence the formation of ${SiMe(OSiMe_3)_2}_2O$ as side reaction product.

¹H NMR studies of the reaction of **6** with HSiMe(OSiMe₃)₂ and CO₂ (4 bar)^[21] at 328 K showed the consumption of the starting siloxane to afford **2a** and the symmetric complex **7**, which has been characterized in solution by multinuclear NMR spectroscopy (Scheme 3). Analogously to that previously described for species **5**, the highly symmetry observed in the NMR spectra of complex **7** could be consequence of a fast equilibrium between species **7a** and **7b** (Scheme 3, Figure S.1.8.).

Computational Study.

Theoretical studies at the DFT level have been carried out in order to shed light into selectivity and activity dependence with the temperature that has been experimentally observed for the 1-catalyzed CO₂-hydrosilylation. Trimethylsilane and the monoanionic tridentate NSiN (NSiN = bis-{pyridine-2-yloxy}) ligand *fac*-coordinated to iridium have been used as model systems. The reported energetic data are Gibbs energies calculated at 328 K and 1M. Two reaction paths are proposed in Scheme 4 for explaining the 1-catalyzed CO₂-hydrosilylation (paths **a** and **b**). In addition, the observation of by-products experimentally detected at higher temperature (>328 K) has

found to be due to the trifluoroacetate ligand reduction (Scheme 4, path **c**)



Scheme 4. Representation of three paths proposed for the 1-catalyzed \mbox{CO}_2 hydrosilylation.

The theoretical study starts at intermediate A (Figure 4), which is the model structure of 5a (or b), bearing a hydrosilane molecule η^2 -(Si-H)-coordinated to the metal. It is reasonable to think that the outer sphere mechanism proposed for the 4a-catalyzed CO2hydrosilylation,^[18a] could also take place in the case of catalyst 1. Thus, the trifluoroacetate ligand may promote the Si-H bond heterolytic cleavage, affording the corresponding Ir-NSiNhydride-(k^1 -O-silylester), which may undergo CO₂ hydrosilylation The energetic barrier for this step has found to be 8.2 kcal mol⁻¹ (see TSAB in Figure 4). The formation of intermediate B is exergonic (6.2 kcal mol⁻¹) and three different reaction paths may be followed. Two of them correspond to the CO₂ hydrosilylation process, which may occur via the concerted outer sphere mechanism (a) or in a stepwise fashion, replacing the silvlester ligand by CO₂ (b). Alternatively, the hydride may be transferred to the carbon atom of the carboxylic group forming a silylacetal intermediate (path c in Scheme 4).

The outer sphere concerted silyl/hydride transfer from **B** to CO_2 takes place via **a-TSBC** (Figure 4), which presents an energetic barrier of 27.1 kcal mol⁻¹, excessively high at the low temperature working conditions (328 K).



Figure 4. Outer sphere mechanism (path **a**). DFT Gibbs energy profile (relative to **A** and isolated molecules, in kcal mol⁻¹) for the **A** catalyzed Si-H bond activation in a molecule of $HSiMe_3$ and concerted CO_2 hydrosilylation.



Figure 5. Inner sphere mechanism (path b). DFT Gibbs energy profile (relative to A and isolated molecules, in kcal mol⁻¹) for path b inner sphere CO_2 hydrosilylation.

The alternative pathway proposes the exchange of the silyl-ester ligand at **B** by a CO_2 molecule, leading to **b-C** (see Figure 5) and increasing the energy in 3.8 kcal mol⁻¹. A molecule of silane may be also coordinated instead, yielding **b-D** which is the most stable intermediate calculated so far.

The migratory insertion of one of the C=O bonds in b-C into the Ir-H bond affords the formate intermediate b-E, which takes place via b-TSCE. Although direct insertion into the Ir-H bond gives an excessively high energetic barrier, the hydride transfer may be assisted by a silane molecule present in the reaction medium reducing the barrier to 23.0 kcal mol⁻¹ relative to b-D (Figure S.3.1.). The formate ligand of intermediate b-E may promote Si-H bond cleavage of a molecule of silane coordinated to the metal through b-TSEF, with an energetic barrier of 6.3 kcal mol⁻¹, leading to the silvlformate and recovering the hydride. Finally, releasing of the product and coordination of a CO₂ molecule closes the catalytic cycle. Comparison of overall energy barriers of paths a (27.1 kcal mol⁻¹) and b (23.0 kcal mol⁻¹) 1) shows that the latter is preferred for CO₂ hydrosilvlation. Therefore, while an outer sphere mechanism was proposed for the 4a-catalyzed CO₂ hydrosilylation,^[18a] when using species 1 as catalyst precursor the inner sphere mechanism showed in Figure 5 has found to be the most kinetically favourable below 328 K

A mechanistic pathway involving the reduction of the ancillary trifluoroacetate ligand, which has been experimentally observed above 328 K, begins at **B** by migratory insertion of carboxylic group into the Ir-H bond to give c-C (Figure 6). Once again, this process is facilitated when a silane molecule assists the hydride transfer through c-TSBC showing a relative energy of 13.8 kcal mol⁻¹ (Figure S.3.2.). Then, the overall energetic barrier for path c is 24.0 kcal mol⁻¹, relative to b-D. As the difference in the energetic barrier between paths **a** and **c** is only 1.0 kcal mol⁻¹, it is expected that at higher temperature a larger amount of molecules will follow c. After the transition state c-TSBC the formed silylacetal c-C may evolve quickly to give the intermediate c-D with a bis(silyl)acetal coordinated to the metal. This step is characterized by the low energy transition state c-**TSCD** (3.6 kcal mol⁻¹) which corresponds to a four member sigma bond methatesis involving the H-Si bond of a coordinated silane molecule and the Ir-O bond. Intermediate c-D is very stable and the reversible reaction is energetically unaffordable.

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Figure 6. DFT Gibbs energy profile (relative to A and isolated molecules, in kcal mol⁻¹) for the reduction of trifluoroactetate ancillary ligand following path c.

Although the conversion of bis(silyl)acetal to the corresponding ethers and even methane is catalyzed by Lewis acids (such as $B(C_6F_5)_3)^{[13b], [15g]}$, in our case, such species are not present in the reaction media and larger energetic barriers can be expected. Hence, the silyl ether (SiR₃)₂O and an aldehyde coordinated to the metal, c-E, are obtained by direct reductive elimination via c-TSDE. The energy barrier for this step is 29.8 kcal mol⁻¹, much higher than the barriers found for path **b**. Then, molecules following this path should retard the catalytic process. As the aldehyde is very instable due to the CF3 group, the insertion of the C=O bond into the Ir-H bond through c-TSEF transition state is very favorable, and leads to the metal alkoxy complex c-F after coordination of another silane molecule at the vacancy. Finally, another sigma bond methatesis process between the H-Si/Ir-O bonds releases the experimentally observed silvlether 3, and a CO₂ molecule can coordinate to the hydride complex forming b-C, which is the starting point of the catalytic cycle previously described in path b. Therefore, according to experimental data and theoretical calculations, it is reasonable to propose that the 1-catalyzed CO₂-hydrosilylation could follow the catalytic cycle summarized in Figure 7. The first step consists in the catalyst activation to give the active species A, which reacts with silane via path b to give species B at T < 328 K. Path c could also take place at higher temperatures generating by-products (Figure 7).



Figure 7. Catalytic cycle proposal for the 1-catalyzed CO₂-hydrosilylation.

Conclusions

The results from the studies of the 1-catalyzed CO₂hydrosilylation with HSiEt₃, HSiMe₂Ph, HSiMePh₂, HSiMe(OSiMe₃)₂ and HSi(OSiMe₃)₃ evidenced a clear dependence of the activity with the nature of the reducing agent, being HSiMe(OSiMe₃)₂ the most active. Therefore, not only hindrance but also electronic factors influence the reactivity of the Si-H bond. In all the cases, the reactions were found to be selective to the formation of the corresponding silylformate.

On the other hand, the activity and selectivity of the solvent-free CO_2 -hydrosilylation catalytic system based on complex **1** and HSiMe(OSiMe₃)₂ strongly depends on the temperature. Thus, when the reaction mixtures were heated above 328 K a drastic decrease of both parameters activity and selectivity of the reaction was observed. NMR studies of this reaction suggest that this effect could be attributable to the partial consumption of the catalytic active species during the catalysis. In this regard, the reduction of the ancillary trifluoroacetate ligand in **1** to afford the silyl ether **3** has been observed during the catalytic studies.

Accordingly, theoretical calculations show that the energetically preferred reaction mechanism is the stepwise CO2hydrosilylation path b, which means, migratory insertion of the CO₂ C=O bond into metal hydride bond followed by H-Si bond heterolytic cleavage of a silane molecule by the metal and the formate group, respectively. These results evidenced that the ancillary ligand clearly influences the mechanism of Ir-NSiN based catalytic processes. Indeed, while the catalytic system based on 4a (with a triflate ligand) undergoes an outer sphere mechanism for the CO₂ activation, the inner sphere (path b) is kinetically favored at (T < 328 K) when using 1 (with a trifluoroacetate ligand) as catalyst precursor. In addition, path c, involving the reduction of the trifluoroacetate ligand is energetically unfavored but accessible at higher temperatures $(\Delta G^{\neq} = 1 \text{ kcal mol}^{-1})$. Along path **c**, a higher energetic barrier is found corresponding to the bis(silyl)acetal reductive elimination. Then, path c can be considered as a thermally competitive reaction pathway that consumes the catalytically active species. In conclusion, it has been found that the 1-catalyzed CO2hydrosilylation depends on the nature of the silane. Moreover, the reasons why an increase in the temperature of the reaction produces a decrease in the activity and selectivity of the catalytic system have been clarified.

Experimental Section

General Details. All reactions and manipulations were carried out under an argon atmosphere using Schlenk-type techniques. Organic solvents were dried by standard procedures and distilled under argon prior to use or obtained oxygen- and water-free from a Solvent Purification System (Innovative Technologies). NMR spectra were obtained on a Bruker AV-300 and AV-400 spectrometer using TMS as the internal reference. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) are reported in Hz to apparent peak multiplications.¹H-¹H-COSY, ¹³C-APT, ¹H/¹³C HSQC, ¹H/¹³C HMBC and ¹H/²⁹Si HMBC sequences were used for help in the assignments of the ¹H and ¹³C spectra. Complex **1** was prepared according to the reported method.^[19] HSiMe(OSiMe₃)₂, HSi(OSiMe₃)₃, HSiMePh₂, HSiMe₂Ph and HSiEt₃ were purchased from commercial sources and used without further purifications. Compounds **2a**,^[18a] **2c**,^[4d,4e] **2d**,^[5] and **2e**^[4d,15b,15g] were characterized by ¹H NMR, ¹³C{¹H} NMR and ²⁹Si(¹H} NMR by comparison with reported data. **CAUTION**, it is important to avoid the presence of water since Ir-NSiN species have proven to be highly active catalysts for the hydrogen generation by hydrolysis of hydrosilanes.^[25]

General procedure for the NMR studies of the 1-catalyzed reactions of CO₂ with HSiR₃. A Young NMR tube was charged with 0.14 mmol of the corresponding HSiR₃ (SiR₃ = SiMe(OSiMe₃)₂, SiMe₂Ph, SiMePh₂, SiEt₃ or Si(OSiMe₃)₃), complex **1** (10 mg, 0.014 mmol), C₆D₆ (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 the desired temperature.

Data for HC(0)O{SiMe(OSiMe₃)₂} (2a). ¹H NMR plus HSQC (400 MHz, C₆D₆, 298 K): δ 7.68 (s, 1H, *H*C(O)O), 0.27 (s, 3 H, SiMe), 0.15 (s, 18 H, OSiMe₃). ¹³C(¹H) NMR plus HSQC (100 MHz, C₆D₆, 298K) δ 158.8 (s, *H*C(O)O), 1.45 (s, OSiMe₃), -2.82 (s, SiMe). ²⁹Si{¹H} NMR plus ¹H-²⁹Si HMBC (80 MHz, C₆D₆, 298 K): δ 10.6 (s, OSiMe₃), -58.3 (s, OSi(OSiMe₃)₂).

Data for HC(0)OSi(OSiMe₃)₃ (2b). ¹H NMR plus HSQC (400 MHz, C₆D₆, 298 K): δ 7.66 (s, 1H, *H*C(O)O), 0.18 (s, 27 H, OSiMe₃). ¹³C(¹H) NMR plus HSQC (100 MHz, C₆D₆, 298K) δ 158.4 (s, *H*C(O)O), 1.40 (s, OSiMe₃). ²⁹Si(¹H) NMR plus ¹H-²⁹Si HMBC (80 MHz, C₆D₆, 298 K): δ 11.8 (s, 3Si, OS*i*Me₃), -104.0 (s, 1Si, OS*i*(OSiMe₃)₃).

Selected data for HC(0)OSiMe₂Ph (2c). ¹H NMR plus HSQC (400 MHz, C₆D₆, 298 K): δ 7.74 (s, 1H, *H*C(0)O), 0.42 (m, 6H, SiMe₂). ²⁹Si{¹H} NMR plus ¹H-²⁹Si HMBC (80 MHz, C₆D₆, 298 K): δ 13.0 (s, *Si*Me₂Ph).

Selected data for HC(0)OSiMePh₂ (2d). ¹H NMR plus HSQC (300 MHz, C₆D₆, 298 K): δ 7.72 (s, 1H, *H*C(0)O), 0.74 (m, 3H, SiMe). ²⁹Si{¹H} NMR plus ¹H.²⁹Si HMBC (80 MHz, C₆D₆, 298 K): δ 1.5 (s, *Si*Me₂Ph).

Selected data for HC(O)OSiEt₃ (2e). ¹H NMR plus HSQC (400 MHz, C₆D₆, 298 K): δ 7.79 (s, 1H, *H*C(O)O), 0.90 (m, 9H, CH₃), 0.66 (m, 6H, CH₂). ²⁹Si{¹H} NMR plus ¹H-²⁹Si HMBC (80 MHz, C₆D₆, 298 K): δ 26.2 (s, *Si*Et₃).

1-catalyzed reaction of CF₃CH₂OH with HSiMe(OSiMe₃)₂. A Schlenk tube, provided with a gas bubbler, was charged with C₆D₆ (0.5 mL), CF₃CH₂OH (1.0 mmol, 76.0 μL)), HSiMe(OSiMe₃)₂ (281µL, 1.01 mmol), and **1** (6.47 mg, 0.01 mmol). The reaction mixture was stirred at 298K for 4 h. After that the resulting C₆D₆ solutions was monitored by NMR. Data for compound **3**: ¹H NMR plus HSQC (400 MHz, C₆D₆, 298 K): δ 3.82 (q, *J*_{F-H} = 8.7, 2H, C*H*₂), 0.09 (br, 18H, OSiMe₃), 0.05 (br, 3H, SiMe). ¹³C{¹H} NMR plus HSQC and HMBC (100 MHz, C₆D₆, 298K): δ 124.9 (q, *J*_{F-C} = 278.2, CF₃), 60.93 (q, *J*_{F-C} = 36.1, CH₂), 1.46 (s, OSiMe₃), -4.09 (s, SiMe) ²⁹Si{¹H} NMR plus ¹H-²⁹Si HMBC (60 MHz, C₆D₆, 298 K): δ 9.4 (OSiMe₃), -56.6 (SiMe). ¹⁹F NMR (282.23 MHz, C₆D₆, 298 K): δ -76.7 (t, *J*_{F-H} = 8.7, 2H, C*H*₂).

General procedure for the NMR studies of the symmetric compounds 5 and 7. A Young NMR tube was charged with complexes 1 or 6 (30 mg, 0.014 mmol). The complexes were dissolved in C_6D_6 (0.5 mL) and then 0.16 mmol of HSiMe(OSiMe₃)₂, were added. The tube was pressurized with CO_2 (4 bar) and heated to 328 K.

Data for [Ir{Si(OSiMe₃)₂}{κ²-Si,H-Si(OSiMe₃)₂}(CF₃CO₂)(NSiN^{*})] (5). ¹H NMR plus COSY, HSQC and HMBC (400 MHz, C₆D₆, 298 K): δ 7.91, (d,

 $\begin{array}{l} J_{H+H} = 5.1, \, 2H, \, CH\text{-}py), \, 6.46 \, (s, \, 2H, \, CH\text{-}py), \, 6.32 \, (d, \, J_{H+H} = 5.1, \, 2H, \, CH\text{-}py), \, 1.78 \, (s, \, 6H, \, CH_3\text{-}py), \, 0.55 \, (s, \, 6H, \, Si\underline{Me}(OSiMe_3)_2), \, 0.22 \, (s, \, SiMe\mbox{ligand, overlapped with the SiMe(OSiMe_3)_2 resonances of traces of $ {SiMe(OSiMe_3)_2}_2O \, and \, CH_3OSiMe(OSiMe_3)_2^{[25]} formed during the catalysis), \, 0.10 \, (s, \, 36H, \, OSiMe_3). \, ^{13}C(^1H) \, NMR \, plus \, HSQC \, and \, HMBC \, (100 \, \text{MHz}, \, C_6D_6, \, 298K): \, \delta \, 162.4 \, (C_{ipso}\text{-}O\text{-}py), \, 150.4 \, (C_{ipso}\text{-}Me\text{-}py), \, 147.0 \, (CH\text{-}py), \, 118.9 \, (CH\text{-}py), \, 113.2 \, (CH\text{-}py), \, 20.5 \, (CH_3\text{-}py), \, 1.2 \, (OSiMe_3), \, -1.7 \, (Si\underline{Me}(OSiMe_3)_2), \, -1.8 \, (SiMe\text{-}ligand). \, ^{29}Si(^1H) \, NMR \, plus \, ^{1}H\text{-}^{29}Si \, HMBC \, (60 \, \text{MHz}, \, C_6D_6, \, 298 \, \text{K}): \, \delta \, \, 12.4 \, (OSMe_3), \, 7.5 \, (SMe), \, -58.3 \, (\underline{SM}e(OSiMe_3)_2). \, ^{19}F \, \text{NMR} \, (282.23 \, \text{MHz}, \, C_6D_6, \, 298 \, \text{K}): \, \delta \, -76.4 \, (s, \, CF_3). \end{array}$

Synthesis of $[Ir(H){CF_3(CF_2)_2CO_2}(NSiN^*)(coe)]$ (6). CH_2Cl_2 (15 mL) was added to a light-protected Schlenk tube containing a mixture of [Ir(H)(CI)(NSiN^{*})(coe)] (334 0.558 mg, mmol) and silver heptafluorobutyrate (180 mg, 0.560 mmol). The resulting suspension was stirred during 90 min at room temperature, after which the reaction mixture was filtered out through Celite. The solvent was removed and the residue was washed with pentane to give the product as a white-off solid. Yield (0.34g) (78%). Data for 6: Elemental analysis for C₂₅H₃₀F₇IrN₂O₄Si; Calculated: C 38.70%; H 3.90%; N 3.61%. Found: C 38.47%; H 3.88%; N 3.67%. ¹H NMR plus COSY, HSQC and HMBC (300 MHz, C₆D₆, 298 K): δ 8.89 (d, J = 6.1, 1H, CH-py), 8.62 (d, J = 6.3 Hz, 1H, CH-py), 6.43 and 6.32 (m, 1H, CH-py), 6.11 (dd, J = 6.1, 1.7 Hz, 1H, CH-py), 5.84 (dd, J = 6.3, 1.8 Hz, 1H, CH-py), 5.10 (m, 1H, =CH-coe), 3.69 (m, 1H, =CH-coe), 2.59 (m, 1H, -CH2-coe), 1.78 (m, 1H, -CH2-coe), 1.52 (s, 3H, Me-py), 1.46 (m, 6H, CH-coe), 1.42 (s, 3H, Me-py), 1.12 (m, 4H, -CH₂-coe), (0.67, s, 3H, Si-Me), -14.12 (s, 1H, H-Ir). ¹³C{¹H} NMR plus HSQC and HMBC (75 MHz, C₆D₆, 298 K): δ 166.2 (s, C_{ipso}-O-py), 164.8 (s, C_{ipso}-O-py), 153.7 (s, C_{ipso} -Me-py), 153.0 (s, C_{ipso} -Me-py), 146.3 (s, CH-py), 145.6 (s, CH-py), 119.1 (s, CH-py), 118.3 (s, CH-py), 112.4 (s, CH-py), 111.4 (s, CH-py), 68.7 and 65.8 (s, =CH-coe), 33.4, 32.6, 31.4, 28.1, 26.1 and 25.9 (s, CH₂-coe), 20.2 (s, Me-py), 20.0 (s, Me-py), -2.0 (s, Si-Me). ²⁹Si{¹H} NMR plus ¹H-²⁹Si HMBC (60 MHz, C₆D₆, 298 K): δ 25.3 (Ir-Si¹⁹F NMR (282 MHz, Benzene-d₆): δ -80.5 (t, J = 8.8 Hz, 3F), -116.30 (m, 2F), -125.9 (brs, 2F).

Data for [Ir{Si(OSiMe₃)₂}{κ²-Si,H-Si(OSiMe₃)₂}(CF₃CF₂CC₂)(NSiN⁵)] (7). ¹H NMR plus COSY, HSQC and HMBC (400 MHz, C₆D₆, 298 K): δ 7.89, (d, J_{H-H} = 5.2, 2H, CH-py), 6.44 (s, 2H, CH-py), 6.34 (d, J_{H-H} = 5.2, 2H, CH-py), 1.80 (s, 6H, CH₃-py), 0.52 (s, 6H, Si<u>Me</u>(OSiMe₃)₂), 0.20 (s, SiMe-ligand, overlapped with the SiMe(OSiMe₃)₂ resonances of traces of {SiMe(OSiMe₃)₂)₂O and CH₃OSiMe(OSiMe₃)₂^[25] formed during the catalysis), 0.10 (s, 36H, OSiMe₃). ¹³Ct¹H NMR plus HSQC and HMBC (100 MHz, C₆D₆, 298K): δ 162.4 (C_{ipso}-O-py), 150.4 (C

^{ipso-}Me-py), 147.0 (CH-py), 118.9 (CH-py), 113.2 (CH-py), 20.5 (CH₃-py), 1.2 (OSi*Me*₃), -1.8 (Si<u>*Me*</u>(OSiMe₃)₂), -1.9 (Si*Me*-ligand). ²⁹Sit¹H} NMR plus ¹H-²⁹Si HMBC (60 MHz, C₆D₆, 298 K): δ 12.7 (OS*M*e₃), 7.6 (S*M*e), -58.4 (<u>S</u>Me(OSiMe₃)₂). ¹⁹F NMR (282 MHz, C₆D₆): δ -81.0 (t, *J* = 8.6 Hz, 3F), -119.4 (q, *J* = 8.6 Hz, 2F), -126.9 (brs, 2F).

General procedure for the solvent-free 6-catalyzed reactions of CO₂ with HSiMe(OSiMe₃)₂. A 25 mL batch reactor with Teflon lining inside was charged with dry HSiMe(OSiMe₃)₂ (3 mL, 11.04 mmol). Then the reactor was closed, purged with CO₂ gas and heated to the corresponding temperature. After stabilization to the corresponding temperature and CO₂ pressure, the reactor was opened under argon atmosphere and complex **6** (85.6 mg, 0.11 mmol), which was weighed in a glove box, was added. After closing the reactor, the system was purged using vacuum and CO₂ gas. Then the pressure of CO₂ was adjusted to 8 bar. The reaction mixture was stirred with mechanical stirrer. The liquid samples were taken periodically after releasing the CO₂ pressure, without opening the reactor, using a long needle through the sample withdrawal valve and analyzed by GC-MS. The reactor was purged with vacuum and

 \mbox{CO}_2 after each sample withdrawal and the pressure was returned back to the desired value bar using \mbox{CO}_2 .

GC-MS samples preparation. The collected samples were diluted in dry tetrahydrofuran (1.0 mL) and analyzed by quantifiable GC-MS. The product yield was obtained by comparison of the area corresponding to the peaks assigned to the reaction products with the area of the peak corresponding to $HSiMe(OSiMe_3)_2$.

Crystal structure determination for complex 6. X-ray diffraction data were collected at 100(2) K on a Bruker Smart APEX area detector diffractometer with graphite-monochromated MoK_α radiation (λ =0.71073 Å) by using narrow ω rotations (0.3°). Data reduction was carried out with APEX 2 package, intensities were integrated with SAINT+,^[26] SADABS^[27] was used to correct the data from absorption effects. The structure was solved by direct methods with SHELXS-2013,^[28] and refined by full-matrix least squares on P^2 with SHELXL-2014^[29] included in WINGX package.^[30] All hydrogen atoms have been observed in Fourier difference maps. In order to increase the data over parameter ratio, most of the hydrogen atoms have been included in the model in calculated positions and refined with a riding model. Hydride position has been located in Fourier difference maps, and refined with a restraint in Ir-H bond length. At the end of the refinement residual density peaks are observed around the metal atom. They have no chemical sense.

Crystal data for complex 6: C₂₅H₃₀F₇IrN₂O₄Si; *M* = 775.80; white prism; 0.070 x 0.140 x 0.150 mm³; triclinic; *P*-1; *a* = 9.8017(7), *b* = 11.4040(8), *c* = 13.7379(10) Å; *α* = 88.1970(10), *β* = 72.2710(10), *γ* = 69.2860(10)°; *Z* = 2; *V* = 1363.10(17) Å³; *ρ_{calc}*= 1.890 g cm⁻³; *μ* = 5.025 mm⁻¹; min. and max. transmission factors: 0.455 and 0.645; 2*θ_{max}* = 56.308°; 13120 reflection collected, 6149 unique [*R_{int}* = 0.0501]; number of data/restraints/parameters: 6149/7/376; final GoF: 1.102; *R*₁= 0.0632 [5319 reflections *I*> 2*σ*(*I*)], *wR*2 = 0.1556 for all data; largest difference peak: 3.005 e Å⁻³.

CCDC 1548786 contains the supplementary crystallographic data for this paper. These data are provided free of charge by the Cambridge Crystallographic Data Centre.

Computational details. All DFT theoretical calculations were carried out using the Gaussian program package.^[31] The B3LYP method,^[32] including the D3 dispersion correction scheme developed by Grimme^[33] with Becke Johnson damping, has been used for both energies and gradient calculations. All atoms were treated with the def2-SVP basis set^[34] together with the corresponding core potential for Ir for geometry optimizations. Energies were further refined by single point calculations using the def2-TZVP basis set. The "ultrafine" grid was employed in all calculations. All reported energies are Gibbs free energies referred to a 1 M standard state at 328.15 K removing the contribution to the translational entropy, as indicated by Morokuma et al^[35]. The nature of the stationary points was confirmed by analytical frequency analysis, and transition states were characterized by a single imaginary frequency corresponding to the expected motion of the atoms.

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146(4)° ²E conformation ; molecule **2** q = 0.150(3) Å, $\varphi = -160.0(18)^{\circ}$ ²T₁ conformation.

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