

Effective Fixation of CO₂ by Iridium-Catalysed Hydrosilylation

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Development of new chemical processes using CO₂ as raw material has become a high priority for scientists.^[1] Utilisation of CO₂ as feedstock would have the advantages of being naturally occurring, abundant, and inexpensive.^[2] However, due to the thermodynamic and kinetic stability of CO₂ its activation represents a challenge for chemists. In this context, the low reactivity of CO₂ can be overcome by catalytic activation and functionalization. For example, a number of transition-metal catalysts are known to be effective for the hydrogenation of CO₂ to formic acid.^[3] However, these catalytic systems have not yet been applied industrially.^[4] The main reason is that direct catalysed hydrogenation of CO₂ to formic acid is thermodynamically unfavourable ($\Delta G = +33$ kJ/mol)^[3] requiring high H₂ and CO₂ pressures,^[5] exhibiting low activities even at these conditions.^[6, 7]

The catalytic hydrosilylation of CO₂ shows great promise for large scale transformation of this greenhouse gas into value-added chemicals. For instance silyl formates, which are easily hydrolysable to afford formic acid,^[8] have been applied for the production of silicon-based polymeric materials in industry and as reactive intermediates in organic syntheses.^[9] Thus, metal-catalysed hydrosilylation of CO₂ to silyl formates is emerging as an alternative methodology for catalytic CO₂ fixation.

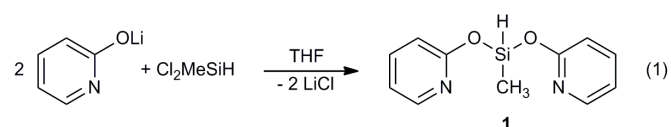
Ruthenium-catalysed hydrosilylation of CO₂ allows formation of silyl formates,^[10,11,12] being disiloxanes the only by-products observed in these reactions. Despite, the good selectivities exhibited by these ruthenium catalytic systems high CO₂ pressure is needed.^[12] On the other hand, iridium-catalysed hydrosilylation of CO₂ to the methoxide level, first reported by Eisenberg and Eisenschmid in 1989,^[13] takes place under mild conditions (r.t. and 1 atm). The authors monitored the reaction of CO₂ with Me₃SiH at 40 °C in the presence of [Ir(CN)(CO)(dppe)] as catalyst by ¹H and ¹³C NMR spectroscopy. This study revealed that reduction of CO₂ produced, in a first stage, the silyl formate Me₃Si-O-CHO. This species was further reduced to (Me₃SiO)₂(μ-CH₂), which finally reacts with an additional equivalent of Me₃SiH to afford Me₃Si-

OCH₃ and (Me₃SiO)₂(μ-O).^[13] In situ generated zirconium cationic species, known to be air and moisture sensitive, have also been used as effective catalyst for the hydrosilylation of CO₂ to the methane level under mild conditions.^[14] ¹H and ¹³C NMR studies of these reactions evidenced formation of (R₃SiO)₂(μ-CH₂) and/or (R₃SiO)₂(μ-O) together with CH₄.^[14] Some transition metal free catalytic systems are also effective for CO₂ hydrosilylation.^[15,16]

The large-scale applicability of the catalytic reduction of CO₂ to silyl formates, which would represent a real breakthrough, lies on the improvement of the selectivity and activity under mild reaction conditions. For this purpose, hydrosiloxanes, as for instance 1,1,1,3,3,5,5,5-heptamethyltrisiloxane (HTMS), are attractive reducing agents since they are commercially available, non-toxic, soluble in most organic solvents and stable to air and moisture.^[17]

Herein, we report the first example of a solvent free gram-scale synthesis and isolation of a silyl formate by iridium-catalysed reduction of CO₂ with HMTS. This reaction is selective, proceeds effectively under mild conditions and generates no waste. Additionally, a mechanistic insight into the catalytic hydrosilylation of CO₂ is also provided.

We have synthesized a new tridentate bis-(pyridine-2-yloxy)methylsilyl (NSiN) ligand precursor with a geometry that favours facial coordination modes, in which the *trans*-labilising properties of the silicon atom are reduced by the electronic effect of the two Si-O bonds (Eq. 1).



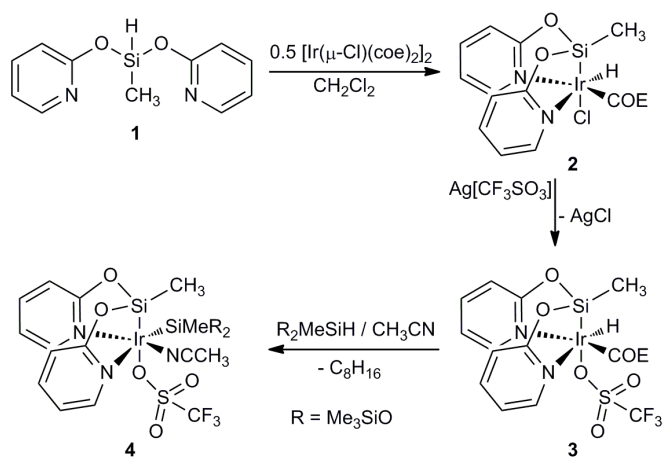
Reaction of bis-(pyridine-2-yloxy)methylsilane (**1**) with [Ir(coe)(μ-Cl)]₂ leads quantitatively to the iridium(III) complex [Ir(H)(coe)(Cl)(NSiN)] (**2**) which was isolated as a pale yellow powder (Scheme 1). The treatment of **2** with Ag[CF₃SO₃] affords the [Ir(H)(CF₃SO₃)(NSiN)(coe)] (**3**) species, which was obtained as an air stable white crystalline solid in 80 % yield according to Scheme 1.

The new iridium(III) complexes **2** and **3** have been fully characterised by elemental analysis, mass spectrometry, ¹H, ¹³C{¹H} and ²⁹Si{¹H} NMR spectroscopy. The ¹H NMR spectra of **2** and **3** is the resonance corresponding to the Ir-H proton, which appears as a singlet at δ -15.44 ppm (**2**) and δ -14.55 ppm (**3**), respectively. The ²⁹Si{¹H} NMR spectra of these complexes showed the SiMe resonance as a singlet at δ 31.5 ppm (**2**) and δ 13.6 ppm (**3**), clearly shifted to low field with respect to the corresponding resonance observed for the ligand precursor **1** at δ -17.5 ppm.

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Scheme 1. Synthesis of the catalyst precursor **4**.

X-ray crystallography^[18] reveals two molecules (Ir1 and Ir2) in the asymmetric unit of **3**. They essentially differ in the orientation of the triflate ligands (Figure 1). Both iridium atoms, which display slightly distorted octahedral coordination geometries, are facially coordinated to the tridentate NSiN ligand (Ir1–N1a, 2.097(4) Å; Ir1–N1b, 2.197(4) Å; Ir1–Si1, 2.2196(14) Å; Ir2–N1d, 2.106(4) Å; Ir2–N1e, 2.169(4) Å; Ir2–Si2, 2.2278(15) Å). The pyridine-N atoms are *trans* positioned to hydride (Ir1–H1 1.58(2) Å; Ir2–H2 1.557(19) Å) and η^2 -cyclooctene (Ir–C from 2.174(5) to 2.191(5) Å) ligands. As expected, Ir–N distances *trans* to the hydride ligand are considerably longer. Triflate ligands (Ir1–O11, 2.340(3) Å; Ir2–O21, 2.385(3) Å) coordinate *trans* to the Si atoms.

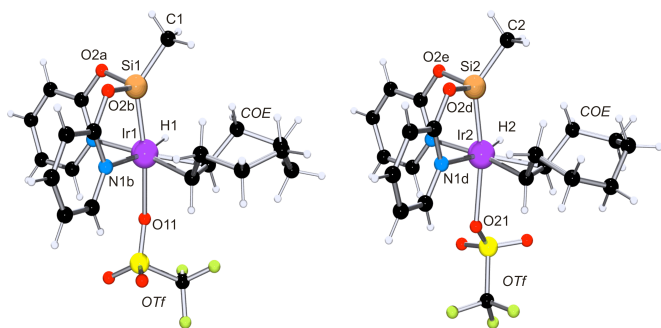


Figure 1. View of both molecules enclosed in the asymmetric unit of **3**, displaying different orientations of the triflate ligand.

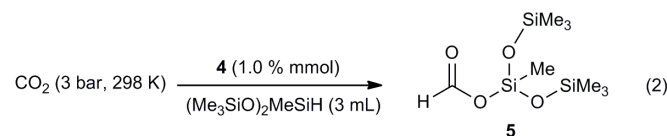
Interestingly, treatment of solutions of **3** in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (ratio 4:1) with HMTS at 50 °C affords quantitatively the solvento species $[\text{Ir}(\text{SiMeR}_2)(\text{CF}_3\text{SO}_3)(\text{NSiN})(\text{CH}_3\text{CN})]$ ($\text{R} = \text{Me}_3\text{SiO}$) (**4**). ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR studies of this reaction confirm the formation of cyclooctane together with **4** (Scheme 1), proving that in this case hydrogenation of cyclooctene is favoured against its hydrosilylation. Conversely, $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ solutions of **2** and HTMS are stable under the same reaction conditions, suggesting a relevant role of the triflate ligand in **3**.

Iridium(III) complexes with a facial disposed tridentate bis(8-quinolyl)methylsilyl (NSi*N) ligand have been reported by Tilley's group.^[19] Namely, complex $[\text{Ir}(\text{H})(\text{CF}_3\text{SO}_3)(\text{NSi*N})(\text{coe})]$, comparable to **3**, reacts with hydrosilanes in presence of acetonitrile to afford $[\text{Ir}(\text{SiR}_3)(\text{NSi*N})(\text{CH}_3\text{CN})_2][(\text{CF}_3\text{SO}_3)]$,^[20] in which the

triflate ligand leaves the coordination sphere of the iridium(III) centre enabling the coordination of two molecules of acetonitrile. Remarkably, this different reactivity proves that in our NSiN ligand, the silyl group exerts a lesser *trans*-effect which results in a stronger Ir–OTf bond interaction in **4**.

Compound **4** has been fully characterised by elemental analysis, mass spectrometry, ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectroscopy. The $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of **4** showed the SiMe resonance of the NSiN ligand as a singlet at δ 15.7 ppm together with two resonances at δ 2.6 ppm and at δ –28.1 ppm corresponding to the SiMe₃ and SiMe silicon atoms of the Ir–SiMe(OSiMe₃)₂ moiety.

CO_2 hydrosilylation under mild conditions was achieved using complex **4** as catalyst. The treatment of HMTS with CO_2 (3–8 bar, 298 K) in the presence of a catalytic amount of **4** (1.0 % mmol) yields after 6 days (3 days when the amount of **4** is increased to 10 % mmol) the silyl formate $\text{Me}(\text{Me}_3\text{SiO})_2\text{Si-OCHO}$ (**5**) as a yellow oil (Eq. 2), which was obtained in 90 % yield after purification. NMR conversion is close to 100% and no traces of the starting hydrosilane or by products were observed. Compound **5** was characterised by ^1H , ^{13}C , $^{29}\text{Si}\{^1\text{H}\}$ NMR spectroscopy and mass spectrometry.

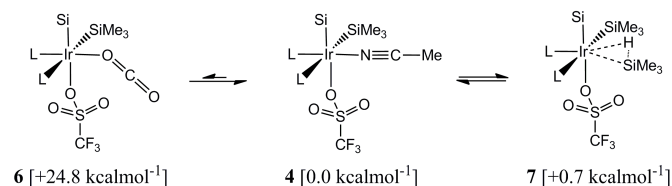


^1H NMR spectra of **5** confirm the presence of the formate group which displays a singlet resonance at δ 8.07 ppm, corresponding to the CHO proton. This resonance shows a direct C–H bond correlation in the heteronucleus single-quantum correlation (HSQC) spectra with a doublet resonance centered at δ 160.2 ppm ($J_{\text{C-H}} = 224$ Hz), assigned to the CHO carbon in the ^{13}C NMR spectra. The remaining resonances of the ^1H and ^{13}C NMR spectra are consistent with the structure proposed for the silyl formate **5**. The $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of **5** showed two singlet resonances, due to the three silicon atoms of the $\text{SiMe}(\text{OSiMe}_3)_2$ moiety, at δ 11.0 ppm $\text{Si}(\text{CH}_3)_3$ and δ –58.4 ppm $\text{Si}(\text{CH}_3)$, shifted to lower and higher field with respect to the corresponding resonances observed in the $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of HMTS at δ 3.6 ppm $\text{Si}(\text{CH}_3)_3$ and δ –42.3 ppm $\text{Si}(\text{CH}_3)$.

Kinetic studies performed using **4** (10.0 mol %) as catalyst, CO_2 (1.5 bar, 298 K), HTMS and CD_2Cl_2 as solvent revealed a 50 % conversion after 30 h, and a $\text{TOF}_{1/2}$ of 0.17 (h^{-1}). Under these conditions ^1H NMR spectroscopy shows that **4** is present throughout the reaction. This fact supports that compound **4** could be considered the catalyst resting state of the catalytic cycle.

Theoretical calculations at the DFT level, using the M06 approach, have been carried out in order to explain the catalytic behaviour of complex **4** towards CO_2 hydrosilylation. It is generally assumed that dissociation of MeCN ligand provides an active site for carbon dioxide or silane binding. Ligand substitution of acetonitrile by CO_2 to yield complex **6** is energetically disfavoured (24.8 kcalmol^{–1}, see Scheme 2). On the other hand, replacement of acetonitrile by silane to form complex **7** is only 0.7 kcalmol^{–1} energetically less stable than **4**. Hence, it is reasonable to assume that catalytic cycle starts by the ligand substitution of acetonitrile by silane to yield complex **7**. The stability of complex **7** can be attributed to the strong coordination of the silane to the metal, based

on the Dewar-Chatt-Ducanson model which comprises both ligand-to-metal σ bonding and metal $d\pi$ back-donation. The optimised structure of complex **7** shows that the Si-H distance is 1.872 Å which corresponds to a Ir- η^2 -(Si-H) interaction.^[21]

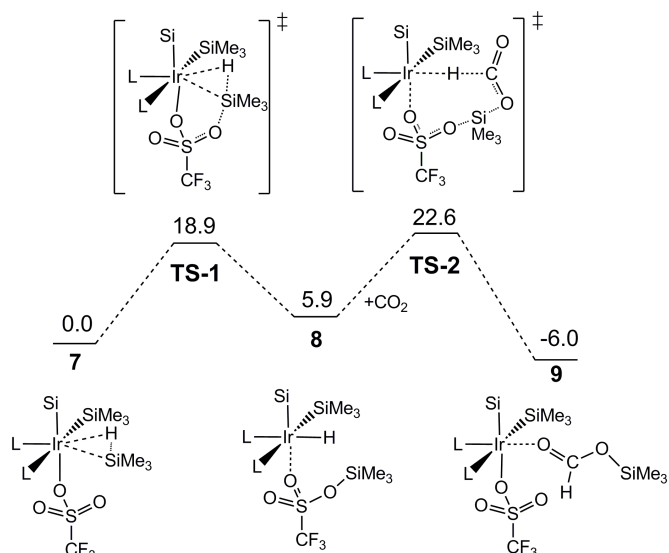


Scheme 2. Relative energies for acetonitrile ligand substitution by carbon dioxide or silane. The coordination sites of the NSiN ligand are represented by L, L and Si.

In order to shed light into the reaction mechanism, three different mechanistic pathways have been explored computationally starting from complex **7**. First, a stepwise ionic reaction mechanism, analogous to those reported by Brookhart,^[22] has been proposed. However, the necessary ionic intermediate bearing a [O=C-O-SiMe₃]⁺ moiety has been found with an energy of 30.8 kcalmol⁻¹ relative to complex **7** and carbon dioxide. A second alternative pathway could be an inner sphere reaction mechanism where the CO₂ is coordinated to the metal, but the dissociation energy calculated for the triflate decooordination and creation of a vacancy yields a value of 109.1 kcalmol⁻¹.

As a third possible pathway, it seems reasonable to assume that the reaction could take place through an outer sphere mechanism, without Ir-CO₂ interaction.^[23] Thus, in a first step, the triflate ligand may interact with the silane leading to **TS-1** structure (see Scheme 3 and Figure 2) in which the silyl group from the Ir- η^2 -(Si-H) moiety may be transferred to a terminal oxygen of the triflate ligand^[24] while Ir-H bond is formed and elongation of the Ir-O bond distance is observed. The activation energy is reasonable (18.9 kcalmol⁻¹) and it yields the intermediate complex **8**. This mechanism can be described as a ambiphilic metal ligand activation of 6 members (AMLA-6)^[25] where the bulky silyl group is transferred to the ligand, releasing the steric hindrance around the metal and forming a relatively stable silyl triflate intermediate coordinated to the metal centre. In a second step, an outer sphere mechanism for the CO₂ hydrosilylation can be proposed where both hydride transfer from the metal and silyl transfer from the triflate to the O=C=O occur in a concerted way through an eight member cycle characterised by the transition structure **TS-2** (see Figure 2) and being the activation energy of 16.7 kcalmol⁻¹. This step can be described as a double group transfer from the H-Ir-triflate-SiMe₃ moiety to the carbon dioxide substrate resulting in complex **9** in which the silyl formate can be released.

It seems interesting to mention that alternative reaction mechanisms such as the dissociation of silyl triflate from complex **8** followed by CO₂ coordination to Ir and stepwise silyl and hydrogen transfers have also been explored. However, the outlined mechanisms proceed through transition states and intermediates that are systematically of higher energy.



Scheme 3. Representation of the energetic profile calculated at DFT level for the catalytic hydrosilylation of carbon dioxide. The coordination sites of the NSiN ligand are represented by L, L and Si.

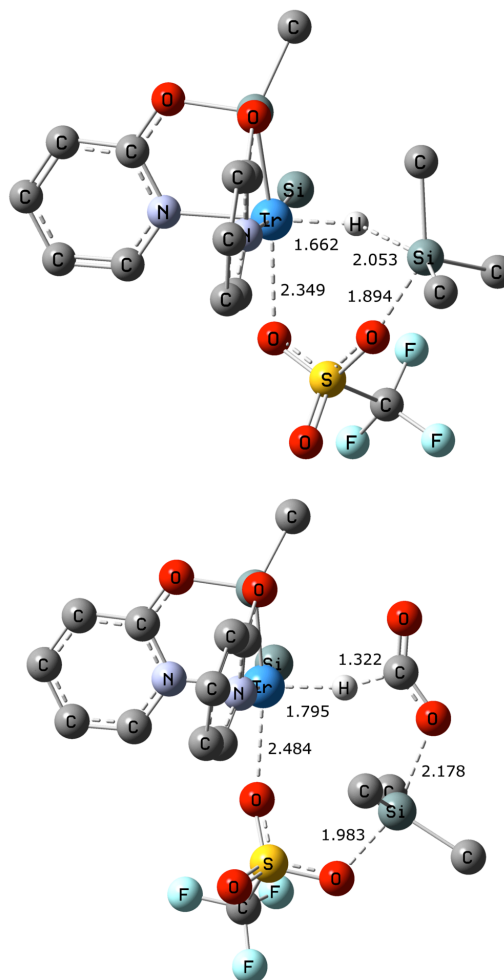


Figure 2. DFT optimised geometries of **TS-1** (up) and **TS-2** (down). Selected distances in Å. Hydrogen atoms and some methyl groups not displayed for clarity.

Summarizing, we have synthesised a new air and moisture stable iridium(III) catalyst precursor effective for CO₂ catalytic hydrosilylation. This hydrosilylation reaction is highly selective to silyl formate and proceeds efficiently under mild conditions, most likely by an out-sphere mechanism as suggested by theoretical calculations. Thus, the CO₂ hydrosilylation catalysed by complex **4** takes place in three steps: a) substitution of acetonitrile ligand by η²-(Si-H) coordination of the silane, b) silyl transfer from the Ir-η²-(Si-H) moiety to the triflate ligand and concomitant Ir-hydride bond formation and c) transfer of silyl and hydride ligands to the CO₂ in a concerted way.

Experimental Section

Full experimental details and spectroscopic data are available in Supporting Information. Coupling constant are given in Hz.

5: A Fisher-Porter tube was charged with (Me₃SiO)₂MeSiH (3.2 mL, 11.7 mmol) and **4** (80 mg, 0.12 mmol) and was pressurised with CO₂ (ca. 3 bar). The reaction mixture was stirred at room temperature for 6 days after that the resulting mixture was passed through a silica gel column prepared with hexane and the sample was eluted with CH₂Cl₂. The CH₂Cl₂ solution was removed in *vacuo* to give yellowish oil. Yield 2.81 g, (90 %). ¹H NMR (CD₂Cl₂, 300 MHz): δ 8.07 (OCHO), 0.26 (s, 3H, SiCH₃), 0.15 (br, 18 H, Si(CH₃)₃). ¹³C NMR (CD₂Cl₂, 75.45 MHz): δ 160.2 (d, J_{C-H} = 224 Hz, OCHO), 2.3 (q, J_{C-H} = 118 Hz, Si(CH₃)₃), -2.1 (q, J_{C-H} = 119 Hz, SiCH₃). ²⁹Si{¹H}NMR (CD₂Cl₂): δ 11.0 (s, Si(CH₃)₃), -58.4 (s, SiCH₃).

Kinetic studies: A Young NMR tube was charged with (Me₃SiO)₂MeSiH (79 μL, 0.30 mmol), **4** (23 mg, 0.03 mmol), CD₂Cl₂ (0.5 mL) and a sealed capillar filled with a CD₂Cl₂ solution of hexamethylbenzene (0.9 M, as internal standard). The tube was pressurised with CO₂ (1.5 bar) and the reaction was monitored by ¹H NMR at 295 K.

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