CO$_2$ Hydrosilylation

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Effective Fixation of CO$_2$ by Iridium-Catalyzed Hydrosilylation**

Ralte Lalrempuia, Manuel Iglesias, Victor Polo, Pablo J. Sanz Miguel, Francisco J. Fernández-Alvarez, Jesús J. Pérez-Torrente, and Luis A. Oro**

Development of new chemical processes with CO$_2$ as raw material has become a high priority for scientists.[1] Utilization of CO$_2$ as feedstock has the advantages that the gas is naturally occurring, abundant, and inexpensive.[2] However, the activation of CO$_2$ represents a challenge for chemists because of its thermodynamic and kinetic stability. In this context, the low reactivity of CO$_2$ 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 CO$_2$ to formic acid.[3] However, these catalytic systems have not yet been applied industrially.[4] The main reason is that direct catalyzed hydrogenation of CO$_2$ to formic acid is thermodynamically unfavorable ($\Delta G = +33\,\text{kJ}\,\text{mol}^{-1}$),[3] requires high H$_2$ and CO$_2$ pressures,[5] and exhibits low activities even at these conditions.[6,7]

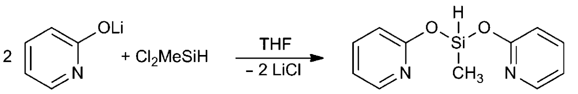
The catalytic hydrosilylation of CO$_2$ shows great promise for large-scale transformation of this greenhouse gas into value-added chemicals. For instance, silyl formates, which are easily hydrolysable to formic acid,[8] have been applied for the production of silicon-based polymeric materials in industry and as reactive intermediates in organic syntheses.[9] Thus, metal-catalyzed hydrosilylation of CO$_2$ to silyl formates is emerging as an alternative methodology for catalytic CO$_2$ fixation.

Ruthenium-catalyzed hydrosilylation of CO$_2$ allows formation of silyl formates,[10–12] with disiloxanes being the only by-products observed in these reactions. Despite the good selectivities exhibited by these ruthenium-based catalytic systems, high CO$_2$ pressure is needed.[12] On the other hand, iridium-catalyzed hydrosilylation of CO$_2$ to the methoxide level, first reported by Eisenberg and Eisenschmid in 1989,[13] takes place under mild conditions (RT and 1 atm). The authors monitored the reaction of CO$_2$ with Me$_3$SiH at 40 °C in the presence of [Ir(CN)(CO)(dppe)] (dppe = 1,2-bis(diphenyphosphanyl)ethane) as catalyst by ^{1}H and ^{13}C NMR spectroscopy. This study revealed that reduction of CO$_2$ first produced the silyl formate Me$_3$Si−O−CHO. This species was further reduced to (Me$_3$SiO)$_2$(μ-CH$_2$), which finally reacted with an additional equivalent of Me$_3$SiH to afford Me$_3$Si−OCH$_3$ and (Me$_3$SiO)$_2$(μ-O).[13] In situ generated zirconium cationic species, known to be air and moisture sensitive, have also been used as effective catalysts for the hydrosilylation of CO$_2$ to the methane level under mild conditions.[14] ^{1}H and ^{13}C NMR studies of these reactions showed formation of (R$_3$SiO)$_2$(μ-CH$_2$) and/or (R$_3$SiO)$_2$(μ-O) together with CH$_4$.[14] Some transition-metal-free catalytic systems are also effective for CO$_2$ hydrosilylation.[15,16]

The large-scale applicability of the catalytic reduction of CO$_2$ to silyl formates, which would represent a real breakthrough, depends on the improvement of the selectivity and activity of the reaction under mild reaction conditions. For this purpose, hydrosiloxanes, as for instance 1,1,1,3,5,5,5-heptamethyltrisiloxane (HMTS), are attractive reducing agents, because they are commercially available, nontoxic, 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-catalyzed reduction of CO$_2$ with HMTS. This reaction is selective, proceeds effectively under mild conditions, and generates no waste. Additionally, a mechanistic insight into the catalytic hydrosilylation of CO$_2$ is also provided.

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



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(1)

Reaction of bis(pyridine-2-yloxy)methylsilane (**1**) with [Ir(μ-Cl)(coe)$_2$]$_2$ (coe = *cis*-cyclooctene) led quantitatively to the iridium(III) complex [Ir(H)(coe)(Cl)(NSiN)] (**2**), which was isolated as a pale yellow powder (Scheme 1). Treatment of **2** with AgCF$_3$SO$_3$ afforded [Ir(H)(coe)(CF$_3$SO$_3$)(NSiN)] (**3**), which was obtained as an air-stable white crystalline solid in 80 % yield (Scheme 1).

The new iridium(III) complexes **2** and **3** have been fully characterized by elemental analysis, mass spectrometry, and ^{1}H, ^{13}C{^{1}H}, and ^{29}Si{^{1}H} NMR spectroscopy. The ^{1}H NMR

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[*] Dr. R. Lalrempuia, Dr. M. Iglesias, Dr. P. J. Sanz Miguel, Dr. F. J. Fernández-Alvarez, Prof. J. J. Pérez-Torrente, Prof. L. A. Oro
Departamento de Química Inorgánica—ISQCH
Universidad de Zaragoza—CSIC
E-mail: paco@unizar.es
oro@unizar.es
Dr. V. Polo
Departamento de Química Física, Universidad de Zaragoza (Spain)

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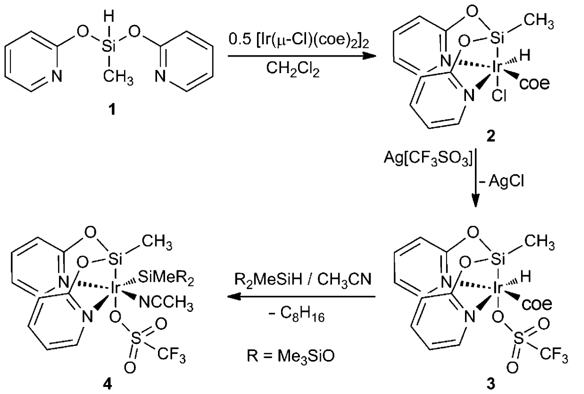


Scheme 1. Synthesis of the catalyst precursor **4**.

spectra of **2** and **3** showed the resonance corresponding to the Ir–H moiety as a singlet at $\delta = -15.44$ ppm (**2**) and $\delta = -14.55$ ppm (**3**), respectively. The $^{29}Si\{^1H\}$ NMR spectra of these complexes showed the resonances of the silicon atoms as a singlet at $\delta = 31.5$ ppm (**2**) and $\delta = 13.6$ ppm (**3**), clearly shifted to low field with respect to the corresponding resonance observed for the ligand precursor **1** at $\delta = -17.5$ ppm.

X-ray crystallography[18] shows 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 N atoms of the pyridine units are in *trans* position 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 in *trans* position 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 silicon atoms.

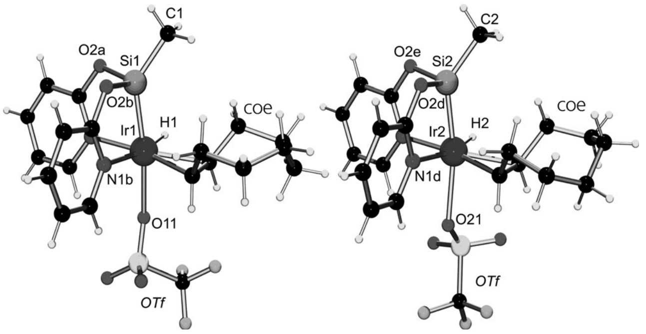


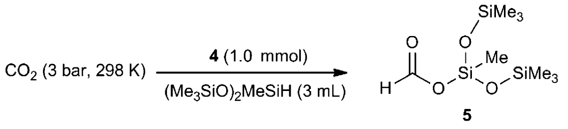
Figure 1. View of both molecules enclosed in the asymmetric unit of **3**, displaying different orientations of the triflate ligand.

Interestingly, treatment of solutions of **3** in CH_2Cl_2/CH_3CN (ratio 4:1) with HMTS at 50 °C afforded the solvento species $[Ir(SiMeR_2)(CF_3SO_3)(NSiN)(CH_3CN)]$ (**4**, R = Me_3SiO) quantitatively. ^1H and $^{13}C\{^1H\}$ NMR studies of this reaction confirmed the formation of cyclooctane together with **4** (Scheme 1), in this case hydrogenation of cyclooctene is favored against its hydrosilylation. Conversely, solutions of **2** in CH_2Cl_2/CH_3CN and HTMS are stable under the same reaction conditions, thus suggesting a relevant role of the triflate ligand in **3**.

Iridium(III) complexes with a facially disposed tridentate bis(8-quinolyl)methylsilyl (NSi*N) ligand have been reported by Tilley's group.[19] Namely, complex $[Ir(H)(coe)(CF_3SO_3)(NSi*N)]$, which is comparable to **3**, reacts with hydrosilanes in the presence of acetonitrile to afford $[Ir(SiR_3)(NSi*N)(CH_3CN)_2][(CF_3SO_3)]$,[20] in which the triflate ligand leaves the coordination sphere of the iridium(III) center, thus enabling the coordination of two molecules of acetonitrile. Remarkably, this different reactivity proves that in our NSiN ligand, the silyl group exerts a weaker *trans* effect, which results in a stronger Ir–OTf bond interaction in **4**.

Compound **4** has been fully characterized by elemental analysis, mass spectrometry, and ^1H, $^{13}C\{^1H\}$, and $^{29}Si\{^1H\}$ NMR spectroscopy. The $^{29}Si\{^1H\}$ NMR spectra of **4** showed the silicon atom resonance of the NSiN ligand as a singlet at $\delta = 15.7$ ppm together with two resonances at $\delta = 2.6$ ppm and at $\delta = -28.1$ ppm, which correspond to the silicon atoms of the $SiMe(OSiMe_3)_2$ moiety.

CO_2 hydrosilylation under mild conditions was achieved by using complex **4** as catalyst. Treatment of HMTS (3 mL) with CO_2 (3–8 bar, 298 K) in the presence of a catalytic amount of **4** (1.0 mmol) gives after 6 days (3 days when the amount of **4** is increased to 10 mmol) the silyl formate $Me(Me_3SiO)_2Si{-}OCHO$ (**5**) as a yellow oil [Eq. (2)], which was obtained in 90 % yield after purification. According to NMR analysis, conversion was close to 100 % and no traces of the starting hydrosilane or by-products were observed. Compound **5** was characterized by ^1H, ^{13}C, $^{13}C\{^1H\}$, and $^{29}Si\{^1H\}$ NMR spectroscopy, and mass spectrometry.



(2)

^1H NMR spectra of **5** confirm the presence of the formate group, which shows a singlet resonance at $\delta = 8.07$ ppm, corresponding to the CHO proton. This resonance shows a direct C–H bond correlation in the heteronuclear single-quantum correlation (HSQC) spectra with a doublet resonance centered at $\delta = 160.2$ ppm ($^1J_{C\text{-}H} = 224$ Hz), which can be assigned to the CHO carbon atom in the ^{13}C NMR spectra. The remaining resonances of the ^1H, ^{13}C, and $^{13}C\{^1H\}$ NMR spectra are consistent with the structure proposed for the silyl formate **5**. The $^{29}Si\{^1H\}$ NMR spectra of **5** showed two singlet resonances (for the three silicon atoms of the $SiMe(OSiMe_3)_2$ moiety) at $\delta = 11.0$ ppm $Si(CH_3)_3$ and $\delta = -58.4$ ppm $Si(CH_3)$. These resonances are shifted to lower and higher field, respectively, with regard to the corresponding resonances of HMTS that were found at $\delta = 3.6$ ppm ($Si(CH_3)_3$) and $\delta = -42.3$ ppm ($SiCH_3$).

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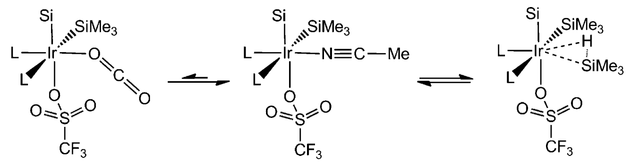
Kinetic studies performed using **4** (10.0 mol %) as catalyst, CO_2 (1.5 bar, 298 K), HTMS, and CD_2Cl_2 as solvent showed a 50 % conversion after 30 hours, and a $TOF_{1/2}$ (turnover frequency at 50 % conversion) of 0.17 h^{-1}. Under these conditions, ^1H NMR spectroscopy shows that **4** is present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

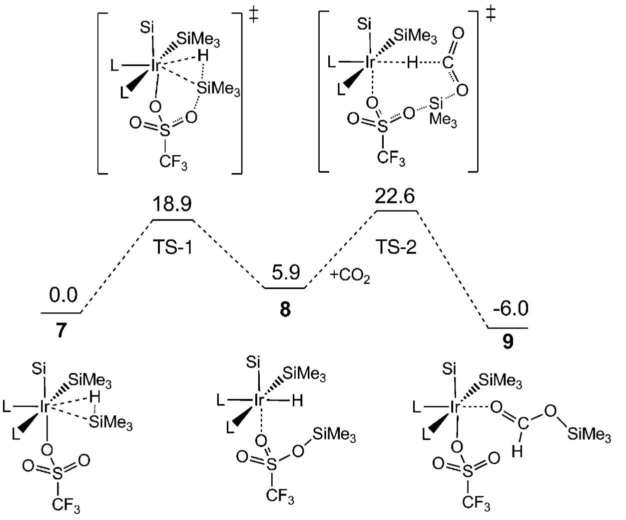
Theoretical calculations at the DFT level, using the M06 approach, have been carried out in order to explain the catalytic behavior of complex **4** toward CO_2 hydrosilylation. It is generally assumed that dissociation of the acetonitrile ligand provides an active site for binding of CO_2 or silane. Ligand substitution of acetonitrile by CO_2 to give complex **6** is energetically disfavored (24.8 kcal mol^{-1}, see Scheme 2). On the other hand, replacement of acetonitrile by one equivalent of silane would give complex **7**, which is energetically less stable than **4** by only 0.7 kcal mol^{-1}. Hence, it is reasonable to assume that the catalytic cycle starts with the ligand substitution of acetonitrile by silane to give complex **7**. The stability of **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 dπ back-donation. The optimized 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]


6 [+24.8 kcal mol^{-1}] **4** [0.0 kcal mol^{-1}] **7** [+0.7 kcal mol^{-1}]

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

In order to shed light onto 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 evaluated. However, the necessary ionic intermediate, which bears a $[O{=}C\text{-}O\text{-}SiMe_3]^+$ moiety, was found with an energy of + 30.8 kcal mol^{-1} relative to complex **7** and CO_2. A second, alternative pathway could be an inner-sphere reaction mechanism, in which the CO_2 is coordinated to the metal, but the dissociation energy calculated for the decoordination of the triflate ligand and creation of a vacancy gave a value of + 109.1 kcal mol^{-1}.

As a third possible pathway, it seems reasonable to assume that the reaction could take place through an outer-sphere mechanism, without Ir–CO_2 interaction.[23] Thus, in a first step, the triflate ligand may interact with the silane to lead to TS-1 (see Scheme 3), in which the silyl group from the Ir-η^2-(Si-H) moiety may be transferred to a terminal oxygen atom of the triflate ligand,[24] while the Ir—H bond is formed and elongation of the Ir—O bond is observed. The activation energy for this step is reasonable (18.9 kcal mol^{-1}), and it gives the intermediate complex **8**. This mechanism can be described as an ambiphilic metal–ligand activation of six members (AMLA-6),[25] in which the bulky silyl group is transferred to the ligand, thus decreasing the steric hindrance around the metal and forming a relatively stable silyl triflate intermediate that is coordinated to the metal center. In a second step, an outer-sphere mechanism for the CO_2 hydrosilylation can be proposed, in which 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-membered cycle that proceeds via transition state TS-2 with an activation energy of 16.7 kcal mol^{-1}. This step can be described as a double group transfer from the H-Ir-triflate-$SiMe_3$ moiety to CO_2 to afford complex **9**, from which the silyl formate can be released.



Scheme 3. Representation of the energetic profile (kcal mol^{-1}) calculated at DFT level for the catalytic hydrosilylation of carbon dioxide. The coordination sites of the NSiN ligand are represented by L and Si.

Alternative reaction mechanisms have also been explored, such as the dissociation of silyl triflate from complex **8** followed by CO_2 coordination to Ir and stepwise silyl and hydrogen transfers. However, the outlined mechanisms proceed through transition states and intermediates that are systematically of higher energy.

In summary, we have synthesized a new air- and moisture-stable iridium(III) catalyst precursor that is effective in the catalytic hydrosilylation of CO_2. This hydrosilylation reaction is highly selective to silyl formate and proceeds efficiently under mild conditions, most likely by an outer-sphere mechanism, as suggested by theoretical calculations. Thus, the CO_2 hydrosilylation, which is catalyzed by complex **4**, takes place in three steps: a) substitution of the acetonitrile ligand by η^2-(Si-H) coordination of the silane, b) silyl transfer from the Ir-η^2-(Si-H) moiety to the triflate ligand and concomitant Ir-hydride bond formation, and c) transfer of silyl and hydride ligands to CO_2 in a concerted way.

Experimental Section

Full experimental details, spectroscopic data, and electronic supplementary information are available in the Supporting Information. Coupling constants are given in Hz.

5: A Fisher–Porter tube was charged with $(Me_3SiO)_2MeSiH$ (3.2 mL, 11.7 mmol) and **4** (80 mg, 0.12 mmol) and pressurized with CO_2 (ca. 3 bar). The reaction mixture was stirred at RT for 6 days, after which the resulting mixture was passed through a column packed with silica gel that was prepared with hexane, and the sample was eluted with CH_2Cl_2. The solvent was removed in vacuo to give the product as a yellowish oil. Yield 2.81 g, (90 %). ^{1}H NMR (CD_2Cl_2, 300 MHz): $\delta = 8.07$ (OCHO), 0.26 (s, 3 H, $SiCH_3$), 0.15 ppm (s, 18 H, $Si(CH_3)_3$). ^{13}C NMR (CD_2Cl_2, 75.45 MHz): $\delta = 160.2$ (d, $J_{C\text{-}H} = 224$ Hz, OCHO), 2.3 (q, $J_{C\text{-}H} = 118$ Hz, $Si(CH_3)_3$), −2.1 ppm (q, $J_{C\text{-}H} = 119$ Hz, $SiCH_3$). ^{29}Si{^{1}H NMR (CD_2Cl_2): $\delta = 11.0$ (s, $Si(CH_3)_3$), −58.4 ppm (s, $SiCH_3$).

Kinetic studies: A Young NMR tube was charged with $(Me_3SiO)_2MeSiH$ (79 μL, 0.30 mmol), **4** (20 mg, 0.03 mmol), CD_2Cl_2 (0.5 mL), and a sealed capillar filled with a solution of hexamethylbenzene (0.9 M, as internal standard) in CD_2Cl_2. The tube was pressurised with CO_2 (1.5 bar) and the reaction was monitored by ^{1}H NMR spectroscopy at 295 K.

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[18] Compound **3** ($C_{20}H_{26}F_3Ir_1N_2O_5S_1Si_1$): triclinic, space group $P\bar{1}$, $a = 10.1970(17)$, $b = 13.435(2)$, $c = 18.585(3)$ Å, $\alpha = 75.695(2)$, $\beta = 81.745(2)$, $\gamma = 71.614(2)°$, $Z = 4$, $M_r = 683.78\ \mathrm{g\,mol^{-1}}$, $V = 2335.3(7)\ \mathrm{Å^3}$, $D_{calcd} = 1.945\ \mathrm{g\,cm^{-3}}$, $\lambda(\mathrm{Mo\ K\alpha}) = 0.71073$ Å, $T = 100$ K, $\mu = 5.917\ \mathrm{mm^{-1}}$, 18336 reflections collected, 7239 observed ($R_{int} = 0.0330$), $R1(F_o) = 0.0261$ [$I > 2\sigma(I)$], $wR2(F_o^2) = 0.0622$ (all data), GOF = 1.024. CCDC 892567 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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