Cationic Platinum(II) σ-SiH Complexes in Carbon Dioxide Hydrosilation


Dedication (optional)

Abstract: The low electron count cationic platinum complex [Pt(IBu)(I Bu)][BAF4], interacts with primary and secondary silanes to form the corresponding σ-SiH complexes. According to DFT calculations the most stable coordination mode is the uncommon η1-SiH. The reaction of 1 with Et3SiH leads to the X-ray structurally characterized 14-electron PtII species [Pt(SiEt2H)(I Bu)][BAF4], 2, that is stabilized by an agostic interaction. Complexes 1, 2 and the hydride [Pt(H)(I Bu)][BAF4], 3, catalyze the hydrosilation of CO2 leading to the exclusive formation of the corresponding silyl formates at room temperature.

Silane σ-complexes lie at the very heart of numerous catalytic transformations.[1] Coordination of the Si–H bond of a silane to a coordinatively unsaturated metal center in either η1-, η2-, or even η3-fashion (Figure 1) enhances the electrophilicity at silicon making it susceptible of nucleophilic attack to form new Si–X bonds (X = O, N, C, etc), and in some cases transferring one of its hydrides to the metal atom.[2] On the other hand, isolation or even unfavorable thermodynamics in the reduction of CO2 to formate,[4c,d;6] acetal,[5] methoxy[6] and even methane levels (Figure 2).[a,b] Controlling the selectivity of the reaction to generate a single product is particularly challenging. Brookhart et al. reported that the iridium η1-SiH complex [(POCOP)Ir(H)(η1-SiH)] [B(C6F5)4] catalyzes the conversion of CO2 into methane.[4a] The reaction was suggested to occur through activation of the Si–H bond by the electrophilic iridium complex leading to a transient “silylium” cation that is sufficiently reactive towards CO2. In fact, Müller and co-workers have demonstrated the role of silyl cations in the reduction of carbon dioxide.[10] Brookhart’s system seems to act in part as a mere Lewis acid, in analogy to other Lewis acids based on main group elements, particularly boron.[11]

![Figure 1. Coordination modes of silanes.](image)

![Figure 2. Possible reduction products of CO2 with hydrosilanes.](image)

Earlier, we have shown that the platinum(II) complex [Pt(I Bu)(I Bu)][BAF4], 1,[12] behaves as a highly electrophilic metal in the dehydrogenation of amine-boranes.[13] In this case, the metal is able to abstract a hydrogen atom from the borane leading to a neutral platinum species [Pt(H)(I Bu)(I Bu)] and a boronium cation, a process that takes place through the intermediacy of η1-BH complexes. Thus, we set out to explore the reactivity of 1 towards silanes and CO2 keeping in mind that silanes can also transfer a hydride atom in the presence of metal Lewis acids. In this communication we report the catalytic activity of formally 14-electron PtII complexes in CO2 hydrosilation with primary and secondary silanes. The process takes place through the initial formation of PtII σ-silane complexes in which the preferred coordination mode is η1 according to DFT calculations.

We first analyzed the interaction of silanes with complex [Pt(I Bu)(I Bu)][BAF4], 1, at different temperatures in an NMR tube (Scheme 1). Triethylsilane, Et3SiH, proved to be too bulky to detect any interaction with the metal center. On the other hand, diethylsilane, Et2SiH2, does not show evidence for an interaction at room temperature. According to NMR data, the chemical shift of the Si–H protons in the 1H NMR spectrum appeared at the same δ than in free Et3SiH2. However, upon cooling the solution at -60 °C, the SiH protons shifted up-field, appearing at ca. δ 2.20, while the signal vanished in the baseline.

---

[a] P. Ríos, Dr. J. López-Serrano, Dr. A. Rodríguez, Dr. S. Conejero Instituto de Investigaciones Químicas (IIQ), Departamento de Química Inorgánica, Centro de Innovación en Química Avanzada (ORFEO-CINCA) CSIC and Universidad de Sevilla. Avda. América Vespucio 49, 41092 Sevilla, Spain E-mail: marrodrguez@iq.csic.es; sconejero@iq.csic.es

[b] Dr. J. Díez Laboratorio de Compuestos Organometálicos y Catalítica (Unidad asociada al CSIC), Departamento de Química Orgánica e Inorgánica Universidad de Oviedo C/Julián Clavería 8, 33006, Oviedo, Spain

Supporting information for this article is given via a link at the end of the document. (Please delete this text if not appropriate)
at -80 °C. This behavior is consistent with the formation of a σ-SiH platinum complex in which fast exchange between terminal and bridging Si–H is taking place.\textsuperscript{[16]} It should be pointed out that complex 1 rearranges into a new species in the presence of Et\textsubscript{3}SiH\textsubscript{2} after a few hours (see below) at rt.

When the less hindered primary silane Bu\textsubscript{3}SiH\textsubscript{2} was used, the interaction with the platinum atom at room temperature was still too weak to observe a significant change in chemical shifts and coupling constants to platinum.\textsuperscript{[14]} As the temperature decreases the SiH proton signals are displaced in the \textsuperscript{1}H NMR spectra to higher field as expected for formation of a σ-SiH complex. The \textsuperscript{1}H-\textsuperscript{29}Si HMOC NMR spectrum shows a down-field shift of the resonance of the silicon atom. As a way of an example, at -50 °C the Si atom resonates at ca. -48 ppm, that is, 12 ppm down-field shifted with respect to the free silane (-60 ppm). The J\textsubscript{SiH} coupling constant decreases slightly on cooling (see Table S1). At lower temperatures, the fast exchange between bridging and terminal SiH protons is frozen. At -65 °C no signals for these protons are discernible whereas at the lowest temperature of the experiment (-90 °C) two broad signals centered at ca. 4 and -4.4 ppm with relative intensities of 2:1 are observed. The broadness of the peaks hampered observation of the corresponding coupling constants with \textsuperscript{29}Si. The presence of cross-peaks between them in a NOESY experiment indicate that these two signals are undergoing exchange on the NMR timescale, thus supporting an structure as depicted in Scheme 1. Phenylsilane PhSiH\textsubscript{2} behaves in a similar way to Bu\textsubscript{3}SiH\textsubscript{2}, but the dynamic exchange between terminal and bridging hydrogens was not observed even at -90 °C.

As mentioned above, complex 1 evolves cleanly into two new species in the presence of 1 equiv. Et\textsubscript{3}SiH\textsubscript{2} at room temperature after a few days. These have been characterized as the low-electron count Pt\textsuperscript{I} silyl derivative [Pt(SiHEt\textsubscript{3})(Bu\textsubscript{3}Si)][BAF\textsubscript{4}], 2 and the platinum hydride [Pt(H)(Bu\textsubscript{3}Si)][BAF\textsubscript{4}], 3 (Scheme 2). The reaction can be accelerated by using a large excess of Et\textsubscript{3}SiH\textsubscript{2}. Interaction of hydrosilanes with complex 1 rearranges cleanly into two new species in the presence of adventitious water, leading to the formation of 3. Importantly, 3 does not convert into silyl complex 2 under these experimental conditions.

On the contrary, the reaction of primary silanes Bu\textsubscript{3}SiH\textsubscript{2} and PhSiH\textsubscript{2} with 1 lead to complex reaction mixtures. Cationic complex 2 is a rare example of a coordinatively unsaturated Pt\textsuperscript{II} silyl species. This type of compounds has been postulated as intermediates in the generation of silylene species.\textsuperscript{[16]} The SiH proton resonates in the \textsuperscript{1}H NMR spectrum as a multiplet centered at 3.64 ppm coupled to \textsuperscript{195}Pt (\textsuperscript{3}J\textsubscript{Pt,H} = 115 Hz) consistent with the formulation of 2 as a platinum silyl species.\textsuperscript{[17]} The \textsuperscript{1}H,\textsuperscript{29}Si-HMQC NMR spectrum shows a signal at 18.1 ppm for the silyl group. These experimental observations were further borne out by X-ray diffraction studies (Figure 3), which show the platinum atom surrounded by two \textsuperscript{1}Bu ligands in a mutually trans disposition and a silyl fragment with no ligand trans to it. One of the CH bonds of a tert-butyl group is in close proximity to the metal center (Pt–C\textsubscript{Bu} distances of 2.06(1) and 2.950(1) Å), suggesting that an agostic interaction is stabilizing the highly electrophilic platinum atom. The angle defined by the two carbones and the platinum atom (C\textsubscript{1}−Pt\textsubscript{1}−C\textsubscript{12}) deviates from linearity (167.4(3)°) as a consequence of the buttressing effect of the silyl ligand exerted on the NHC that establishes the agostic interaction. The Pt1–Si1 bond distance of 2.314(3) Å falls in the expected region for Pt\textsuperscript{II} silyl species.

At variance with hydride 3 that was not possible to be isolated in the solid state due to its propensity reform 1, cyclometalation of 2 with concomitant extrusion of Et\textsubscript{3}SiH\textsubscript{2} takes place at rt (25% of conversion after 5 days) or under mild heating for a few hours. On the other hand compound 2 does not react with H\textsubscript{2} leading to Et\textsubscript{3}SiH\textsubscript{2} and 3 which contrast with the fast hydrogenation of the cyclometalated species 1.
The interaction of ⁵BuSiH₃ and Et₃SiH₂ with silyl and hydrido derivatives 2 and 3 was also explored. VT NMR studies have proven that formation of their α-SiH complexes is less favored than in the case of 1. For example, ¹H NMR spectra of the silyl species [Pt(SiEt₂H)(²Bu)₃][BAr₆] in the presence of 1 equiv of ⁵BuSiH₃ shows only a marginally different chemical shift of the SiH₂ protons at −90 °C (0.1 ppm downfield shifted with respect to the ¹H NMR spectrum recorded at r.t.). Expectedly, the silicon nucleus of ⁵BuSiH₃ resonates in the ²⁹Si NMR spectra at ca. −58 ppm. Similarly, negligible interaction is observed in the case of hydride [Pt(H)(²Bu)₃][BAr₆] and Et₃SiH₂ (SiH protons of Et₃SiH₂ 0.2 ppm downfield shifted with respect to the ¹H NMR spectrum recorded at r.t.).

All attempts to obtain crystals suitable for X-ray diffraction for the α-SiH complexes at low temperature failed. Thus, we turned to DFT calculations ((M06/6-31g(d,p) + SDD; see ESI)[¹⁹] to analyze the stability and coordination mode of the silanes to complexes 1-3 (Figure 4). According to the calculations, coordination of the silane molecules to complexes 1-3 in a α-SiH fashion is exothermic in all cases with energy returns in the range -12.8 to -8.2 kcal mol⁻¹ (Table S8), which lays within the expected loss of entropy at r.t.[¹⁹] and agrees with coordination of the silanes to the metal complexes at temperatures lower than room temperature. Also, the calculations predict a slight preference for the coordination of Et₃SiH₂ to all metal fragments and, in agreement with our observations, of both silanes to 1.

![Figure 4. DFT calculated structures of complexes 1-3-3-HSiBu.](image)

The Pt···Si distances (greater than the sum of the covalent radii) and Pt···H–Si angles are consistent with a preferred η¹-Si–H coordination mode,[¹⁸] but some differences in the structural parameters have been observed (Table 1). Complex 1 is the one that forces to a greater extent the η¹ coordination mode according to the angle defined by the Pt···H–Si atoms and the Pt···Si bond distances (Table 1). This is likely due to the cyclometalated nature of the NHC that, at variance to the non-cyclometalated ᵅBu ligands in complexes 2 and 3, cannot rotate about the Pt–C carbene bond to accommodate the silane. The Pt···H and Pt···Si distances in complexes 2 ᵅBuSiBu and 2 ᵅSiEt₂ are considerably longer (see Table 1). A closer look at the angles defined by the two carbene carbon atoms and the platinum center hints at a possible explanation. These angles are nearly 182° for these species, compared to the ca. 175° in 3 ᵅBuSiBu and 3 ᵅSiEt₂, that is, the Et₃SiH fragment in complexes 2 ᵅBuSiBu and 2 ᵅSiEt₂ is pushing the ᵅBu ligands towards the silane, hampering its interaction with the platinum atom. Obviously, the C(carbene)–Pt–C(carbene) angles in

<table>
<thead>
<tr>
<th>Complex</th>
<th>Pt···H(Å)</th>
<th>Pt···Si(Å)</th>
<th>Si···H(Å)</th>
<th>Pt···H-Si(°)</th>
<th>C–Pt–C(°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 ᵅBuSiBu</td>
<td>1.96</td>
<td>3.33</td>
<td>1.53</td>
<td>145.25</td>
<td>173.28</td>
</tr>
<tr>
<td>2 ᵅBuSiBu</td>
<td>2.24</td>
<td>3.54</td>
<td>1.51</td>
<td>140.73</td>
<td>182.52</td>
</tr>
<tr>
<td>3 ᵅBuSiBu</td>
<td>1.95</td>
<td>3.24</td>
<td>1.53</td>
<td>137.09</td>
<td>174.75</td>
</tr>
<tr>
<td>1 ᵅSiEt₂</td>
<td>1.96</td>
<td>3.44</td>
<td>1.53</td>
<td>159.07</td>
<td>171.46</td>
</tr>
<tr>
<td>2 ᵅSiEt₂</td>
<td>2.18</td>
<td>3.63</td>
<td>1.52</td>
<td>157.25</td>
<td>182.35</td>
</tr>
<tr>
<td>3 ᵅSiEt₂</td>
<td>1.94</td>
<td>3.39</td>
<td>1.53</td>
<td>154.81</td>
<td>175.45</td>
</tr>
</tbody>
</table>

Table 1. Selected structural parameters of the DFT-optimized geometries for the silane adducts.

This result is in stark contrast with the reduction of CO₂ usingtrialkylsilanes catalyzed by the iridium complex [(POCOP)Ir(η¹-HSiBu)]⁺, for which over-reduction to methane was observed, but resembles pretty much that observed by Chen et al. with the aluminium Lewis acid Al(C₆F₅)₃ in the absence of B(C₆F₅)₃ as co-catalyst.[⁹⁺] The selectivity of the process towards the monoformate is also remarkable. In spite of the limited studies on the reduction of CO₂ by primary silanes, incorporation of two or even three molecules of carbon dioxide leading to bis- and tris-formates is prevalent in most of the
cases. On the other hand, under the same catalytic conditions, complexes 2 and 3 (0.5%) required 10 h to fully convert \( ^{1} \text{BuSiH}_2 \) into silyl-formate \( ^{1} \text{BuSiH}_2 \text{(OCO)} \). At the end of these catalytic reactions, catalysts 2 and 3 remained intact, while catalyst 1 was partially transformed into hydride 3 due to the presence of adventitious water.

\( \text{PhSiH}_4 \) was also used for the hydrosilylation of CO\(_2\). However, in spite of the presence of silylformate compounds, several other unidentified products were produced. \( \text{Et}_2\text{SiH}_2 \) does also generate the corresponding silylformate \( \text{Et}_2\text{SiH}(\text{OCO}) \) with catalyst 1. Nevertheless, the reaction proceeded at considerably slower rates in comparison with the reactions carried out with butylsilane and, in addition, higher catalyst loadings (3%) were required to achieve full conversion after 6 h at rt. Once more, we have noticed that hydrosilylation of \( \text{Et}_2\text{SiH}_2 \) with release of \( \text{H}_2 \) is detrimental for the catalytic activity of complex 1 due to formation of the less catalytically active complex 3. Likewise, complexes 2 and 3 catalyzed the transformation of \( \text{Et}_2\text{SiH}_2 \) into \( \text{Et}_2\text{SiH}(\text{OCO}) \) but very long reaction times were necessary (see Table S2).

In summary, we have detected by NMR the formation of silane \( \sigma \)-complexes with the highly electrophilic platinum complex 1. According to DFT calculations, the most favored coordination mode is the rare \( \eta^1 \)-SiH for which only one example has been reported. In one of the cases, the coordination of the silane precedes the Si–H bond cleavage leading to the first structurally characterized cationic Pt(\( \sigma \))-silyl complex \( \text{Pt}[\text{SiHEt}_2(\text{EtSi})_2]^{2+} \) \( \text{Ba}^+ \). The interaction of the silanes with the platinum atom depends strongly on the orientation of the NH with respect to the metal center, being more favored when it is cyclometalated. The enhanced electrophilicity of the silicon atom in the silane through its coordination to platinum (in a similar way than the iridium complex reported by Brookhart) makes it reactive enough to hydrosilylate CO\(_2\) in a selective way towards mono-silylformates. Ongoing efforts are geared toward crystallographical characterization of a \( \sigma \)-SiH platinum complex and understanding the mechanism for the hydrosilylation of CO\(_2\).

**Acknowledgements**

Financial support (FEDER contribution) from the MINECO (Projects CTQ2013-45011-P and CTQ2014-51912-Redc) and the Junta de Andalucía (Project FQM-2126) is gratefully acknowledged. P.R. thanks the Junta de Andalucía for a research grant.

**Keywords**: Platinum • Carbon Dioxide • Silane • \( \sigma \)-complex • Hydrosilylation

---


[18] For results using PBE0, PBE0-D3 and wb97XD functionals see ESI.


Entry for the Table of Contents (Please choose one layout)

Layout 1:

COMMUNICATION

$\eta^1$-SiH platinum complexes are intermediates in the hydrosilation of carbon dioxide.

Pablo Ríos, Josefina Díez, Joaquín López-Serrano, Amor Rodríguez*, Salvador Conejero*

Page No. – Page No.

Title