Rhodium-catalyzed formation of silylcarbamates from the reaction of secondary amines with CO2 and hydrosilanes


Departamento de Química Inorgánica-Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), Universidad de Zaragoza – CSIC, Facultad de Ciencias, 50009, Zaragoza, Spain

1. Introduction

Pyridine-2-iloxy-silyl based anions could be considered promising ligands due to their electronic and steric versatility, which includes their potential as monooanionic bidentate (k^2-NSi), tridentate (k^3-N_Si) or tetradentate (k^4-N_Si) ligands [1,2]. In addition, their steric hindrance, sigma donor ability of the nitrogen atom(s) and trans influence of the silyl group could be easily tuned by choosing the proper substituents at the pyridinic ring(s) and/or the silicon atom (Fig. 1). However, this type of ligands presents the disadvantage that the functionalized silanes used as precursors are very reactive and hydrolyze easily in the presence of traces of moisture. This may be one of the reasons why the transition metal coordination chemistry of this type of ligands has been scarcely explored so far [1,2].

In this context, it is worth mentioning that in recent years we have demonstrated that rhodium and iridium complexes with pyridine-2-iloxy-silyl based ligands are excellent catalysts for hydrosilylation and/or silylation processes [2]. For example, iridium-(fac-k^3-N_Si) complexes (N_Si = fac-bis(pyridine-2-iloxy)-methylsilyl or fac-bis(4-methylpyridine-2-iloxy)methylsilyl) are effective catalysts for the solvent-free selective reduction of CO2 to silyl-formates [3], the hydrolysis of hydrosilanes to afford the corresponding silanol and hydrogen [4], the synthesis of silylamines by dehydrogenative silylation of secondary amines [5], the synthesis of silylesters by dehydrogenative silylation of carboxylic acids [6], the synthesis of sillyphosphinecarboxylates by insertion of CO2 into the P-Si bond of sillyphosphines [7] and the synthesis of silylcarbamates by insertion of CO2 into the N-Si bond of silyl-amines [5]. In addition, rhodium-(fac-k^3-N_Si) (N_Si = fac-bis(pyridine-2-iloxy)methylsilyl) species catalyzes the formation of silylenolethers by dehydrogenative silylation of acetophenone derivatives [8].

Examples of hydrosilylation catalysts based on iridium complexes with monooanionic bidentate NSi ligands have also been reported. Thus, Ir-(k^2-NSi^{Bu}) (NSi^{Bu} = 4-(methylpyridine-2-iloxy)dierterbutylylsilyl) species are effective catalysts for the selective reduction of formamides to O-silylated hemiaminals or to amines [9]. Moreover, Ir-(k^2-NSi^{Me}) (NSi^{Me} = 4-(methylpyridine-2-iloxy)dimethylsilyl) complexes are effective catalyst precursors for the selective reduction of CO2 to silylformate or methoxysilane [10].

Herein, the synthesis and characterization of Rh-(k^2-NSi^{Me})_2 species together with the study of their potential as catalysts for the reaction of secondary amines with CO2 and hydrosilanes is...
described. The outcomes of these studies revealed that Rh-(\(k^2\)-NSiMe)_2 species promoted the selective formation of silylcarbamates from the reaction of aliphatic secondary amines with CO_2 and hydrosilanes.

2. Results and discussion

2.1. Synthesis and characterization of the rhodium catalyst precursors

The reaction of two equivalents of the freshly prepared functionalized silane NSiMe-H, (4-methylpyridine-2-iloxy)dimethylsilane, (1) with half equivalent of [Rh(\(k^2\)-Cl)(coe)_2] (coe = cis-cyclooctene) in toluene quantitatively gives the rhodium(III) species [Rh(Cl)(\(k^2\)-NSiMe)_2](2) (NSiMe = 4-methylpyridine-2-iloxy) (Scheme 1). ^1H NMR studies of this reaction showed the presence of free coe and the formation of cyclooctane (coa) along with 2.

Species 2 reacts with one equivalent of silver trifluoroacetate in CH_2Cl_2 to afford the compound [Rh(CF_3CO_2)(\(k^2\)-NSiMe)_2](3), which has been isolated as a white solid in 73% yield (Scheme 1). ^1H NMR studies of this reaction showed the presence of free coe and the formation of cyclooctane (coa) along with 2.

Species 2 reacts with one equivalent of silver trifluoroacetate in CH_2Cl_2 to afford the compound [Rh(CF_3CO_2)(\(k^2\)-NSiMe)_2](3), which has been isolated as a white solid in 73% yield (Scheme 1). ^1H NMR studies of this reaction showed the presence of free coe and the formation of cyclooctane (coa) along with 2.

The reaction of two equivalents of the freshly prepared functionalized silane NSiMe-H, (4-methylpyridine-2-iloxy)dimethylsilane, (1) [10] with half equivalent of [Rh(\(k^2\)-Cl)(coe)_2] (coe = cis-cyclooctene) in toluene quantitatively gives the rhodium(III) species [Rh(Cl)(\(k^2\)-NSiMe)_2] (2) (NSiMe = 4-methylpyridine-2-iloxy) (Scheme 1). ^1H NMR studies of this reaction showed the presence of free coe and the formation of cyclooctane (coa) along with 2.

Species 2 reacts with one equivalent of silver trifluoroacetate in CH_2Cl_2 to afford the compound [Rh(CF_3CO_2)(\(k^2\)-NSiMe)_2](3), which has been isolated as a white solid in 73% yield (Scheme 1). ^1H NMR studies of this reaction showed the presence of free coe and the formation of cyclooctane (coa) along with 2.

Figure 1. Examples of monoanionic pyridine-2-iloxy-silyl based ligands (E and R alkyl or aryl groups).

Figure 2. Molecular structure of complex 3. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (^\circ): Rh–Se(1), 2.2277(8); Rh–Se(2), 2.2388(10); Rh–Se(3), 2.414(2); Rh–O(4), 2.391(2); Rh–N(1), 2.062(3); Rh–N(2), 2.056(3); Si(1)–Rh–Si(2), 91.47(3); Si(1)–Rh–O(3), 158.19(6); Si(1)–Rh–O(4), 104.21(6); Si(1)–Rh–N(1), 81.82(7); Si(1)–Rh–N(2), 93.56(7); Si(2)–Rh–O(3), 109.59(6); Si(2)–Rh–O(4), 163.86(6); Si(2)–Rh–N(1), 93.51(8); Si(2)–Rh–N(2), 81.88(8); O(3)–Rh–O(4), 55.29(7); O(3)–Rh–N(1), 91.03(9); O(3)–Rh–N(2), 94.83(9); O(4)–Rh–N(1), 92.47(9); O(4)–Rh–N(2), 92.31(10); N(1)–Rh–N(2), 173.42(10).

The rhodium atom in complex 3 exhibits a distorted octahedral geometry, with the oxygen atoms of the carboxylate ligand and the silicon atoms in the equatorial plane, and apical positions filled by nitrogen atoms. The rhodium-silicon bond lengths in 3 are in the range 2.2277(8)-2.2388(10) Å. The (\(k^2\)-O) coordination of the carboxylate ligand to the metal is characterized by two long but similar Rh–O bond lengths (around 2.4 Å) and trans Si–Rh–O angles close to 160^\circ. The pyridinic rings around the metallic centers in 3 are trans disposed one to each other, with similar Rh–N bond lengths 2.056(3) and 2.062(3) Å. The N–Rh–N arrangement is deviated from the ideal value of 180^\circ (N(1)–Ir(1)–N(2), 173.42(10)^\circ), which could be related to the chelating bonding of NSiMe ligands which leads to the formation of two Ir–Si–O–C–N metallacycles, with ring puckering parameters typical of 2T1 and 2T1 with a small contribution of 2E conformations, respectively [11].

The mononuclear structure proposed in Scheme 1 for complex 2 was corroborated by means of ^1H-DOSY NMR spectroscopy [12]. The resonances of the aromatic protons of the NSiMe ligand in CD_2Cl_2 were used for the determination of the diffusion coefficients (D) of complexes 2 and 3 at 300 K. The D value measured for 2 in CD_2Cl_2, 1.163 \times 10^{-9} m^2 s^{-1}, compares well with the D value obtained for 3 under the same conditions, 1.186 \times 10^{-9} m^2 s^{-1}. Therefore, assuming the mononuclear structure found for 3 (Fig. 2), it is reasonable to propose that 2 also possesses a mononuclear structure in solution. In addition, ^1H and ^13C NMR spectra of complexes 2 and 3 also support the structure proposed for these species. ^29Si{^1H} NMR spectra show a doublet resonance at \(\delta\) 85.7 ppm (\(^1J_{Rh-Si} = 36.6\) Hz) and \(\delta\) 86.2 ppm (\(^1J_{Rh-Si} = 39.3\) Hz), respectively, which agrees with the equivalence of the two silicon atoms in both complexes.

Scheme 1. Synthesis of the rhodium complexes 2 and 3.
2.2. 3-Catalyzed reaction of secondary amines with hydrosilanes

The development of catalytic methodologies that allow the utilization of CO2 as C1 raw material for organic synthesis is of great interest [13]. The reaction of amines with CO2 and hydrosilanes has proven to be an effective methodology for obtaining formamides, methylenamines, aminals and/or carbamates [14]. Thus, in presence of a catalyst, secondary and/or primary amines usually react with CO2 and hydrosilanes to yield formamides. Furthermore, some catalysts can reduce the formamide to the corresponding methylamine (Scheme 2) [14].

In recent years, it has been demonstrated that silylcarbamates could also be obtained from the catalytic reaction of amines with CO2 and hydrosilanes. The formation of silylcarbamates as minor by-products of the transition metal catalyzed formylation of secondary amines with CO2 and hydrosilanes was first observed by García et al., in 2013 [15]. Few years later, we found that using the iridium complex [Ir(H)(CF3SO3)(NSiN)(coe)] (NSiN = fac-bis-(pyridine-2-ylxylylmethylyl) and coe = cis-cyclooctene) as catalyst (1.0 mol %), it was possible to selective and quantitatively prepare the corresponding silylcarbamate from the reaction of aliphatic secondary amines with CO2 (3 bar) and one equivalent of HSiMe(OSiMe3)2 under solvent-free conditions [5]. Examples of heterogeneous catalytic systems based on 10% wt Pd on dry matrix carbon have also proven to be effective for the dehydrogenative formation of silylcarbamates from amines, CO2 and hydrosilanes [16].

In this context, it has been found that complexes 2 and 3 (1.0 mol%) catalyze the selective reaction of pyrrolidine with CO2 and HSiMe2Ph to give the corresponding silylcarbamate c-(C6H5)NCO2SiMe2Ph (4a). The ancillary ligand plays a role on the catalytic activity. Thus, complex 3 with a trifluorocetate ligand allows the conversion of 94% of the starting silane after 6 h, while using 2 around 80% of conversion was obtained in the same time.

The above described outcomes aimed us to explore the performance of the catalytic system based on 3. The activity of the 3-catalyzed reaction of pyrrolidine with CO2 and hydrosilanes depends on the nature of the silicon compound. In all the cases, the reactions were selective to the formation of the corresponding silylcarbamate c-(C6H5)NCO2SiR3 (SiR3 = SiMe2Ph, 4a; SiMePh2, 5; SiEt2, 6; SiMe(OSiMe3)2) (Scheme 3). HSiMePh2 is more reactive than HSiMePh and HSiEt2, and using HSiMe(OSiMe3)2 only 12% of the corresponding silylcarbamate was observed after 24 h (Fig. 3).

This reactivity trend could be explained considering the lower hindrance around the Si–H bond in HSiMe2Ph in comparison with the other silicon derivatives studied.

1H NMR studies of the reaction of pyrrolidine with CO2 (3 bar) and HSiMe2Ph in C6D6 at 323 K in presence of 0.5, 1.0 and 5.0 mol% of 3 evidenced that the catalyst loading moderately influences on the catalytic activity (Fig. S39). In addition, it has been found that the nature of the amine strongly influences the catalytic activity, where the best results were obtained for cyclic secondary amines such as pyrrolidine and piperidine, while the reactions with N,N-disopropylamine bearing a hindered N–H bond were slower (Table 1 and Fig. 4). In addition, no reaction was observed with N-methylaniline.

The silylcarbamates 4a-e, 5 and 6 were characterized by means of 1H, 13C and 29Si NMR spectroscopy (see experimental and supporting). Compound 7 was characterized by comparison with the reported data [5]. The most noticeable resonances in their 13C (1H) NMR spectra were those corresponding to the carboxylic carbon atom that appears around δ 154 ppm, which agrees with the reported data for analogous compounds [5].

In the absence of complexes 2 and 3, C6D6 solutions of pyrrolidine and HSiMe2Ph react with CO2 (3 bar) to quantitatively give a mixture of the corresponding carbamic acid and HSiMe2Ph. This mixture slowly evolves at 323 K to produce the corresponding silylcarbamate and traces of formamide. Thus, after 60 h a 36% of conversion of the carboxylic acid into silylcarbamate (30%) and formamide (6%) is observed. These outcomes prove that species 2 and 3 play a relevant role on the above-mentioned catalytic process.

- 4 mol% base on 1H NMR integration; [b] mol% of the starting amine consumed after 14 h of reaction.

![Scheme 2. Catalytic formylation of secondary aliphatic amines (R2NH) with CO2 and hydrosilanes.](image)

![Scheme 3. Preparation of silylcarbamates from the 3-catalyzed (1.0 mol%) reaction of secondary amines with CO2 (3 bar) and HSiMe2Ph in C6D6 at 323 K. (R2 = c-(C6H5), 4a; c-(C4H8O), 4b; c-(C6H10), 4c; Et2, 4d; iPr2, 4e).](image)

Table 1

<table>
<thead>
<tr>
<th>Amine</th>
<th>Carbamate (%)</th>
<th>Conversion (%)</th>
<th>Formamide (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrrolidine</td>
<td>4a (99)</td>
<td>94</td>
<td>1</td>
</tr>
<tr>
<td>Morpholine</td>
<td>4b (96)</td>
<td>78</td>
<td>3</td>
</tr>
<tr>
<td>Piperidine</td>
<td>4c (97)</td>
<td>80</td>
<td>4</td>
</tr>
<tr>
<td>N,N-diethylylamine</td>
<td>4d (97)</td>
<td>92</td>
<td>3</td>
</tr>
<tr>
<td>N,N-diisopropylamine</td>
<td>4e (100)</td>
<td>36</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 3.

![Fig. 3. Representation of hydrosilane conversion (mol %) to c-(C6H5)NCO2SiR3 (SiR3 = SiMe2Ph, 4a; SiMePh2, 5; SiEt2, 6; SiMe(OSiMe3)2, 7) vs time for the 3-catalyzed (1.0 mol%) reaction of pyrrolidine with CO2 (3 bar) and the corresponding silane at 323 K in C6D6.](image)
Two different reaction pathways have been proposed to explain the catalytic formation of silylcarbamates from the reaction of amines with CO₂ and hydrosilanes (Scheme 4). The first one consists in the insertion of a CO₂ molecule into the Si–N bond of an in situ generated silylamine (Scheme 4, path a) [5,17–19]. This path requires a previous step consisting in a dehydrogenative silylation of the corresponding carbamic acid (Scheme 4, path b).

It has been demonstrated that, differently to that observed for Ir–N₂Si based catalysts [5], in absence of CO₂, solutions of pyrrolidine and HSiMe₂Ph in presence of catalytic amounts of 3 (1.0 mol%) are stable over time. Indeed, no reaction was observed after 6 h at 343 K. Analogous behavior was observed for piperidine and morpholine. Therefore, under the studied conditions complex 3 is not an active catalyst for the dehydrogenative silylation of secondary amines. Therefore, it is reasonable to discard path a of Scheme 4 for explaining the formation of silylcarbamates.

It is worth mentioning that under the reaction conditions, 3 bar of CO₂, the equilibrium between the amine and the corresponding carbamic acid [22] is shifted towards the latter (Fig. 5). This suggest that formation of the silylcarbamate could be consequence of the poor activity of 3-catalyzed dehydrogenative silylation of the corresponding carbamic acid according to path b in Scheme 4.

In agreement with that possibility, it has been proven that, similarly to other group 9 metal complexes [6], species 3 catalyzes the dehydrogenative silylation of formic acid to afford the silylformate HCO₂SiMe₂Ph (8). Thus, the 3-catalyzed (1.0 mol%) reaction of formic acid with one equivalent of HSiMe₂Ph quantitatively affords 8 and H₂ (Scheme 5). The silylformate 8 has been characterized by comparison of its ¹H NMR spectra with reported data [3a].

Table 1 illustrates that formamides were obtained as minor side products of these reactions in around 1–4% yield. The obtention of formamides from the catalytic reaction of secondary amines with CO₂ using hydrosilanes as reductants, has been commonly explained because of the reaction of the in situ produced silylformates, by CO₂ hydrolysis, with the corresponding amine [13], or by the catalytic reaction of silylcarbamates with hydrosilanes to yield formamides and the corresponding siloxane [23] (Scheme 6).

In this regard, it should be mentioned that the ¹H NMR studies of the 3-catalyzed reaction of CO₂ (3 bar) with HSiMe₂Ph in C₆D₆ at 323 K revealed that after 24 h of reaction only traces of the corresponding silylformate 8 were formed. Moreover, the 3-catalyzed reaction of pyrrolidine with CO₂ (3 bar) in presence of four equivalents of HSiMe₂Ph quantitatively affords the silylcarbamate 4a, which did not react with the excess of HSiMe₂Ph present in the reaction mixture, even after 24 h at 323 K. Therefore, the low concentration of formamide observed along the above described reactions (Table 1) could be consequence of the poor activity of 3 as CO₂ and/or silylcarbamates hydrosilylation catalyst.

3. Experimental

3.1. General information

All manipulations were performed with rigorous exclusion of air at an argon/vacuum manifold using standard Schlenk-tube techniques or in MBraun glovebox when necessary. Solvents were dried and distilled under argon by standard procedures prior to use or purified by a Solvent Purification System (Innovative Technologies). NMR spectra were obtained on a Bruker ARX-300, Bruker AV-300 MHz or Varian Gemini 2000. Chemical shifts (δ), reported in ppm, were referenced to the residual peaks of deuterated solvents. Compound 1 was prepared according to the method reported in the literature [10]. Carbon dioxide (99.99% purity) was purchased from commercial sources.

3.2. Synthesis of [Rh( Cl)( κ²-N₂SiMe₂)]₂ (2)

A toluene solution (5 mL) of compound 1 (0.300 g, 1.800 mmol) was slowly added to a suspension of [Rh(μ-Cl)(coe)]₂ (0.760 g, 0.848 mmol) in toluene (10 mL) and the resulting mixture was stirred at room temperature for 2 h. The solvent was removed in vacuo and the residue washed with pentane cooled at 273 K (3 × 10 mL) to afford a pale brown solid. Yield: 0.320 g (76%). Anal. Calcd. For C₁₀H₅₄ClRh₄N₄O₂Si₂: C, 40.81; H, 5.14; N, 5.95. Found: C, 40.84; H, 5.15; N, 6.09. ¹H NMR plus HSQC ¹H–¹³C (300 MHz, 298 K, CD₂Cl₂): δ 8.58 (d, JHH = 6.1 Hz, 2H, py-6), 6.67 (m, 2H, py-3), 6.59 (dd, JHH = 6.1 Hz, JHH = 1.8 Hz, 2H, py-5), 2.30 (s, 6H, CH₂-py), 0.65 (s, 6H, SiMe), 0.40 (s, 6H, SiMe). ¹³C(¹H) APT plus HSQC ¹H–¹³C (75 MHz, 298 K, CD₂Cl₂): δ 166.8 (C₂-py), 152.8 (C₂-py), 150.3 (C₂-py), 118.4 (C₂-py), 112.0 (C₂-py), 21.3 (C₂-py), 6.8 (SiMe), 3.8 (d, JHH = 4.0 Hz, SiMe). 29Si(¹H) NMR (HMBC ¹H–²⁹Si, 298 K, CD₂Cl₂): δ 85.7 (d, JHH = 36.6 Hz). High Resolution Mass Spectrometry (ESI+): calc. m/z = 435.0434; found m/z = 434.9765 (M⁺ – Cl).

3.3. Synthesis of [Rh(CF₃CO₂)( κ²-N₂SiMe₂)]₂ (3)

CH₂Cl₂ (15 mL) was added to a light-protected Schlenk tube containing a mixture of complex 2 (0.300 g, 0.320 mmol) and silver trifluoroacetate (0.150 g, 0.680 mmol). The resulting suspension was stirred at room temperature for 4 h and filtered out through Celite. The solvent was removed in vacuo and the residue washed
with cold pentane (198 K, 3 × 10 mL) to afford a white solid. Yield 0.255 g (73%). Anal. Calcd. For C18H24F3RhN2O4Si2: C, 39.42; H, 4.41; N, 5.11. Found: C, 39.32; H, 4.25; N, 4.98. 1H NMR plus HSQC (300 MHz, 298 K, CD2Cl2): δ 7.96 (d, 3J_H-H = 6.0 Hz, 2H, py-6), 6.69 (s, 2H, py-3), 6.67 (d, 3J_H-H = 6.0 Hz, 2H, py-5), 2.30 (s, 6H, C(CH3)3-py), 0.61 (s, 6H, SiMe), 0.41 (s, 6H, SiMe). 13C{1H} NMR APT plus HSQC (75 MHz, 298 K, CD2Cl2): δ 166.7 (s, C2-py), 153.1 (s, C4-py), 147.7 (s, C6-py), 118.9 (s, C5-py), 112.4 (s, C3-py), 21.3 (s, CH2-py), 4.6 (s, SiMe), 3.2 (d, 2J_Rh-H = 4.4 Hz, SiMe). 19F{1H} NMR (282 MHz, 298 K, CD2Cl2): δ -75.6 (CF3CO2). 29Si{1H} NMR (HMBC, 298 K, CD2Cl2): δ 86.2 (d, 1J_Rh-Si = 39.3 Hz). High Resolution Mass Spectrometry (ESI+): calc. m/z = 435.0432; found m/z = 435.0423 (M+ - CF3CO2).

3.4. 3-Catalyzed (1.0 mol%) reactions

A Young cap NMR tube was filled with the catalyst precursor 3 (2.00 mg, 3.64 μmol), HSiMe2Ph (0.401 mmol, 61.5 μL), amine (0.364 mmol) and 0.5 mL of C6D6. Argon was removed under reduced pressure after freezing the solution, and the tube was then pressurized with CO2 (3 bar) and heated to 323 K. The same procedure was followed for the reactions of pyrrolidine with other silanes (HSiMePh2, 80.0 μL; HSiEt3, 64 μL; HSiMe(OSiMe3)2, 109.0 μL).

3.5. 3-Catalyzed (1.0 mol%) dehydrogenative silylation of formic acid

A Young cap NMR tube was filled with the catalyst precursor 3 (2.00 mg, 3.64 μmol), HSiMe2Ph (0.401 mmol, 61.5 μL), formic acid (0.364 mmol, 13.7 μL) and 0.5 mL of C6D6. The mixture was then heated at 323 K and monitored by 1H NMR spectroscopy.

3.6. Selected NMR data of the catalytic products

3.6.1. c-(C6H6)N—C(O)OSiMe2Ph (4a)

1H NMR (300 MHz, C6D6, 298 K): δ 7.78–7.75 (m, 2H, Ph), 7.28–7.20 (m, 3H, Ph), 7.23–7.05 (m, 4H, N–C6H5), 1.26–1.20 (m, 5H, –CH2–), 0.66 (s, 6H, Si(CH3)2). 13C NMR (75 MHz, C6D6, 298 K): δ 153.6 (s, CO2Si), 137.4 (s, C3me–Ph), 134.1 (s, Ph), 130.1 (s, Ph), 128.2 (s, Ph), 46.5 (s, N–C6H5), 46.1 (s, N–C6H5). 19F NMR (75 MHz, C6D6, 298 K): δ -75.6 (CF3CO2). 29Si NMR (HMBC, 298 K, CD2Cl2): δ 86.2 (d, 1J_Rh-Si = 39.3 Hz). High Resolution Mass Spectrometry (ESI+): calc. m/z = 435.0432; found m/z = 435.0423 (M+ - CF3CO2).

3.6.2. c-(C6H5O)N—C(O)OSiMe2Ph (4b)

1H NMR (300 MHz, C6D6, 298 K): δ 7.71–7.68 (m, 2H, Ph),
7.25–7.21 (m, 3H, Ph), 3.23–3.13 (m, 8H, –CH2–), 0.61 (s, 6H, SiCH3).

13C NMR APT (75 MHz, C6D6): δ 154.0 (s, CO2Si), 136.8 (s, Cipso-Ph), 134.1 (s, Ph), 130.3 (s, Ph), 128.2 (s, Ph), 66.4 (s, O–CH2), 45.3 (s, N–CH2), 44.0 (s, N–CH2), –1.1 (s, SiCH3). 29Si{1H} NMR (HMBC 23Si–1H; 298 K): δ 10.9 (s, SiCH3).

3.6.3. c-(C6H10)N–O–SiMe2Ph (4e)

1H NMR (300 MHz, C6D6, 298 K): δ 7.72–7.69 (m, 2H, Ph), 7.25–7.19 (m, 3H, Ph), 3.11–2.98 (m, 4H, N–CH2), 0.89 (br s, 6H, CH3), 0.61 (s, SiCH3). 13C NMR APT (75 MHz, C6D6): δ 154.6 (s, CO2Si), 137.4 (s, Cipso-Ph), 134.0 (s, Ph), 130.1 (s, Ph), 128.2 (s, Ph), 42.0, 41.7 (s, N–CH2), 14.3, 13.5 (s, CH3), –0.9 (s, SiCH3). 29Si{1H} NMR (HMBC 23Si–1H; 298 K): δ 10.1 (s, SiCH3).

3.6.4. Et2N–O–SiMe2Ph (4d)

1H NMR (300 MHz, C6D6, 298 K): δ 7.72–7.69 (m, 2H, Ph), 7.23–7.19 (m, 3H, Ph), 3.90–3.56 (m, 2H, N–CH2), 1.04 (d, J = 6.8 Hz, 12H, CH3), 0.62 (s, SiCH3). 13C NMR APT (75 MHz, C6D6): δ 154.2 (s, CO2Si), 137.5 (s, Cipso-Ph), 134.1 (s, Ph), 130.0 (s, Ph), 128.1 (s, Ph), 46.2 (s, N–CH2), 21.5, 20.5 (br s, CH3), –0.8 (s, SiCH3). 29Si{1H} NMR (HMBC 23Si–1H; 298 K): δ 9.4 (s, SiCH3).

3.6.5. pPhN–O–SiMe2Ph (4e)

1H NMR (300 MHz, C6D6, 298 K): δ 7.74–7.71 (m, 2H, Ph), 7.25–7.24 (m, 6H, Ph), 3.29 (br s, 4H, N–CH2), 1.36 (m, 4H, CH2), 0.99 (s, 3H, SiCH3). 13C NMR APT (75 MHz, C6D6): δ 153.2 (s, CO2Si), 137.9 (s, Cipso-Ph), 135.1 (s, Ph), 130.3 (s, Ph), 128.2 (s, Ph), 46.2 (br s, N–CH2), 25.4 (br s, CH2), 25.2 (s, CH2), –1.7 (s, SiCH3). 29Si{1H} NMR (HMBC 23Si–1H; 298 K): δ –1.0 (s, SiCH3).

3.6.6. c-(C6H8)N–O–SiMePh2 (5)

1H NMR (300 MHz, C6D6, 298 K): δ 7.84–7.82 (m, 4H, Ph), 7.25–7.24 (m, 6H, Ph), 3.29 (br s, 4H, N–CH2), 1.36 (m, 4H, CH2), 0.99 (s, 3H, SiCH3). 13C NMR APT (75 MHz, C6D6): δ 151.3 (s, CO2Si), 137.9 (s, Cipso-Ph), 135.1 (s, Ph), 130.3 (s, Ph), 128.2 (s, Ph), 46.2 (br s, N–CH2), 25.4 (br s, CH2), 25.2 (s, CH2), 8.4 (s, CH3), 5.4 (s, SiCH3). 29Si{1H} NMR (HMBC 23Si–1H; 298 K): δ 22.3 (s, SiCH3).

3.7. Crystal structure determination of complex 3

X-ray diffraction data were collected at 100(2)K on an automatic Smart APEX Bruker diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) using Ω scans with narrow oscillation frames (0.3°). Diffractions intensities were integrated and corrected from absorption effects with SAINT [24] and SADABS [25] programs, included in APEX 3 package. The structure was solved by direct methods and refined with SHELXS-2013 [26] and refined with full-matrix least-squares refinement with SHELXL-2018 [27] programs included in WinGX package [28].

Crystal Data for 3: C23H29F3N2O2RhSi2; M = 873.66-P and DGA/FSE project E42_17R is gratefully acknowledged.

Hydrogen atoms were included in the model in calculated positions and refined with a riding model. Fluorine atoms have been found to be disordered. They have been included in the model in three sets of positions with 0.42/0.30/0.28(1) occupancy factors and isotropically refined.

CCDC 1906237 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

4. Conclusions

The reaction of (4-methyl-pyridine-2-iloxy)dimethylsilane (NSiMe2–H, 1) with [RhCl(cod)]2 gives [RhCl(κ2–NSiMe2–H)] (2), which reacts with a stoichiometric amount of AgCF3CO2 to afford [Rh(κ2–CF3CO2–CF3)(κ2–NSiMe2–H)] (3). Complexes 2 and 3 have been fully characterized by elemental analysis and NMR spectroscopy. In addition, the solid-state structure of 3 has been confirmed by X-ray diffraction studies.

Complex 3 is an effective catalyst for the selective formation of silylbacarminates from the reaction of aliphatic secondary amines with CO2 and hydroisloxanes. Moreover, it has been demonstrated that 3 is an active catalyst for dehydrogenative silylation of carboxylic acids. However, under the studied conditions, 3 is a poor catalyst for the hydrosilylation of CO2 and for the dehydrogenative silylation of amines.

These outcomes allow to conclude that the 3-catalyzed dehydrogenative silylation of the carbamic acid in situ generated by reaction of the corresponding secondary amine with CO2 is the determining step for explaining the selective formation of silylbacarminates from the 3-catalyzed reaction of secondary amines with CO2 and HSiMe2Ph.

Acknowledgements

The financial support from MINECO/FEDER project CTQ2015-67366-P and DGA/FSE project E42_17R is gratefully acknowledged. Dr. P. García-Orduña acknowledges CSIC, European Social Fund and Ministerio de Economía y Competitividad of Spain for a PTA contract. Authors would like to acknowledge the use of Servicio General de Apoyo a la Investigación-SAI, Universidad de Zaragoza.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorgchem.2019.06.010.

References

(For recent reviews see:)(a) F.J. Fernández-Alvarez, Dalton Trans. 48 (2019) 4255–4262.
(e) (2016) 12112–12118.