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# Reactivity of Ir-NSiN Complexes: Ir-Catalyzed Dehydrogenative Silylation of Carboxylic Acids

Alejandro Julián,<sup>[a]</sup> Karin Garcés,<sup>[a]</sup> Ralte Lalrempuia,<sup>[a][b]</sup> E. A. Jaseer,<sup>[c]</sup> Pilar García-Orduña,<sup>[a]</sup> Francisco J. Fernández-Alvarez,<sup>\*,[a]</sup> Fernando J. Lahoz,<sup>[a]</sup> and Luis A. Oro<sup>\*,[a][c]</sup>

**Abstract:** This work describes the results from the studies on the potential of  $[\text{Ir}(\mu\text{-Cl})(\text{cod})_2]$  ( $\text{cod} = 1,5\text{-cyclooctadiene}$ ) as metallic precursor for the preparation of Ir(NSiN) complexes (NSiN = *fac*-bis-(pyridine-2-yloxy)methylsilyl). It is noteworthy that the reaction of  $[\text{Ir}(\mu\text{-Cl})(\text{cod})_2]$  with bis-(pyridine-2-yloxy)methylsilane has allowed the synthesis of  $[\text{Ir}(\text{H})(\text{Cl})(\text{NSiN})(\eta^2\text{-cod})]$  with an uncommon  $\eta^2$ -coordination mode for the cod ligand. Moreover, the application of Ir-NSiN species as catalysts precursors for the dehydrogenative silylation of carboxylic acids has also been explored. The outcomes from these catalytic studies revealed a clear influence of the ancillary ligand on the catalytic activity of Ir-NSiN species. Thus, while  $[\text{Ir}(\text{H})(\text{CF}_3\text{SO}_3)(\text{NSiN})(\text{coe})]$  shows a poor catalytic activity, the related complex  $[\text{Ir}(\text{H})(\text{CF}_3\text{CO}_2)(\text{NSiN})(\text{coe})]$  with a trifluoroacetate ligand has demonstrated to be a highly active catalyst precursor.

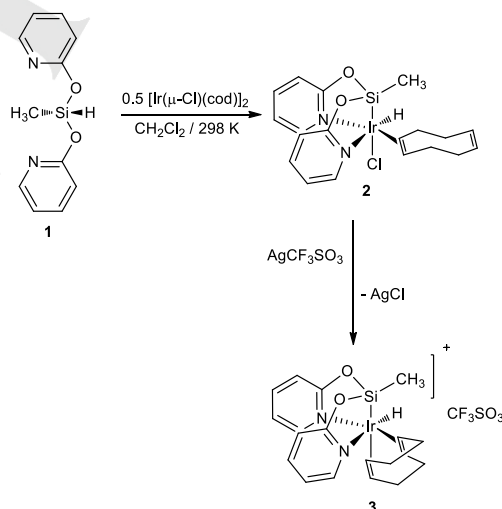
## Introduction

Catalytic hydrosilylation has proven to be an effective methodology for the reduction of unsaturated organic molecules including alkenes, alkynes, ketones, nitriles, imines, carboxylic acids and carbonic acid derivatives.<sup>[1,2]</sup> Besides that, a number of catalytic systems has been efficiently employed for the selective reduction of  $\text{CO}_2$  with hydrosilanes to give the corresponding silylformate, bis-silylacetal, methoxysilane or methane.<sup>[3]</sup> It should be noted that the selective reaction of carboxylic acids with hydrosilanes to afford silylesters,<sup>[4]</sup> alcohols<sup>[5]</sup> or aldehydes<sup>[6]</sup> still represents a challenge. Rh and Ir complexes with tridentate monoanionic NSiN ligands<sup>[7]</sup> were found to be effective catalysts for  $\text{CO}_2$ -hydrosilylation,<sup>[3,8]</sup> dehydrogenative silylation of arenes<sup>[9]</sup> and acetophenone<sup>[10]</sup> derivatives and for processes involving  $\text{CO}_2$ -insertion into N-Si<sup>[11]</sup> and P-Si<sup>[12]</sup> bonds. In this context, it should be mentioned that the formation of the silylether  $\text{CF}_3\text{CH}_2\text{OSiMe}(\text{OSiMe}_3)_2$  by reduction of the trifluoroacetate ligand during the  $\text{Ir}(\text{CF}_3\text{CO}_2)(\text{NSiN})$ -catalyzed hydrosilylation of  $\text{CO}_2$  with

$\text{HSiMe}(\text{OSiMe}_3)_2$ <sup>[13,14]</sup> has been observed. These outcomes stimulated us to study the potential of Ir-NSiN species as catalyst precursors for the reduction of carboxylic acids with  $\text{HSiMe}(\text{OSiMe}_3)_2$ .

## Results and Discussion

**Synthesis and reactivity of Ir-NSiN complexes.** Ir-NSiN species (NSiN = *fac*-bis-(pyridine-2-yloxy)methylsilyl, or *fac*-bis-(4-methylpyridine-2-yloxy)methylsilyl)<sup>[7]</sup> have been so far prepared using  $[\text{Ir}(\mu\text{-Cl})(\text{coe})_2]$  ( $\text{coe} = \text{cis-cyclooctene}$ ) as metallic precursor. This work shows that  $[\text{Ir}(\mu\text{-Cl})(\text{cod})_2]$  ( $\text{cod} = 1,5\text{-cyclooctadiene}$ ) could also be used as metallic precursor for the preparation of Ir-NSiN species.



**Scheme 1.** Preparation of Ir-NSiN complexes with 1,5-cyclooctadiene.

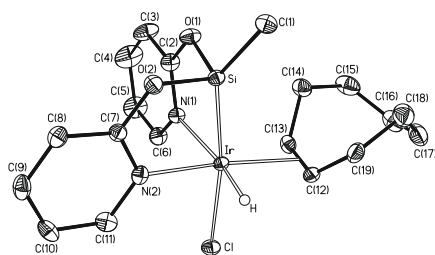
The treatment of  $[\text{Ir}(\mu\text{-Cl})(\text{cod})_2]$  with bis-(pyridine-2-yloxy)methylsilane (**1**) in  $\text{CH}_2\text{Cl}_2$  quantitatively leads to the iridium(III) complex  $[\text{Ir}(\text{H})(\text{Cl})(\text{NSiN})(\eta^2\text{-cod})]$  (**2**), which has been isolated as a white solid in 87% yield (Scheme 1). The Ir-NSiN species **2** has been fully characterized by elemental analysis, mass spectrometry and NMR spectroscopy. In addition, the  $\eta^2$ -coordination mode of the cod ligand to the iridium atom in **2** has been confirmed by X-ray diffraction studies (Figure 1).

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**Figure 1.** Molecular structure of complex **2**. Selected bond lengths (Å) and angles (°) for compound **2**. Ir-Si, 2.2356(12); Ir-Cl, 2.5229(10); Ir-Ct<sup>[a]</sup>, 2.068(4); Ir-N1, 2.197(3); Ir-N2, 2.114(4); Ir-H, 1.53(7); Si-Ir-Cl, 170.51(4); Si-Ir-Ct<sup>[a]</sup>, 100.47(13); Si-Ir-N1, 79.93(9); Si-Ir-N2, 80.60(11); Si-Ir-H, 96(2); Cl-Ir-Ct<sup>[a]</sup>, 86.29(13); Cl-Ir-N1, 92.26(9); Cl-Ir-N2, 93.61(10); Cl-Ir-H, 90(2); Ct<sup>[a]</sup>-Ir-N1, 101.58(15); Ct<sup>[a]</sup>-Ir-N2, 172.08(15); Ct<sup>[a]</sup>-Ir-H, 89(2); N1-Ir-N2, 86.34(13); N1-Ir-H, 169(2); N2-Ir-H, 83(2). <sup>[a]</sup>Ct represents the centroid of the C12=C13 olefinic bond in compound **2**.

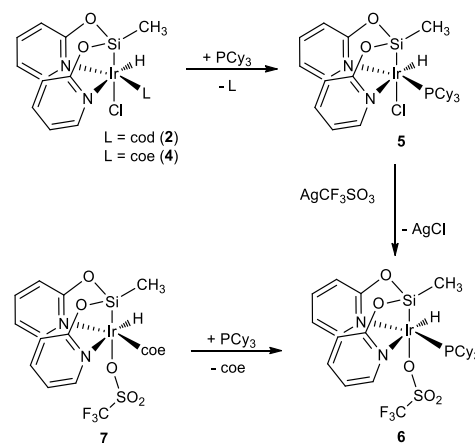
The NSiN ligand in **2** is facially coordinated to the iridium center. Si-Ir-N *cis* angles (Si-Ir-N1, 79.93(9)° and Si-Ir-N2, 80.60(11)°) are deviated from the ideal value of 90° due to the NSiN chelating bonding through the formation of two Ir-Si-O-C-N metallacycles, with ring puckering parameters (Ir-Si-O1-C2-N1:  $q = 0.148(2)$  Å,  $\phi = 29.6(15)^\circ$ , Ir-Si-O2-C7-N2:  $q = 0.135(2)$  Å,  $\phi = -141.0(15)^\circ$ )<sup>[15]</sup> typical of envelope E<sub>2</sub> and <sup>2</sup>E enantiomorphic configurations. The pyridine-N atoms are located *trans* to the hydride and to the  $\eta^2$ -cyclooctadiene ligands. The Ir-N1 bond length (2.197(3) Å) is longer than Ir-N2 (2.114(4) Å), most likely associated to the high structural *trans* effect of the hydride ligand compared to that exerted by the olefin. The chloride ligand (Ir-Cl, 2.5229(10) Å) is coordinated *trans* to the Si atom. Structural parameters describing the metal coordination sphere are close to those reported in related Rh and Ir-(NSiN) metal complexes.<sup>[8,10,13,14]</sup>

The coordination mode of the cod fragment to the metal in compound **2** deserves special attention. The bond length found between the metal atom and the olefin in compound **2** (2.068(4) Å) is similar to those observed in related Ir(NSiN)( $\eta^2$ -coe) complexes (in the range 2.062(12)-2.102(2) Å).<sup>[8,13,14]</sup> Although the versatility of cyclooctadiene ligand to coordinate to iridium in different forms has been well established,<sup>[16]</sup> it tends to chelate to the metal in a  $\eta^4$  coordination mode. It should be mentioned that the equilibrium between Ir( $\eta^2$ -cod) and Ir( $\eta^4$ -cod) has been proposed as key step in some catalytic processes.<sup>[17]</sup> In addition, to the best of our knowledge only three mononuclear complexes containing an Ir( $\eta^2$ -cod) fragment have been crystallographically characterized: [( $\eta^5$ -Cp)Ir( $\eta^2$ -cod)(NHC)]<sup>[18]</sup>, [( $\eta^5$ -Cp)Ir( $\eta^2$ -cod)(biph)]<sup>[19]</sup> and [Ir( $\eta^2$ -cod)(4-Ph)Tr(NP(<sup>*i*</sup>Pr)<sub>2</sub>)(NHP(<sup>*i*</sup>Pr)<sub>2</sub>)]<sup>[20]</sup>. The coordinated olefinic bond length in compound **2** (C12=C13: 1.411(6) Å) has been found to be longer than that of the uncoordinated one (C16=C17: 1.334(9) Å), a feature that has been related to a  $\pi$ -back donation from the metal atom.<sup>[18,19]</sup>

The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of **2** in CD<sub>2</sub>Cl<sub>2</sub> support the  $\eta^2$ -coordination of the cod ligand in solution. Thus, the <sup>1</sup>H NMR spectra of **2** exhibit one multiplet resonance between  $\delta$  5.67 and 5.51 ppm, assigned to the two Csp<sup>2</sup>-H protons of the free olefinic moiety of the cyclooctadiene ligand, which show correlation in the heteronuclear single quantum correlation (HSQC) spectra

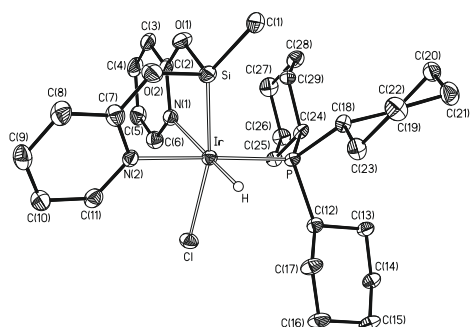
with two resonances which appear at  $\delta$  130.2 and 130.1 ppm, respectively, in the <sup>13</sup>C{<sup>1</sup>H} NMR spectra of **2**. It should be mentioned that <sup>13</sup>C{<sup>1</sup>H} NMR spectra of free 1,5-cyclooctadiene show the olefinic carbon atoms around  $\delta$  129 ppm. As it should be expected, the carbon atoms of the coordinated olefinic fragment appear shifted at higher field at  $\delta$  68.7 and 65.9 ppm, respectively. The <sup>1</sup>H NMR spectra of species **2** in CD<sub>2</sub>Cl<sub>2</sub> also show a singlet resonance corresponding to the hydride ligand at  $\delta$  -15.35 ppm, which is in the same range of that observed for related species [Ir(H)(Cl)(NSiN)(coe)] (**4**)<sup>[8]</sup> with a cyclooctene instead of the cyclooctadiene ligand. The <sup>29</sup>Si{<sup>1</sup>H} NMR spectra of **2** in CD<sub>2</sub>Cl<sub>2</sub> exhibit a singlet at  $\delta$  31.3 ppm, which compares well with the corresponding resonances reported for **4**. Compound **2** reacts with one equivalent of silver trifluoromethanesulfonate in CH<sub>2</sub>Cl<sub>2</sub>, in the absence of light, to give a light-orange solid, which has been fully characterized by means of elemental analysis, mass spectrometry and NMR spectroscopy as the ionic iridium(III) species **3** (Scheme 1).

<sup>1</sup>H NMR studies of the reaction of **2** with PCy<sub>3</sub> in C<sub>6</sub>D<sub>6</sub> show the resonances due to free cyclooctadiene together with those corresponding to the complex [Ir(H)(Cl)(NSiN)(PCy<sub>3</sub>)] (**5**). It should be mentioned that analogous behavior was observed when using complex **4** instead of **2** (Scheme 2). In addition, when the reactions of **2** (or **4**) with one equivalent of PCy<sub>3</sub> were carried out at preparative level, the corresponding phosphane derivative [Ir(H)(Cl)(NSiN)(PCy<sub>3</sub>)] (**5**) was obtained in high yield. The reaction of complex **5** with AgCF<sub>3</sub>SO<sub>3</sub> quantitatively gives the triflate derivative [Ir(H)(CF<sub>3</sub>SO<sub>3</sub>)(NSiN)(PCy<sub>3</sub>)] (**6**) (Scheme 2). The triflate derivatives **3** or [Ir(H)(CF<sub>3</sub>SO<sub>3</sub>)(NSiN)(coe)] (**7**)<sup>[13]</sup> also reacts with one equivalent of PCy<sub>3</sub> to afford complex **6**. However, this methodology allows the formation of other minor reaction side products, corresponding to the coordination of two phosphane ligands to the iridium atom.



**Scheme 2.** Synthesis of Ir-NSiN phosphane complexes.

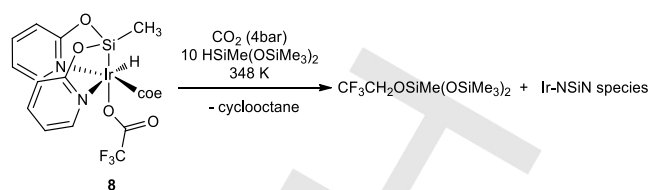
The Ir-NSiN derivatives **5** and **6** have been fully characterized. Moreover, the solid state structure of **5** has been determined by X-ray diffraction studies (Figure 2).



**Figure 2.** Molecular structure of complex **5**. Selected bond lengths (Å) and angles (°) for compound **5**. Ir-Si, 2.2243(13); Ir-Cl, 2.5099(11); Ir-P, 2.2763(11); Ir-N1, 2.204(4); Ir-N2, 2.172(3); Ir-H, 1.641(10); Si-Ir-Cl, 166.07(4); Si-Ir-P, 99.22(4); Si-Ir-N1, 80.14(10); Si-Ir-N2, 79.07(10); Si-Ir-H, 95.0(18); Cl-Ir-P, 92.83(4); Cl-Ir-N1, 90.39(10); Cl-Ir-N2, 90.13(10); Cl-Ir-H, 93.8(18); P-Ir-N1, 103.01(10); P-Ir-N2, 170.78(10); P-Ir-H, 80.7(18); N1-Ir-N2, 85.69(13); N1-Ir-H, 174.2(18), N2-Ir-H, 90.4(18)

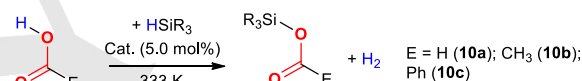
The iridium atom in **5** displays slightly distorted octahedral coordination geometry (Figure 2) with similar structural features than those found in its rhodium analogous.<sup>[10]</sup> The NSiN ligand is facially coordinated to the iridium center, exhibiting Si-Ir-N *cis* angles deviated from the ideal value of 90° due to the chelating bonding of the ligand. Ring puckering parameters of the iridacycles (Ir-Si-O1-C2-N1:  $q = 0.094(3)$  Å,  $\varphi = 11(3)^\circ$ , Ir-Si-O2-C7-N2:  $q = 0.210(3)$  Å,  $\varphi = -156.4(10)^\circ$ ) characterize their twisted  $^1T_2$  and  $^2T_1$  (with an envelope  $^2E$  contribution) conformations. The Ir-Si bond length (2.2243(13) Å) is shorter than that found in complex **2**, and indeed, it is in the lower limit of an iridium-silyl mononuclear species (2.22–2.42 Å).<sup>[21]</sup> The nitrogen atoms are located *trans* to the hydride and the phosphane ligands, and although their different *trans* effect is reflected in the Ir-N bond lengths, the disparity between Ir-N1 and Ir-N2 bond lengths in complex **5** is less marked than that observed in compound **2**. The coordination sphere is completed by a chloride ligand. Interestingly, the Ir-Cl bond length in **5** is shorter (2.5099(11) Å) than that found for compound **2**. This feature may be due to the different intermolecular hydrogen bond patterns involving chlorine atom in each structure ( $R_2^2(10)$  in compound **2** and C(7),  $R_2^2(12)$  and  $R_2^2(14)$  in compound **5**) (see SI).

**Study of the Ir-NSiN catalyzed reaction of carboxylic acids with silanes.** The formation of the silylether  $\text{CF}_3\text{CH}_2\text{OSiMe(OSiMe}_3)_2$  during the hydrosilylation of  $\text{CO}_2$  with  $\text{HSiMe(OSiMe}_3)_2$  using complex  $[\text{Ir}(\text{H})(\text{CF}_3\text{CO}_2)(\text{NSiN})(\text{coe})]$  (**8**) as catalyst precursor has been recently reported (Scheme 3).<sup>[14]</sup> This evidence prompted us to study the potential of Ir-NSiN species as catalysts for the reduction of carboxylic acids using  $\text{HSiMe(OSiMe}_3)_2$  as reducing agent.



**Scheme 3.** Reduction of the ancillary trifluoroacetate ligand in **8** to give  $\text{CF}_3\text{CH}_2\text{OSiMe(OSiMe}_3)_2$  during the **8**-catalyzed hydrosilylation of  $\text{CO}_2$  with  $\text{HSiMe(OSiMe}_3)_2$ .<sup>[14]</sup>

$^1\text{H}$  NMR studies of the reaction of  $\text{E}\text{COOH}$  ( $\text{E} = \text{H, CH}_3, \text{Ph}$ ) with one equivalent of  $\text{HSiMe(OSiMe}_3)_2$  in  $\text{C}_6\text{D}_6$  at 328 K in presence of catalytic amounts of complexes **7** or **8** show a clear influence of the ancillary ligands on the performance of the resulting catalytic system (Table 1). Thus, while using complex **8** as catalyst, it is possible to achieve the quantitative conversion of the parent carboxylic acids into the corresponding silylester in less than 4 hours, the related triflate derivatives **6** and **7** have shown a poorer catalytic activity (Table 1). It should be mentioned that the phosphane complex **6** is slightly more active than **7** but less than **8** (Table 1).



**Table 1.** Reaction products from the reaction of carboxylic acids with one equivalent of  $\text{HSiMe(OSiMe}_3)_2$  in presence of catalytic amounts (5.0 mol%) of Ir-NSiN complexes in  $\text{C}_6\text{D}_6$ .

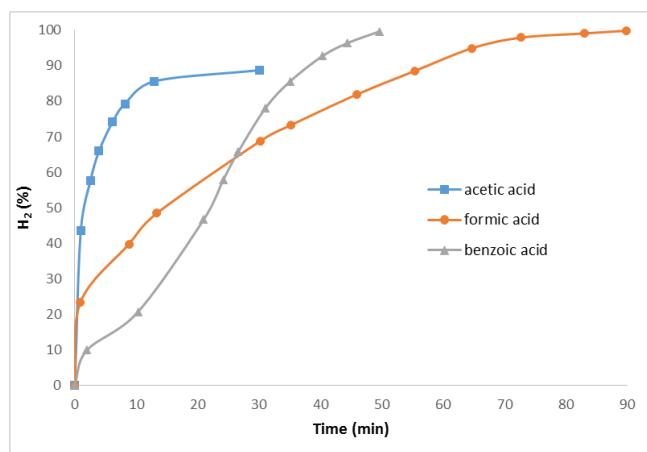
Acid	catalyst	T (K)	Silyl ester (%) <sup>[a],[b]</sup>
HCOOH	<b>6</b>	328	<b>10a</b> (63.7)
HCOOH	<b>7</b>	328	<b>10a</b> (52.0)
HCOOH	<b>8</b>	328	<b>10a</b> (95.0)
$\text{CH}_3\text{COOH}$	<b>7</b>	328	<b>10b</b> (43.5)
$\text{CH}_3\text{COOH}$	<b>8</b>	328	<b>10b</b> (84.5)
$\text{PhCOOH}$	<b>7</b>	328	<b>10c</b> (65.0)
$\text{PhCOOH}$	<b>8</b>	328	<b>10c</b> (90.0)

[a] % calculated by  $^1\text{H}$  NMR integration using hexamethylbenzene (0.07 mmol) as internal standard. [b] Data corresponding to the  $^1\text{H}$  NMR spectra registered after 3.5 h of reaction.

The silylester species **10a-c** were characterized by comparison of their  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectra with the reported data (Figures S1 to S6).<sup>[8,14,4e]</sup> In this context, it should be mentioned that few catalytic systems effective for the selective dehydrogenative silylation of carboxylic acids with silanes have been reported so far.<sup>[4]</sup> It is worth noting that  $^1\text{H}$  NMR studies of the **8**-catalyzed reactions of formic, acetic or benzoic acid, with 3.0 equivalents of  $\text{HSiMe(OSiMe}_3)_2$  in  $\text{C}_6\text{D}_6$  at 328 K showed that, after 24h, the corresponding silylester species **10** remains

as the major reaction product and no evidence of its reduction was observed.

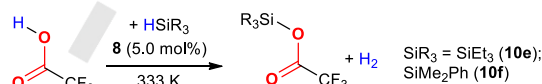
Kinetic studies of the reaction of ECOOH (E = H, CH<sub>3</sub>, Ph) with HSiMe(OSiMe<sub>3</sub>)<sub>2</sub> in presence of **8** (1.0 mol%) using dry-toluene as solvent were carried out in a micro-reactor.<sup>[22]</sup> This allowed measuring the hydrogen pressure generated during the process (Figure 3). As a result from these studies a turnover frequency number at 50% conversion (TOF<sub>1/2</sub>) value of 195, 2000 and 136 h<sup>-1</sup> were found for the H<sub>2</sub> generation from the dehydrogenative Si-O coupling of HSiMe(OSiMe<sub>3</sub>)<sub>2</sub> with formic, acetic and benzoic acid, respectively. Therefore, the dehydrogenative silylation is faster for acetic acid. However, in agreement with the NMR experiments (Table 1) the reaction yield has found to be lower for CH<sub>3</sub>COOH than for HCOOH and PhCOOH. These data showed that the Ir-NSiN based catalytic system for dehydrogenative silylation of carboxylic acids could be considered as one of the most active so far reported.<sup>4</sup>



**Figure 3.** Hydrogen generation (% related to 1.0 mmol as 100%) versus time (min) for the catalytic dehydrogenative Si-O coupling of acetic acid, formic acid and benzoic acid (1.0 mmol) with HSiMe(OSiMe<sub>3</sub>)<sub>2</sub> (1.01 mmol) using **8** (1.0 mol%) as catalyst in dry toluene (1.0 mL) at 328 K.

<sup>1</sup>H and <sup>29</sup>Si{<sup>1</sup>H} NMR studies of the **8**-catalyzed reaction of CF<sub>3</sub>COOH with HSiMe(OSiMe<sub>3</sub>)<sub>2</sub> under the same conditions as above described for others acids evidenced the formation of molecular hydrogen together with a mixture of unidentified species (Table 2). <sup>29</sup>Si{<sup>1</sup>H} NMR spectra of the final reaction product show that the intensity of the resonances assigned to CF<sub>3</sub>COOSiMe(OSiMe<sub>3</sub>)<sub>2</sub> (**10d**) (δ 8.5 and -65.2 ppm)<sup>[4e]</sup> is very low in comparison with the intensity of the resonances corresponding to others not identified species (Figure S7). In addition, no evidence of {SiMe(OSiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>O nor residual CF<sub>3</sub>COOH were observed in the <sup>29</sup>Si{<sup>1</sup>H} and <sup>13</sup>C{<sup>1</sup>H} NMR spectra, respectively. The <sup>13</sup>C{<sup>1</sup>H} NMR spectra of these reaction samples show the presence of two quartet resonances centered at δ 156.8 ppm (<sup>2</sup>J<sub>C-F</sub> = 42.1 Hz) and δ 155.6 ppm (<sup>2</sup>J<sub>C-F</sub> = 42.6 Hz), high field shifted with respect to the corresponding resonance for CF<sub>3</sub>COOH (δ 160.8 ppm, <sup>2</sup>J<sub>C-F</sub> = 43.8 Hz) (Figure S8). These spectra showed another two quartet resonances due CF<sub>3</sub> groups (δ 115.32 ppm, <sup>1</sup>J<sub>C-F</sub> = 286.2 Hz and δ 115.30 ppm,

<sup>1</sup>J<sub>C-F</sub> = 286.0 Hz) that are low field shifted in comparison with the related resonance observed for trifluoroacetic acid (δ 114.8 ppm, <sup>1</sup>J<sub>C-F</sub> = 284.5 Hz) (Figure S8). These results confirm the formation of at least two silyl ester species with the CF<sub>3</sub>CO<sub>2</sub>Si moiety but different from **10d**. This behavior could be explained taking into account that complex **8** promoted the rearrangement of HSiMe(OSiMe<sub>3</sub>)<sub>2</sub> in absence of coordinating substrates to give mixtures of HSi(OSiMe<sub>3</sub>)<sub>3</sub>, HSiMe<sub>2</sub>(OSiMe<sub>3</sub>) and other hydrosiloxanes.<sup>[14]</sup> Indeed, when using HSiEt<sub>3</sub> or HSiMe<sub>2</sub>Ph instead of HSiMe(OSiMe<sub>3</sub>)<sub>2</sub> under the same reaction conditions the selective **8**-catalyzed silylation of CF<sub>3</sub>COOH to give the corresponding silyl-ester CF<sub>3</sub>COOSiEt<sub>3</sub> (**10e**) or CF<sub>3</sub>COOSiMe<sub>2</sub>Ph (**10f**) was achieved in 1.5 h (Table 2). Compounds **10e** and **10f** were characterized by means of <sup>1</sup>H, <sup>29</sup>Si and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy (Figure S9 to S14). It should be noted that the silyl esters **10e** and **10f** were previously obtained in low yield from the reaction of the corresponding silane, HSiEt<sub>3</sub> or HSiMe<sub>2</sub>Ph, with 3 equivalents of CF<sub>3</sub>COOH at 343 K for 10 h.<sup>[23]</sup>

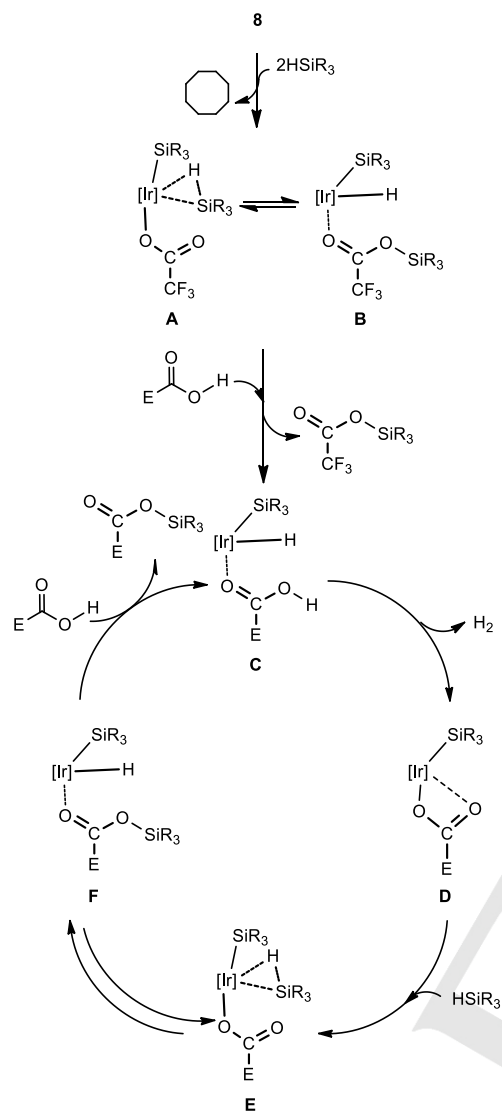


**Table 2.** Reaction products from the reaction of CF<sub>3</sub>COOH with one equivalent of HSiR<sub>3</sub> in presence of catalytic amounts complex **8** (5.0 mol%) in C<sub>6</sub>D<sub>6</sub>.

Silane	catalyst	T (K)	Silyl ester(%) <sup>[a],[b]</sup>
HSiMe(OSiMe <sub>3</sub> ) <sub>2</sub>	<b>8</b>	328	mixture of silyl esters
HSiEt <sub>3</sub>	<b>8</b>	328	<b>10e</b> (91.0)
HSiMe <sub>2</sub> Ph	<b>8</b>	328	<b>10f</b> (93.0)

[a] % calculated by <sup>1</sup>H NMR integration using hexamethylbenzene (0.07 mmol) as internal standard. [b] Data corresponding to the <sup>1</sup>H NMR spectra registered after 1.5 h of reaction.

A mechanism proposed for the **8**-dehydrogenative silylation of the above mentioned carboxylic acids is shown in Scheme 4. It has been proven that C<sub>6</sub>D<sub>6</sub> solutions of **8** did not react with the carboxylic acids in absence of silane. Therefore, it is reasonable to assume that, analogously to that reported for the **8**-catalyzed CO<sub>2</sub>-hydrosilylation processes,<sup>[14]</sup> the first step of the reaction could be the formation of species **A**, which is in equilibrium with **B** (Scheme 4).<sup>[14]</sup> This is also supported by the experimentally observed formation of cyclooctane. Intramolecular elimination of molecular hydrogen from **C** could afford **D**. Subsequently, the (η<sup>2</sup>-Si-H)-coordination of a molecule of silane<sup>[14]</sup> to the free vacancy in **D** affords intermediate **E** (related to **A**). The carboxylate ligand assisted Si-H bond activation leads to the silyl-hydride intermediate **F** (related to **B**), which contains a molecule of the corresponding silyl ester κ<sup>1</sup>-O-bonded to iridium. Finally, the substitution of the silyl ester in **F** by a molecule of the corresponding carboxylic acid regenerates the active species **C**. This mechanistic proposal is based on Ir-NSiN intermediates and/or transition states which have been recently reported.<sup>[14]</sup>



**Scheme 4.** Mechanism proposal for the **8**-catalyzed dehydrogenative silylation of carboxylic acids. [Ir] = [Ir(*fac*-NSiN)]; E = H, CH<sub>3</sub> or Ph).

## Conclusions

The potential of [Ir( $\mu$ -Cl)(cod)]<sub>2</sub> as metallic precursor for the preparation of Ir-NSiN species and the reactivity of the resulting compounds have been successfully studied. The complex [Ir(H)(Cl)(NSiN)( $\eta^2$ -cod)] (**2**) reacts with silver triflate to afford the ionic species [Ir(H)(NSiN)( $\eta^4$ -cod)] [CF<sub>3</sub>SO<sub>3</sub>] (**3**). The uncommon  $\eta^2$ -cod coordination mode of the cod ligand to the iridium atom in **2** has been confirmed by X-ray diffraction methods. The reactivity of the Ir-NSiN(olefin) species with PCy<sub>3</sub> evidenced that the olefin ligand is easily replaced by the phosphane to give [Ir(H)(X)(NSiN)(PCy<sub>3</sub>)] (X = Cl, CF<sub>3</sub>SO<sub>3</sub>) complexes.

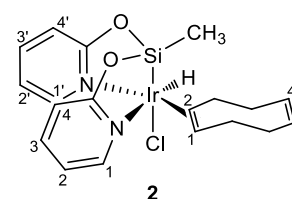
On the other hand, the trifluoroacetate derivative [Ir(H)(CF<sub>3</sub>CO<sub>2</sub>)(NSiN)(coe)] (**8**) has proven to be an efficient

catalyst for the selective dehydrogenative silylation of ECOOH (E = H, CH<sub>3</sub> and Ph) to give the corresponding silyl ester. Conversely, when the reaction with CF<sub>3</sub>COOH was studied under the same reaction conditions the expected silyl ester was obtained as minor product together with a mixture of not identified compounds containing the CF<sub>3</sub>CO<sub>2</sub>Si moiety. This behaviour could be due to **8**-catalyzed rearrangement of HSiMe(OSiMe<sub>2</sub>)<sub>2</sub>. Indeed, the reaction of CF<sub>3</sub>COOH with HSiEt<sub>3</sub> or HSiMe<sub>2</sub>Ph in presence of catalytic amounts of **8** quantitatively affords the corresponding silyl ester CF<sub>3</sub>COOSiEt<sub>3</sub> or CF<sub>3</sub>COOSiMe<sub>2</sub>Ph, respectively.

## Experimental Section

**General Considerations.** 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 ( $\delta$ ) are reported in ppm and coupling constants (*J*) are reported in Hz to apparent peak multiplications. <sup>1</sup>H-<sup>1</sup>H-COSY, <sup>13</sup>C-APT, <sup>1</sup>H/<sup>13</sup>C HSQC, <sup>1</sup>H/<sup>13</sup>C HMBC and <sup>1</sup>H/<sup>29</sup>Si HMBC sequences were used for help in the assignments of the <sup>1</sup>H and <sup>13</sup>C spectra. Compound **1** and the Ir-NSiN precursors **4**,<sup>[8]</sup> **7**<sup>[8]</sup> and **8**<sup>[12]</sup> were prepared according to the reported method. RCO<sub>2</sub>H (R = H, CH<sub>3</sub>, CF<sub>3</sub> and Ph) and PCy<sub>3</sub>, were purchased from commercial sources and used without further purifications.

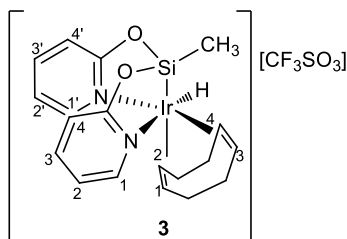
**Preparation of IrHCl( $\eta^2$ -cod)(NSiN) (**2**).** A solution of [IrCl(cod)]<sub>2</sub> (0.202 g, 0.30 mmol) in 7 mL of dichloromethane was treated with 1.0 equiv of bis-(2-(oxy)pyridine)methylsilane **1** (0.140 g, 0.60 mmol) and stirred at room temperature for 3 h. Then, the solvent was removed in vacuum. The addition of hexane (3 mL) led to a white solid, which was separated by decantation, washed with further portions of hexane (3 x 3 mL) and dried in vacuum. Yield: 0.297 g (87 %). Anal. calcd. for C<sub>19</sub>H<sub>24</sub>N<sub>2</sub>IrClO<sub>2</sub>Si (568.165): C, 40.17; H, 4.26; N, 4.93. Found: C, 39.45; H, 4.25; N, 5.85. Mass spectrometry (ESI): *m/z* 533.1, [M-Cl]<sup>+</sup> (100%).



<sup>1</sup>H NMR plus COSY and NOESY (400.13 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta$  9.53 (ddd, *J*<sub>H-H</sub> = 6.1, 1.9, 0.6, 1H, H<sup>1</sup><sub>py</sub>), 9.25-9.22 (m, 1H, H<sup>1</sup><sub>py</sub>), 7.71 (ddd, *J*<sub>H-H</sub> = 8.3, 7.2, 2.0, 1H, H<sup>3</sup><sub>py</sub>), 7.65 (ddd, *J*<sub>H-H</sub> = 8.4, 7.2, 1.9, 1H, H<sup>3</sup><sub>py</sub>), 7.01-6.95 (m, 2H, H<sub>py</sub> (H<sub>4</sub> + H<sub>2</sub>)), 6.93 (ddd, *J*<sub>H-H</sub> = 8.3, 1.3, 0.6, 1H, H<sup>4</sup><sub>py</sub>), 6.79 (ddd, *J*<sub>H-H</sub> = 7.3, 6.1, 1.4, 1H, H<sup>2</sup><sub>py</sub>), 5.67-5.51 (m, 2H, =CH<sup>3,4</sup><sub>cod</sub>), 4.61-4.54 (m, 1H, =CH<sup>2</sup><sub>cod</sub>), 3.83-3.75 (m, 1H, =CH<sup>1</sup><sub>cod</sub>), 2.60-1.32 (m, 8H, -CH<sub>2</sub>-<sub>cod</sub>), 0.69 (s, SiCH<sub>3</sub>, 3H), -15.35 (s, 1H, Ir-H). <sup>13</sup>C-APT NMR plus HMBC and HSQC (100.4 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta$  167.6 and 165.8 (both s, C<sup>ipso</sup>-py and C<sup>ipso</sup>-py, respectively), 150.9, 148.1, 142.1 and 141.7 (all s, C<sup>1</sup><sub>py</sub>, C<sup>1</sup><sub>py</sub>, C<sup>3</sup><sub>py</sub> and C<sup>3</sup><sub>py</sub>, respectively), 130.2 and 130.1 (both s, =CH<sup>3,4</sup><sub>cod</sub>), 118.3, 117.4, 112.7 and 112.0 (all s, C<sup>2</sup><sub>py</sub>, C<sup>2</sup><sub>py</sub>, C<sup>4</sup><sub>py</sub>, C<sup>4</sup><sub>py</sub>,

respectively), 68.7 and 65.9 (both s,  $=CH^2_{cod}$  and  $=CH^1_{cod}$ , respectively), 35.0, 32.7, 31.4 and 30.8 (all s,  $-CH_2-cod$ ), -1.0 (s,  $SiCH_3$ ).  $^{29}Si\{^1H\}$  NMR (59.6 MHz,  $CD_2Cl_2$ , 298 K):  $\delta$  31.3 (s,  $SiCH_3$ ).

**Preparation of  $[IrH(\eta^4-cod)(NSi)(CF_3SO_3)]$  (3).** A solution of **2** (0.179 g, 0.32 mmol) in 12 mL of THF was treated with 1.0 equiv of silver trifluoromethanesulfonate (0.081 g, 0.32 mmol) in the absence of light. After stirring the mixture for 1.5 h at room temperature, the suspension was filtered through Celite and the filtrate was evaporated to dryness. The addition of hexane (3 mL) caused the precipitation of a light orange solid, which was separated by decantation, washed with further portions of hexane (3 x 3 mL), and dried in vacuum. Yield: 0.176 g (82 %). Anal. calcd. for  $C_{20}H_{24}N_2SF_3IrO_5Si$  (681.778): C, 35.23; H, 3.55; N, 4.11; S, 4.70. Found: C, 34.78; H, 3.58; N, 3.99; S, 4.48. Mass spectrometry (ESI):  $m/z$  533.1,  $[M]^+$  (100 %).



$^1H$  NMR plus COSY and NOESY (400.13 MHz,  $CD_2Cl_2$ , 298 K): 8.84 (ddd,  $J_{H-H} = 6.0, 1.6, 0.8$ , 1H,  $H^1_{py}$ ), 7.96 (ddd,  $J_{H-H} = 6.1, 1.3, 0.4$ , 1H,  $H^1_{py}$ ), 7.90 (ddd,  $J_{H-H} = 8.4, 7.3, 1.8$ , 1H,  $H^3_{py}$ ), 7.80 (ddd,  $J_{H-H} = 8.5, 7.3, 1.8$ , 1H,  $H^3_{py}$ ), 7.19 (ddd,  $J_{H-H} = 7.3, 6.0, 1.3$ , 1H,  $H^2_{py}$ ), 7.10-7.08 (m, 1H,  $H^4_{py}$ ), 7.08-7.06 (m, 1H,  $H^4_{py}$ ), 7.00 (ddd,  $J_{H-H} = 7.4, 6.1, 1.4$ , 1H,  $H^2_{py}$ ), 5.97-5.91 (m, 1H,  $=CH^2_{cod}$ ), 4.71-4.64 (m, 1H,  $=CH^4_{cod}$ ), 4.54-4.62 (m, 1H,  $=CH^1_{cod}$ ), 3.74-3.69 (m, 1H,  $=CH^3_{cod}$ ), 3.00-1.84 (m, 8H,  $-CH_2-cod$ ), 0.79 (s,  $SiCH_3$ , 3H), -15.47 (s, 1H, Ir-H).  $^{13}C$ -APT NMR plus HMBC and HSQC (100.4 MHz,  $CD_2Cl_2$ , 298 K):  $\delta$  167.3 and 166.1 (both s,  $C_{ipso-py}$  and  $C_{ipso-py}$ , respectively), 152.1, 149.1, 144.0 and 143.8 (all s,  $C^1_{py}$ ,  $C^1_{py}$ ,  $C^3_{py}$  and  $C^3_{py}$ , respectively), 121.1, 120.3, 114.0 and 113.7 (all s,  $C^2_{py}$ ,  $C^2_{py}$ ,  $C^4_{py}$  and  $C^4_{py}$ , respectively), 112.5, 105.8, 69.2 and 69.0 (all s,  $=CH^2_{cod}$ ,  $=CH^1_{cod}$ ,  $=CH^3_{cod}$ ,  $=CH^4_{cod}$ , respectively), 35.9, 35.1, 31.5 and 22.4 (all s,  $-CH_2-cod$ ), -1.5 (s,  $SiCH_3$ ).  $^{29}Si\{^1H\}$  NMR (59.6 MHz,  $CD_2Cl_2$ , 298 K):  $\delta$  51.5 (s,  $SiCH_3$ ).  $^{19}F$  NMR (282.4 MHz,  $CD_2Cl_2$ , 298 K):  $\delta$  -78.8 (s,  $CF_3$ ).

**Preparation of  $[IrH(Cl)(NSi)(PCy_3)]$  (5).** Complex **2** (0.200 g, 0.35 mmol) and  $PCy_3$  (0.980 g, 0.35 mmol) were mixed inside the glovebox and then 8.0 mL of toluene were added to give a yellow solution, which was stirred at room temperature during 24h. The solvent was removed in vacuum and the resulting residue was washed with hexane (2 x 3 mL) and dried in vacuum to obtain a white powder. Yield: 0.210 g (80%). Anal. calcd. for  $C_{29}H_{45}ClIrN_2O_2PSi$ : C, 47.04; H, 6.13; N, 3.78. Found: C, 46.78; H, 6.20; N, 3.87.  $^1H$  NMR plus HSQC (300 MHz, 298 K,  $CDCl_3$ ):  $\delta$  9.64 (m, 1H, py), 9.40 (m, 1H, py), 7.54 (t,  $J_{H-H} = 7.6$  Hz, 1H, py), 7.48 (t,  $J_{H-H} = 7.6$  Hz, 1H, py), 6.91-6.68 (m, 4H, py), 2.01-1.07 (m, 33H, Cy), 0.81(s, 3H, Me), -20.47 (d,  $J_{H-P} = 23$  Hz, Ir-H).  $^{31}P\{^1H\}$  NMR (121 MHz, 298 K,  $C_6D_6$ )  $\delta$  15.0 (s,  $PCy_3$ ).  $^{13}C$ -APT plus HSQC and HMBC NMR (75 MHz, 298 K,  $CDCl_3$ ):  $\delta$  166.1, 166.0 (s,  $C_{ipso-py}$ ), 148.6, 148.1, 140.0, 139.8, 116.6, 116.5, 111.8 and 111.2, (s, CH-py), 36.8 and 35.0 (br s, CH- $PCy_3$ ), 29.3, 27.6, 26.7 ( $CH_2-Cy$ ).  $^{29}Si$  NMR (DEPT 45, 60 MHz, 298 K,  $C_6D_6$ ):  $\delta$  41.3 (d,  $J_{Si-P} = 14.9$  Hz, SiMe). ESI $^+$ : 705.2  $[M^+-Cl, 100\%]$ .

**Preparation of  $[IrH(CF_3SO_3)(NSi)(PCy_3)]$  (6).** A solution of **5** (0.250 g, 0.32 mmol) in 12 mL of THF was treated with 1.0 equiv of silver trifluoromethanesulfonate (0.081 g, 0.32 mmol) in the absence of light. After stirring the mixture for 1.5 h at room temperature, the suspension was filtered through Celite and the filtrate was evaporated to dryness. The addition of hexane (3 mL) caused the precipitation of a light orange solid, which was separated by decantation, washed with further portions of hexane (3 x 3 mL), and dried in vacuum. Yield: 0.268 g (84%).  $^1H$  NMR (300 MHz,  $CD_2Cl_2$ ):  $\delta$  8.62 (m, 2H, py), 7.63 (m, 2H, py), 6.97 (m, 1H, py), 6.89 (m, 3H, py), 2.24 (brs, 3H, P-CH), 1.70 (m, 15H, Cy), 1.25 (m, 15H, Cy), 0.86 (s, 3H, SiMe), -19.17 (d,  $J_{P-H} = 22.5$  Hz, 1H, Ir-H).  $^{13}C$ -APT NMR plus HSQC and HMBC (75 MHz,  $CD_2Cl_2$ ):  $\delta$  165.2 (br,  $C_{ipso}$ , 2C, py), 147.4 (s, 2C, CH-py), 141.0, 140.9 and 118.1 (s, CH-py), 117.6 (d,  $^3J_{P-C} = 2.5$  Hz, CH-py), 112.8 and 112.3 (s, CH-py), 37.0 (d,  $^1J = 31.4$  Hz, P-C), 30.1 (d,  $^4J = 2.5$  Hz, Cy), 29.3 (br s, Cy), 27.9 (d,  $^3J = 11.0$  Hz, Cy), 27.7 (d,  $^3J = 10.8$  Hz, Cy), 27.0 (s, Cy), 0.20 (s, SiMe).  $^1H$ - $^{29}Si$ -HMBC NMR ( $C_6D_6$ ):  $\delta$  15.3 (SiMe).

**General procedure for the NMR scale reactions of equimolar mixtures of  $HSiMe(OSiMe_3)_2$  with carboxylic acids.** A NMR tube was charged with the precursor catalyst **7** or **8** ( $3.5 \cdot 10^{-3}$  mmol) and  $C_6D_6$  (0.5 mL). After which,  $HSiMe(OSiMe_3)_2$  (22  $\mu$ L, 0.07 mmol) and the corresponding carboxylic acid (0.07 mmol) were added to the homogeneous solution and the resulting mixtures were heated at 333 K and monitored by  $^1H$  NMR spectroscopy.

**Selected data for 10b.**  $^1H$  NMR (300 MHz, 298 K,  $C_6D_6$ ):  $\delta$  1.70 (s, 3H,  $CH_3$ ), 0.37 (s, 3H, SiMe), 0.20 (s, 18H,  $OSiMe_3$ ).  $^{13}C$ -APT NMR plus HSQC and HMBC (75 MHz,  $C_6D_6$ ):  $\delta$  169.7 (s,  $CO_2$ ), 22.3 (s,  $CH_3$ ), 1.6 (s,  $OSiMe_3$ ), -2.6 (s, SiMe).  $^{29}Si\{^1H\}$  plus  $^1H$ - $^{29}Si$ -HMBC NMR (60 MHz, 298 K,  $C_6D_6$ ):  $\delta$  10.0 (s,  $OSiMe_3$ ), -58.2 (s, SiMe).

**Selected data for 10c.**  $^1H$  NMR (300 MHz, 298 K,  $C_6D_6$ ):  $\delta$  8.20 (m, 2H, Ph), 7.06 (m, 3H, Ph), 0.48 (s, 3H, SiMe), 0.23 (s, 18H,  $OSiMe_3$ ).  $^{13}C$ -APT NMR plus HSQC and HMBC (75 MHz,  $C_6D_6$ ):  $\delta$  165.6 (s,  $CO_2$ ), 133.1 (s, CH, Ph), 131.7 (s,  $C_{ipso}$ , Ph), 130.5 (s, CH, Ph) 128.5 (s, CH, Ph), 1.7 (s,  $OSiMe_3$ ), -2.5 (s, SiMe).  $^{29}Si\{^1H\}$  NMR (60 MHz, 298 K,  $C_6D_6$ ):  $\delta$  10.3 (s,  $OSiMe_3$ ), -57.0 (s, SiMe).

**Selected data for 10e.**  $^1H$  NMR (400 MHz, 298 K,  $C_6D_6$ ):  $\delta$  0.56 (q, 6H,  $^3J_{H-H} = 7.7$ ,  $CH_2$ ), 0.78 (t, 9H,  $^3J_{H-H} = 7.7$ ,  $CH_3$ ).  $^{13}C\{^1H\}$  NMR plus HSQC (100 MHz,  $C_6D_6$ ):  $\delta$  156.5 (q,  $^2J_{C-F} = 42.0$ ,  $CO_2$ ), 115.2 (q,  $^1J_{C-F} = 286.5$ ,  $CF_3$ ), 5.8 (s,  $CH_3$ ), 4.0 (s,  $CH_2$ ).  $^{29}Si\{^1H\}$  NMR (99.0 MHz, 298 K,  $C_6D_6$ ):  $\delta$  34.5 (s).  $^{19}F\{^1H\}$  NMR (282 MHz, 298 K,  $C_6D_6$ ):  $\delta$  -75.8 (s).

**Selected data for 10f.**  $^1H$  NMR (400 MHz, 298 K,  $C_6D_6$ ):  $\delta$  7.42 (m, 2H, Ph), 7.12 (m, 3H, Ph), 0.30 (s, 6H, SiMe $_2$ ).  $^{13}C\{^1H\}$  NMR plus HSQC (100 MHz,  $C_6D_6$ ):  $\delta$  156.7 (q,  $^2J_{C-F} = 42.0$ ,  $CO_2$ ), 114.9 (q,  $^1J_{C-F} = 282.2$ ,  $CF_3$ ), 128.5, 131.3 and 133.4 (s, CH, Ph), 133.1 (s,  $C_{ipso}$ , Ph), -2.5 (s, SiMe $_2$ ).  $^{29}Si\{^1H\}$  NMR (99.0 MHz, 298 K,  $C_6D_6$ ):  $\delta$  20.5 (s).  $^{19}F\{^1H\}$  NMR (282 MHz, 298 K,  $C_6D_6$ ):  $\delta$  -75.9 (s).

**General procedure for the measurement of  $H_2$  evolution from the 1-catalyzed reactions of carboxylic acids with  $HSiMe(OSiMe_3)_2$ .** The reactions were carried out in a *Man on the Moon X102 kit*<sup>®</sup> micro-reactor (www.manonthemoontech.com), with a total volume of 19.0 mL, placed in a silicone bath at 333 K. In a typical procedure 1.0 mmol of  $HSiMe(OSiMe_3)_2$  (281  $\mu$ L, 1.01 mmol) was added to a solution of the catalyst **8** (0.01 mmol, 6.50 mg) in 1 mL of dry-toluene. The reactor was closed and the pressure measurement started. Once the pressure was stabilized, the corresponding ECOOH ( $E = H$ , 37.7  $\mu$ L;  $CH_3$ , 57.2  $\mu$ L; 1.0 mmol) was added with a syringe. In the case of PhCOOH, 1.0 mmol of

HSiMe(OSiMe<sub>3</sub>)<sub>2</sub> (281  $\mu$ L, 1.01 mmol) was added to a solution of the catalyst **8** (6.50 mg, 0.01 mmol) and PhCOOH (122 mg, 1.0 mmol) in 1 mL of dry-toluene. Hydrogen evolution was measured till inner pressure in the micro-reactor remained constant. The difference in pressure was used to calculate the amount of H<sub>2</sub> produced during the reaction using the Ideal Gas Law,  $P \cdot V = n \cdot R \cdot T$ .

**Crystal Structure Determination of Complexes 2 and 5.** Single crystal X-ray diffraction data were collected at 100(2) K with graphite-monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å) using narrow  $\omega$  rotations (0.3°) on a Bruker APEX DUO (compound **2**) or a Bruker SMART APEX diffractometer (compound **5**). SAINT<sup>[24]</sup> and SADABS<sup>[25]</sup> programs, integrated in APEX2 package, were used to integrate and correct the absorption effect of the intensities. The structures were solved by direct methods with SHELXS-2013<sup>[26]</sup> and refined by full-matrix least-squares refinement in  $F^2$  with SHELXL-2014<sup>[27]</sup> included in Wingx package.<sup>[28]</sup> Hydride ligand has been included in the model in observed position and freely refined (compound **2**) or refined with a restraint in Ir-H bond length (compound **5**).

**Crystal data for 2.** C<sub>29</sub>H<sub>24</sub>ClIrN<sub>2</sub>O<sub>2</sub>Si  $M = 568.14$ ; yellow prism, 0.070 x 0.082 x 0.082 mm<sup>3</sup>; monoclinic  $P2_1/c$ ;  $a = 9.8151(7)$ ,  $b = 12.3333(8)$ ,  $c = 16.2337(11)$  Å,  $\beta = 90.1270(10)^\circ$ ;  $V = 1965.1(2)$  Å<sup>3</sup>;  $Z = 4$ ;  $\rho_{\text{calc}} = 1.920$  g cm<sup>-3</sup>;  $\mu = 7.007$  cm<sup>-1</sup>; min. and max. transmission factors 0.522 and 0.672;  $2\theta_{\text{max}} = 59.056^\circ$ ; 30016 reflections collected; 5214 unique reflections [ $R_{\text{int}} = 0.0441$ ]; number of data/restraints/parameters: 5214/0/256; final GOF 1.046;  $R_1 = 0.0320$  [4438 reflections,  $I > 2\sigma(I)$ ],  $wR_2 = 0.0837$  for all data; largest difference peak: 7.05 e Å<sup>-3</sup>. At the end of the refinement five residual density peaks bigger than 1 e Å<sup>-3</sup> have been found. They are close to iridium atom and reveal bonding effects between the metal and the ligands.

**Crystal data for 5.** C<sub>29</sub>H<sub>45</sub>ClIrN<sub>2</sub>O<sub>2</sub>PSi  $M = 740.38$ ; colorless prism, 0.060 x 0.160 x 0.175 mm<sup>3</sup>; monoclinic  $P2_1/c$ ;  $a = 11.7418(8)$ ,  $b = 12.1443(8)$ ,  $c = 21.6800(14)$  Å,  $\beta = 104.6250(10)^\circ$ ;  $V = 2991.3(3)$  Å<sup>3</sup>;  $Z = 4$ ;  $\rho_{\text{calc}} = 1.644$  g cm<sup>-3</sup>;  $\mu = 4.675$  cm<sup>-1</sup>; min. and max. transmission factors 0.498 and 0.640;  $2\theta_{\text{max}} = 56.214^\circ$ ; 34218 reflections collected; 7094 unique reflections [ $R_{\text{int}} = 0.0552$ ]; number of data/restraints/parameters: 7094/3/394; final GOF 0.982;  $R_1 = 0.0345$  [5637 reflections,  $I > 2\sigma(I)$ ],  $wR_2 = 0.0844$  for all data; largest difference peak: 3.926 e Å<sup>-3</sup>. At the end of the refinement five residual density peaks bigger than 1 e Å<sup>-3</sup> have been found. They are close to iridium atom and have no chemical sense.

CCDC 1574097-1574098 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [http://www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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**Keywords:** Carboxylic acids reduction • Silylation • Ir-NSiN • Homogeneous catalysis • Hydrogen generation

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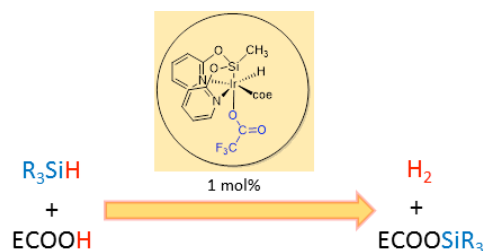
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Layout 1:

## FULL PAPER

Ir-NSiN species have proven to be efficient catalysts for the dehydrogenative silylation of carboxylic acids



A. Julián, K. Garcés, R. Lalrempuia, E. A. Jaseer, P. García-Orduña, F. J. Fernández-Alvarez,\* F. J. Lahoz,<sup>[a]</sup> and L. A. Oro\*

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Reactivity of Ir-NSiN Complexes: Ir-Catalyzed Dehydrogenative Silylation of Carboxylic Acids