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

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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 η^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.

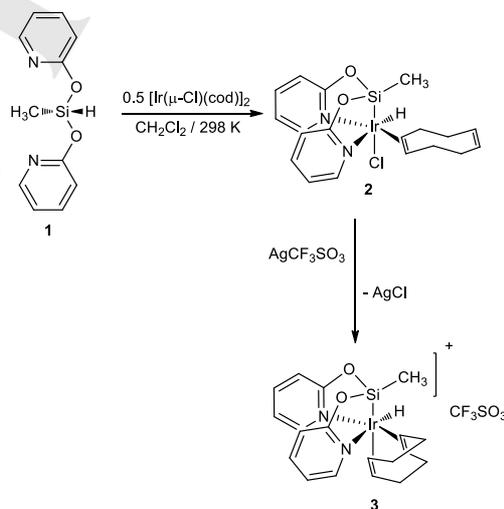
Introduction

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.^[1,2] Besides that, a number of catalytic systems has been efficiently employed for the selective reduction of CO_2 with hydrosilanes to give the corresponding silylformate, bis-silyl acetal, methoxysilane or methane.^[3] It should be noted that the selective reaction of carboxylic acids with hydrosilanes to afford silylesters,^[4] alcohols^[5] or aldehydes^[6] still represents a challenge. Rh and Ir complexes with tridentate monoanionic NSiN ligands^[7] were found to be effective catalysts for CO_2 -hydrosilylation,^[3,8] dehydrogenative silylation of arenes^[9] and acetophenone^[10] derivatives and for processes involving CO_2 -insertion into N-Si^[11] and P-Si^[12] 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 CO_2 with

$\text{HSiMe}(\text{OSiMe}_3)_2$ ^[13,14] 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)^[7] 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 CH_2Cl_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 η^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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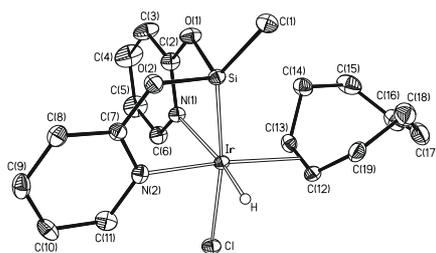


Figure 1. Molecular structure of complex **2**. Selected bond lengths (Å) and angles (°) for compound **2**. Ir-Si, 2.2356(12); Ir-Cl, 2.5229(10); Ir-Ct^[a], 2.068(4); Ir-N1, 2.197(3); Ir-N2, 2.114(4); Ir-H, 1.53(7); Si-Ir-Cl, 170.51(4); Si-Ir-Ct^[a], 100.47(13); Si-Ir-N1, 79.93(9); Si-Ir-N2, 80.60(11);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

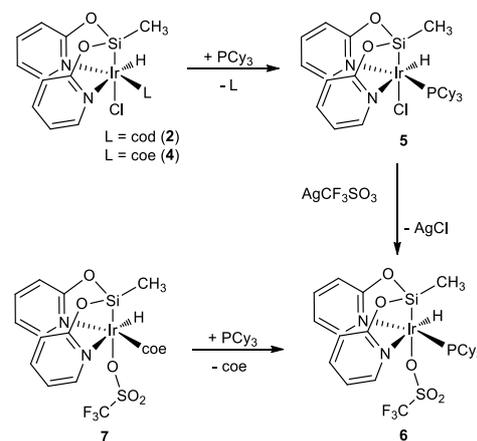
The NSiN ligand in **2** is facially coordinated to the iridium center. Si-Ir-N *cis* angles (Si-Ir-N1, 79.93(9)° and Si-Ir-N2, 80.60(11)°) are deviated from the ideal value of 90° due to the NSiN chelating bonding through the formation of two Ir-Si-O-C-N metallacycles, with ring puckering parameters (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, $\phi = -141.0(15)^\circ$)^[15] typical of envelope E₂ and ²E enantiomeric configurations. The pyridine-N atoms are located *trans* to the hydride and to the η^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.^[8,10,13,14]

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)(η^2 -cod) complexes (in the range 2.062(12)-2.102(2) Å).^[8,13,14] Although the versatility of cyclooctadiene ligand to coordinate to iridium in different forms has been well established,^[16] it tends to chelate to the metal in a η^4 coordination mode. It should be mentioned that the equilibrium between Ir(η^2 -cod) and Ir(η^4 -cod) has been proposed as key step in some catalytic processes.^[17] In addition, to the best of our knowledge only three mononuclear complexes containing an Ir(η^2 -cod) fragment have been crystallographically characterized: [(η^5 -Cp)Ir(η^2 -cod)(NHC)]^[18], [(η^5 -Cp)Ir(η^2 -cod)(biph)]^[19] and [Ir(η^2 -cod)(4-Ph)Tr(NP(ⁱPr)₂)(NHP(ⁱPr)₂)]^[20]. 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 π -back donation from the metal atom.^[18,19]

The ¹H and ¹³C{¹H} NMR spectra of **2** in CD₂Cl₂ support the η^2 -coordination of the cod ligand in solution. Thus, the ¹H NMR spectra of **2** exhibit one multiplet resonance between δ 5.67 and 5.51 ppm, assigned to the two Csp²-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 δ 130.2 and 130.1 ppm, respectively, in the ¹³C{¹H} NMR spectra of **2**. It should be mentioned that ¹³C{¹H} NMR spectra of free 1,5-cyclooctadiene show the olefinic carbon atoms around δ 129 ppm. As it should be expected, the carbon atoms of the coordinated olefinic fragment appear shifted at higher field at δ 68.7 and 65.9 ppm, respectively. The ¹H NMR spectra of species **2** in CD₂Cl₂ also show a singlet resonance corresponding to the hydride ligand at δ -15.35 ppm, which is in the same range of that observed for related species [Ir(H)(Cl)(NSiN)(coe)] (**4**)^[8] with a cyclooctene instead of the cyclooctadiene ligand. The ²⁹Si{¹H} NMR spectra of **2** in CD₂Cl₂ exhibit a singlet at δ 31.3 ppm, which compares well with the corresponding resonances reported for **4**. Compound **2** reacts with one equivalent of silver trifluoromethanesulfonate in CH₂Cl₂, 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).

¹H NMR studies of the reaction of **2** with PCy₃ in C₆D₆ show the resonances due to free cyclooctadiene together with those corresponding to the complex [Ir(H)(Cl)(NSiN)(PCy₃)] (**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 PCy₃ were carried out at preparative level, the corresponding phosphane derivative [Ir(H)(Cl)(NSiN)(PCy₃)] (**5**) was obtained in high yield. The reaction of complex **5** with AgCF₃SO₃ quantitatively gives the triflate derivative [Ir(H)(CF₃SO₃)(NSiN)(PCy₃)] (**6**) (Scheme 2). The triflate derivatives **3** or [Ir(H)(CF₃SO₃)(NSiN)(coe)] (**7**)^[13] also reacts with one equivalent of PCy₃ 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).

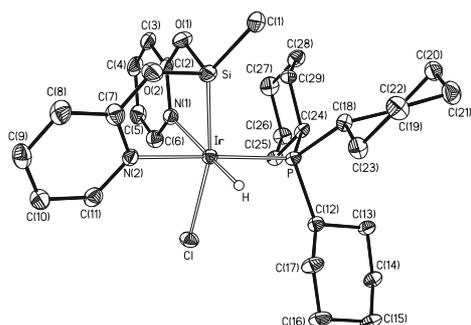
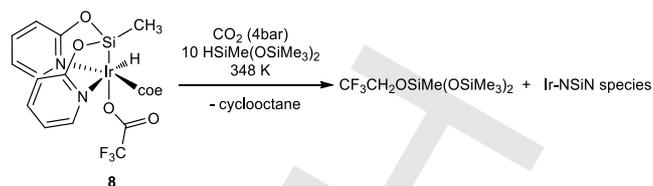


Figure 2. Molecular structure of complex **5**. Selected bond lengths (Å) and angles (°) for compound **5**. Ir-Si, 2.2243(13); Ir-Cl, 2.5099(11); Ir-P, 2.2763(11); Ir-N1, 2.204(4); Ir-N2, 2.172(3); Ir-H, 1.641(10); Si-Ir-Cl, 166.07(4); Si-Ir-P, 99.22(4); Si-Ir-N1, 80.14(10); Si-Ir-N2, 79.07(10); Si-Ir-H, 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.^[10] 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).^[21] 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 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).^[14] 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 CO_2 with $\text{HSiMe(OSiMe}_3)_2$.^[14]

${}^1\text{H}$ NMR studies of the reaction of ECO_2H ($\text{E} = \text{H, CH}_3, \text{Ph}$) with one equivalent of $\text{HSiMe(OSiMe}_3)_2$ in C_6D_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).

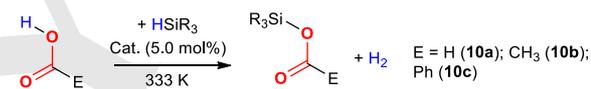


Table 1. Reaction products from the reaction of carboxylic acids with one equivalent of $\text{HSiMe(OSiMe}_3)_2$ in presence of catalytic amounts (5.0 mol%) of Ir-NSiN complexes in C_6D_6 .

Acid	catalyst	T (K)	Silyl ester(%) ^{[a],[b]}
HCOOH	6	328	10a (63.7)
HCOOH	7	328	10a (52.0)
HCOOH	8	328	10a (95.0)
CH_3COOH	7	328	10b (43.5)
CH_3COOH	8	328	10b (84.5)
PhCOOH	7	328	10c (65.0)
PhCOOH	8	328	10c (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).^[8,14,4e] 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.^[4] 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 C_6D_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, CH₃, Ph) with HSiMe(OSiMe₃)₂ in presence of **8** (1.0 mol%) using dry-toluene as solvent were carried out in a micro-reactor.^[22] 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_{1/2}) value of 195, 2000 and 136 h⁻¹ were found for the H₂ generation from the dehydrogenative Si-O coupling of HSiMe(OSiMe₃)₂ 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 CH₃COOH 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.⁴

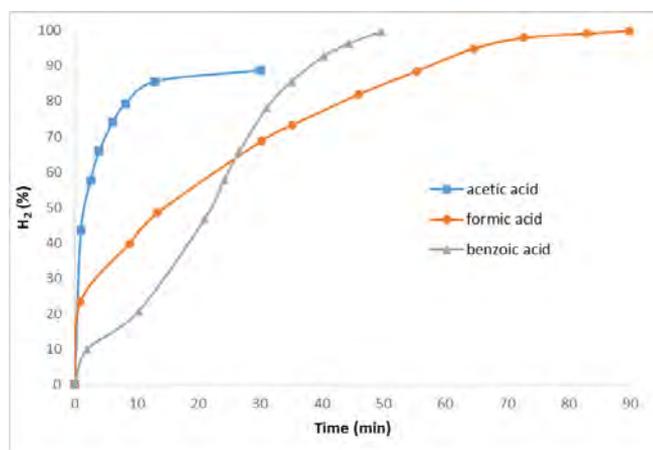


Figure 3. Hydrogen generation (% related to 1.0 mmol as 100%) versus time (min) for the catalytic dehydrogenative Si-O coupling of acetic acid, formic acid and benzoic acid (1.0 mmol) with HSiMe(OSiMe₃)₂ (1.01 mmol) using **8** (1.0 mol%) as catalyst in dry toluene (1.0 mL) at 328 K.

¹H and ²⁹Si{¹H} NMR studies of the **8**-catalyzed reaction of CF₃COOH with HSiMe(OSiMe₃)₂ 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). ²⁹Si{¹H} NMR spectra of the final reaction product show that the intensity of the resonances assigned to CF₃COOSiMe(OSiMe₃)₂ (**10d**) (δ 8.5 and -65.2 ppm)^[4e] 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(OSiMe₃)₂}₂O nor residual CF₃COOH were observed in the ²⁹Si{¹H} and ¹³C{¹H} NMR spectra, respectively. The ¹³C{¹H} NMR spectra of these reaction samples show the presence of two quartet resonances centered at δ 156.8 ppm (²J_{C-F} = 42.1 Hz) and δ 155.6 ppm (²J_{C-F} = 42.6 Hz), high field shifted with respect to the corresponding resonance for CF₃COOH (δ 160.8 ppm, ²J_{C-F} = 43.8 Hz) (Figure S8). These spectra showed another two quartet resonances due CF₃ groups (δ 115.32 ppm, ¹J_{C-F} = 286.2 Hz and δ 115.30 ppm,

¹J_{C-F} = 286.0 Hz) that are low field shifted in comparison with the related resonance observed for trifluoroacetic acid (δ 114.8 ppm, ¹J_{C-F} = 284.5 Hz) (Figure S8). These results confirm the formation of at least two silyl ester species with the CF₃CO₂Si moiety but different from **10d**. This behavior could be explained taking into account that complex **8** promoted the rearrangement of HSiMe(OSiMe₃)₂ in absence of coordinating substrates to give mixtures of HSi(OSiMe₃)₃, HSiMe₂(OSiMe₃) and other hydrosiloxanes.^[14] Indeed, when using HSiEt₃ or HSiMe₂Ph instead of HSiMe(OSiMe₃)₂ under the same reaction conditions the selective **8**-catalyzed silylation of CF₃COOH to give the corresponding silyl-ester CF₃COOSiEt₃ (**10e**) or CF₃COOSiMe₂Ph (**10f**) was achieved in 1.5 h (Table 2). Compounds **10e** and **10f** were characterized by means of ¹H, ²⁹Si and ¹³C{¹H} 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, HSiEt₃ or HSiMe₂Ph, with 3 equivalents of CF₃COOH at 343 K for 10 h.^[23]

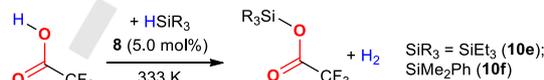
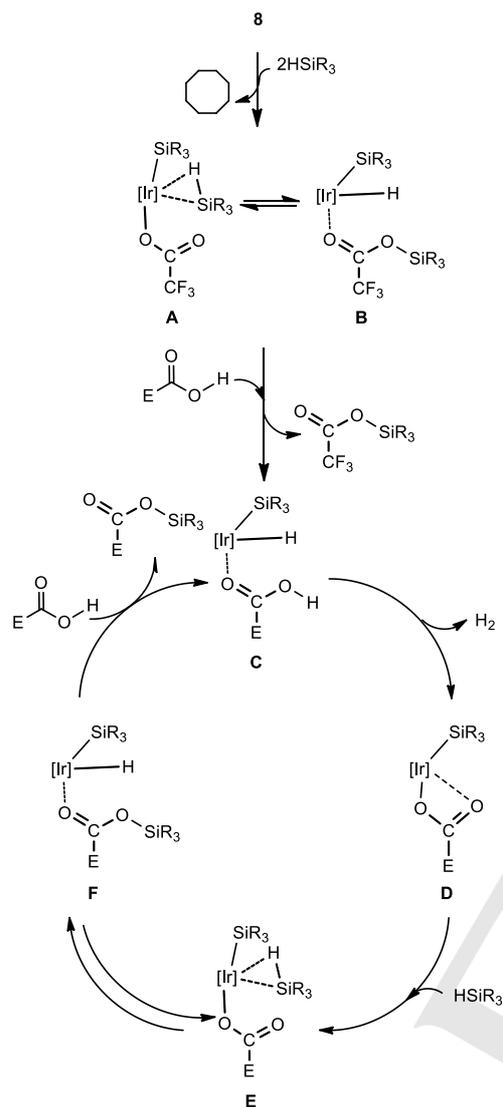


Table 2. Reaction products from the reaction of CF₃COOH with one equivalent of HSiR₃ in presence of catalytic amounts complex **8** (5.0 mol%) in C₆D₆.

Silane	catalyst	T (K)	Silyl ester(%) ^{[a],[b]}
HSiMe(OSiMe ₃) ₂	8	328	mixture of silyl esters
HSiEt ₃	8	328	10e (91.0)
HSiMe ₂ Ph	8	328	10f (93.0)

[a] % calculated by ¹H NMR integration using hexamethylbenzene (0.07 mmol) as internal standard. [b] Data corresponding to the ¹H 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 C₆D₆ 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 CO₂-hydrosilylation processes,^[14] the first step of the reaction could be the formation of species **A**, which is in equilibrium with **B** (Scheme 4).^[14] This is also supported by the experimentally observed formation of cyclooctane. Intramolecular elimination of molecular hydrogen from **C** could afford **D**. Subsequently, the (η²-Si-H)-coordination of a molecule of silane^[14] 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 κ¹-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.^[14]



Scheme 4. Mechanism proposal for the **8**-catalyzed dehydrogenative silylation of carboxylic acids. [Ir] = [Ir(*fac*-NSiN)]; E = H, CH₃ or Ph).

Conclusions

The potential of [Ir(μ -Cl)(cod)]₂ 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)(η^2 -cod)] (**2**) reacts with silver triflate to afford the ionic species [Ir(H)(NSiN)(η^4 -cod)] [CF₃SO₃] (**3**). The uncommon η^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 PCy₃ evidenced that the olefin ligand is easily replaced by the phosphane to give [Ir(H)(X)(NSiN)(PCy₃)] (X = Cl, CF₃SO₃) complexes.

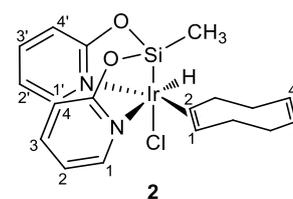
On the other hand, the trifluoroacetate derivative [Ir(H)(CF₃CO₂)(NSiN)(coe)] (**8**) has proven to be an efficient

catalyst for the selective dehydrogenative silylation of ECOOH (E = H, CH₃ and Ph) to give the corresponding silylester. Conversely, when the reaction with CF₃COOH was studied under the same reaction conditions the expected silylester was obtained as minor product together with a mixture of not identified compounds containing the CF₃CO₂Si moiety. This behaviour could be due to **8**-catalyzed rearrangement of HSiMe(OSiMe₃)₂. Indeed, the reaction of CF₃COOH with HSiEt₃ or HSiMe₂Ph in presence of catalytic amounts of **8** quantitatively affords the corresponding silylester CF₃COOSiEt₃ or CF₃COOSiMe₂Ph, 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 (δ) are reported in ppm and coupling constants (*J*) are reported in Hz to apparent peak multiplications. ¹H-¹H-COSY, ¹³C-APT, ¹H/¹³C HSQC, ¹H/¹³C HMBC and ¹H/²⁹Si HMBC sequences were used for help in the assignments of the ¹H and ¹³C spectra. Compound **1** and the Ir-NSiN precursors **4**,^[8] **7**^[8] and **8**^[12] were prepared according to the reported method. RCO₂H (R = H, CH₃, CF₃ and Ph) and PCy₃, were purchased from commercial sources and used without further purifications.

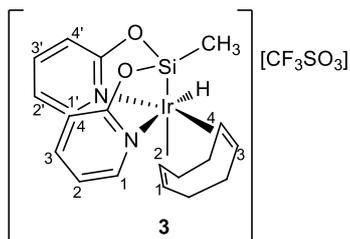
Preparation of IrHCl(η^2 -cod)(NSiN) (2**).** A solution of [IrCl(cod)]₂ (0.202 g, 0.30 mmol) in 7 mL of dichloromethane was treated with 1.0 equiv of bis-(2-(oxy)pyridine)methylsilane **1** (0.140 g, 0.60 mmol) and stirred at room temperature for 3 h. Then, the solvent was removed in vacuum. The addition 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 C₁₉H₂₄N₂IrClO₂Si (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]⁺ (100%).



¹H NMR plus COSY and NOESY (400.13 MHz, CD₂Cl₂, 298 K): δ 9.53 (ddd, *J*_{H-H} = 6.1, 1.9, 0.6, 1H, H¹_{py}), 9.25-9.22 (m, 1H, H¹_{py}), 7.71 (ddd, *J*_{H-H} = 8.3, 7.2, 2.0, 1H, H³_{py}), 7.65 (ddd, *J*_{H-H} = 8.4, 7.2, 1.9, 1H, H³_{py}), 7.01-6.95 (m, 2H, H_{py} (H₄ + H₂)), 6.93 (ddd, *J*_{H-H} = 8.3, 1.3, 0.6, 1H, H⁴_{py}), 6.79 (ddd, *J*_{H-H} = 7.3, 6.1, 1.4, 1H, H²_{py}), 5.67-5.51 (m, 2H, =CH^{3,4}_{cod}), 4.61-4.54 (m, 1H, =CH²_{cod}), 3.83-3.75 (m, 1H, =CH¹_{cod}), 2.60-1.32 (m, 8H, -CH₂^{2-cod}), 0.69 (s, SiCH₃, 3H), -15.35 (s, 1H, Ir-H). ¹³C-APT NMR plus HMBC and HSQC (100.4 MHz, CD₂Cl₂, 298 K): δ 167.6 and 165.8 (both s, C¹_{ipso-py} and C_{ipso-py}, respectively), 150.9, 148.1, 142.1 and 141.7 (all s, C¹_{py}, C¹_{py}, C³_{py} and C³_{py}, respectively), 130.2 and 130.1 (both s, =CH^{3,4}_{cod}), 118.3, 117.4, 112.7 and 112.0 (all s, C²_{py}, C²_{py}, C⁴_{py}, C⁴_{py},

respectively), 68.7 and 65.9 (both s, =CH²_{cod} and =CH¹_{cod}, respectively), 35.0, 32.7, 31.4 and 30.8 (all s, -CH₂-_{cod}), -1.0 (s, SiCH₃). ²⁹Si{¹H} NMR (59.6 MHz, CD₂Cl₂, 298 K): δ 31.3 (s, SiCH₃).

Preparation of [IrH(η⁴-cod)(NSiN)(CF₃SO₃) (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 C₂₀H₂₄N₂SF₃IrO₅Si (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, CD₂Cl₂, 298 K): 8.84 (ddd, *J*_{H-H} = 6.0, 1.6, 0.8, 1H, H¹_{py}), 7.96 (ddd, *J*_{H-H} = 6.1, 1.3, 0.4, 1H, H¹_{py}), 7.90 (ddd, *J*_{H-H} = 8.4, 7.3, 1.8, 1H, H³_{py}), 7.80 (ddd, *J*_{H-H} = 8.5, 7.3, 1.8, 1H, H³_{py}), 7.19 (ddd, *J*_{H-H} = 7.3, 6.0, 1.3, 1H, H²_{py}), 7.10-7.08 (m, 1H, H⁴_{py}), 7.08-7.06 (m, 1H, H⁴_{py}), 7.00 (ddd, *J*_{H-H} = 7.4, 6.1, 1.4, 1H, H²_{py}), 5.97-5.91 (m, 1H, =CH²_{cod}), 4.71-4.64 (m, 1H, =CH⁴_{cod}), 4.54-4.62 (m, 1H, =CH¹_{cod}), 3.74-3.69 (m, 1H, =CH³_{cod}), 3.00-1.84 (m, 8H, -CH₂-_{cod}), 0.79 (s, SiCH₃, 3H), -15.47 (s, 1H, Ir-H). ¹³C-APT NMR plus HMBC and HSQC (100.4 MHz, CD₂Cl₂, 298 K): δ 167.3 and 166.1 (both s, C¹_{ipso-py} and C_{ipso-py}, respectively), 152.1, 149.1, 144.0 and 143.8 (all s, C¹_{py}, C¹_{py}, C³_{py} and C³_{py}, respectively), 121.1, 120.3, 114.0 and 113.7 (all s, C²_{py}, C²_{py}, C⁴_{py}, C⁴_{py}, respectively), 112.5, 105.8, 69.2 and 69.0 (all s, =CH²_{cod}, =CH¹_{cod}, =CH³_{cod}, =CH⁴_{cod}, respectively), 35.9, 35.1, 31.5 and 22.4 (all s, -CH₂-_{cod}), -1.5 (s, SiCH₃). ²⁹Si{¹H} NMR (59.6 MHz, CD₂Cl₂, 298 K): δ 51.5 (s, SiCH₃). ¹⁹F NMR (282.4 MHz, CD₂Cl₂, 298 K): δ -78.8 (s, CF₃).

Preparation of [IrH(Cl)(NSiN)(PCy₃)] (5). Complex **2** (0.200 g, 0.35 mmol) and PCy₃ (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 C₂₉H₄₅ClIrN₂O₂PSi: 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, CDCl₃): δ 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). ³¹P{¹H} NMR (121 MHz, 298 K, C₆D₆) δ 15.0 (s, PCy₃). ¹³C-APT plus HSQC and HMBC NMR (75 MHz, 298 K, CDCl₃): δ 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-PCy₃), 29.3, 27.6, 26.7 (CH₂-Cy). ²⁹Si NMR (DEPT 45, 60 MHz, 298 K, C₆D₆): δ 41.3 (d, *J*_{Si-P} = 14.9 Hz, SiMe). ESI⁺: 705.2 [M⁺-Cl, 100%].

Preparation of [IrH(CF₃SO₃)(NSiN)(PCy₃)] (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, CD₂Cl₂): δ 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). ¹³C-APT NMR plus HSQC and HMBC (75 MHz, CD₂Cl₂): δ 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, ³*J*_{P-C} = 2.5 Hz, CH-py), 112.8 and 112.3 (s, CH-py), 37.0 (d, ¹*J* = 31.4 Hz, P-C), 30.1 (d, ⁴*J* = 2.5 Hz, Cy), 29.3 (br s, Cy), 27.9 (d, ³*J* = 11.0 Hz, Cy), 27.7 (d, ³*J* = 10.8 Hz, Cy), 27.0 (s, Cy), 0.20 (s, SiMe). ¹H-²⁹Si-HMBC NMR (C₆D₆): δ 15.3 (SiMe).

General procedure for the NMR scale reactions of equimolar mixtures of HSiMe(OSiMe₃)₂ with carboxylic acids. A NMR tube was charged with the precursor catalyst **7** or **8** (3.5 · 10⁻³ mmol) and C₆D₆ (0.5 mL). After which, HSiMe(OSiMe₃)₂ (22 μL, 0.07 mmol) and the corresponding carboxylic acid (0.07 mmol) and hexamethylbenzene as internal standard (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, C₆D₆): δ 1.70 (s, 3H, CH₃), 0.37 (s, 3H, SiMe), 0.20 (s, 18H, OSiMe₃). ¹³C-APT NMR plus HSQC and HMBC (75 MHz, C₆D₆): δ 169.7 (s, CO₂), 22.3 (s, CH₃), 1.6 (s, OSiMe₃), -2.6 (s, SiMe). ²⁹Si{¹H} plus ¹H-²⁹Si-HMBC NMR (60 MHz, 298 K, C₆D₆): δ 10.0 (s, OSiMe₃), -58.2 (s, SiMe).

Selected data for 10c. ¹H NMR (300 MHz, 298 K, C₆D₆): δ 8.20 (m, 2H, Ph), 7.06 (m, 3H, Ph), 0.48 (s, 3H, SiMe), 0.23 (s, 18H, OSiMe₃). ¹³C-APT NMR plus HSQC and HMBC (75 MHz, C₆D₆): δ 165.6 (s, CO₂), 133.1 (s, CH, Ph), 131.7 (s, C_{ipso}, Ph), 130.5 (s, CH, Ph) 128.5 (s, CH, Ph), 1.7 (s, OSiMe₃), -2.5 (s, SiMe). ²⁹Si{¹H} NMR (60 MHz, 298 K, C₆D₆): δ 10.3 (s, OSiMe₃), -57.0 (s, SiMe).

Selected data for 10e. ¹H NMR (400 MHz, 298 K, C₆D₆): δ 0.56 (q, 6H, ³*J*_{H-H} = 7.7, CH₂), 0.78 (t, 9H, ³*J*_{H-H} = 7.7, CH₃). ¹³C{¹H} NMR plus HSQC (100 MHz, C₆D₆): δ 156.5 (q, ²*J*_{C-F} = 42.0, CO₂), 115.2 (q, ¹*J*_{C-F} = 286.5, CF₃), 5.8 (s, CH₃), 4.0 (s, CH₂). ²⁹Si{¹H} NMR (99.0 MHz, 298 K, C₆D₆): δ 34.5 (s). ¹⁹F{¹H} NMR (282 MHz, 298 K, C₆D₆): δ -75.8 (s).

Selected data for 10f. ¹H NMR (400 MHz, 298 K, C₆D₆): δ 7.42 (m, 2H, Ph), 7.12 (m, 3H, Ph), 0.30 (s, 6H, SiMe₂). ¹³C{¹H} NMR plus HSQC (100 MHz, C₆D₆): δ 156.7 (q, ²*J*_{C-F} = 42.0, CO₂), 114.9 (q, ¹*J*_{C-F} = 282.2, CF₃), 128.5, 131.3 and 133.4 (s, CH, Ph), 133.1 (s, C_{ipso}, Ph), -2.5 (s, SiMe₂). ²⁹Si{¹H} NMR (99.0 MHz, 298 K, C₆D₆): δ 20.5 (s). ¹⁹F{¹H} NMR (282 MHz, 298 K, C₆D₆): δ -75.9 (s).

General procedure for the measurement of H₂ evolution from the 1-catalyzed reactions of carboxylic acids with HSiMe(OSiMe₃)₂. The reactions were carried out in a *Man on the Moon X102 kit*® 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(OSiMe₃)₂ (281 μL, 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 μL; CH₃, 57.2 μL; 1.0 mmol) was added with a syringe. In the case of PhCOOH, 1.0 mmol of

HSiMe(OSiMe₃)₂ (281 μ 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 H₂ 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 α radiation ($\lambda = 0.71073$ Å) using narrow ω rotations (0.3°) on a Bruker APEX DUO (compound **2**) or a Bruker SMART APEX diffractometer (compound **5**). SAINT+^[24] and SADABS^[25] 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^[26] and refined by full-matrix least-squares refinement in F^2 with SHELXL-2014^[27] included in Wingx package.^[28] 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. C₂₉H₂₄ClIrN₂O₂Si $M = 568.14$; yellow prism, 0.070 x 0.082 x 0.082 mm³; monoclinic $P2_1/c$; $a = 9.8151(7)$, $b = 12.3333(8)$, $c = 16.2337(11)$ Å, $\beta = 90.1270(10)^\circ$; $V = 1965.1(2)$ Å³; $Z = 4$; $\rho_{\text{calc}} = 1.920$ g cm⁻³; $\mu = 7.007$ cm⁻¹; 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⁻³. At the end of the refinement five residual density peaks bigger than 1 e Å⁻³ have been found. They are close to iridium atom and reveal bonding effects between the metal and the ligands.

Crystal data for 5. C₂₉H₄₅ClIrN₂O₂PSi $M = 740.38$; colorless prism, 0.060 x 0.160 x 0.175 mm³; monoclinic $P2_1/c$; $a = 11.7418(8)$, $b = 12.1443(8)$, $c = 21.6800(14)$ Å, $\beta = 104.6250(10)^\circ$; $V = 2991.3(3)$ Å³; $Z = 4$; $\rho_{\text{calc}} = 1.644$ g cm⁻³; $\mu = 4.675$ cm⁻¹; 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⁻³. At the end of the refinement five residual density peaks bigger than 1 e Å⁻³ 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.

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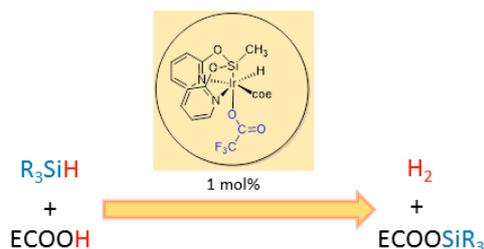
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Layout 1:

FULL PAPER

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



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