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## Iridium(I) complexes with bidentate NHC ligands as catalysts for dehydrogenative directed C-H silylation

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**A series of (NHC)(cod)Ir(I) complexes bearing NHC-carboxylate ligands were efficiently synthesized and fully characterized. Their solid-state structures confirmed the bidentate coordination mode of these LX-type NHC ligands. These unprecedented iridium(I) complexes demonstrated efficient catalytic activities in dehydrogenative directed C-H silylation of arenes, and allowed for excellent *ortho*-selectivity control with aromatic silylating agents.**

Organosilicon compounds exhibit remarkable physicochemical properties that are of interest for applications in organic synthesis, in chemical biology and in material science.<sup>1</sup> Therefore, the development of new efficient methods to access organosilanes from easily accessible raw materials is an important research focus in modern organic chemistry. As an alternative to traditional methods employing stoichiometric amount of metals and to cross-coupling approaches involving pre-functionalized precursors, transition metal-catalyzed direct cross-dehydrogenative coupling of C-H and Si-H bonds to selectively form new C-Si bonds constitutes an atom- and step-efficient approach.<sup>2</sup> The directing-group assisted dehydrogenative C-H bond silylation, which can be catalyzed by a variety of transition metal-based systems, has emerged in recent years as a robust strategy for regioselective functionalization.<sup>3</sup> Among transition metals, iridium is recognized for its high performance in catalyzing dehydrogenative C-H silylation transformations, especially when in association with nitrogen-based ligand.<sup>4</sup> Furthermore, and despite the established advantage of *N*-Heterocyclic Carbene (NHC) ligand in transition-metal catalysis,<sup>5</sup> including for

C-H bond functionalization,<sup>6</sup> the use of such ligands in C-H silylation is very scarce and limited to two independent reports by Mashima and co-workers in 2013 on the one hand,<sup>7</sup> and Oro and co-workers in 2017 on the other (Figure 1).<sup>8</sup> Herein, we described the synthesis of new iridium(I) complexes with bidentate NHC ligands complexes and their application as efficient catalysts for the *ortho*-selective dehydrogenative directed C-H silylation of arenes with bulky aromatic silylating agents.

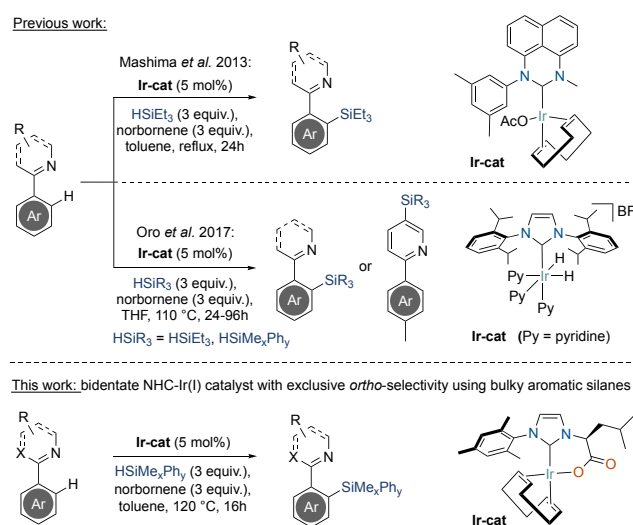


Figure 1. State of the art of NHC-iridium catalysts in directed C-H silylation.

Precursors of unsymmetrical bidentate NHC-carboxylate are accessible through a straightforward multicomponent synthesis which we recently developed.<sup>9</sup> Previous reports have evidenced that these bidentate LX type ligands could strongly bind transition metals such as iridium(III),<sup>10</sup> rhodium(I/III)<sup>11</sup> and ruthenium(II)<sup>12</sup> to form robust cyclometallated complexes that notably demonstrated efficient catalytic activities in C-H borylation under thermic and photocatalytic conditions.<sup>11,12</sup> In a continued effort to design novel NHC-based transition-metal catalysts for C-H bond functionalization reactions, we investigated the synthesis of well-defined iridium(I) complexes combining an electron rich bidentate NHC-carboxylate ancillary

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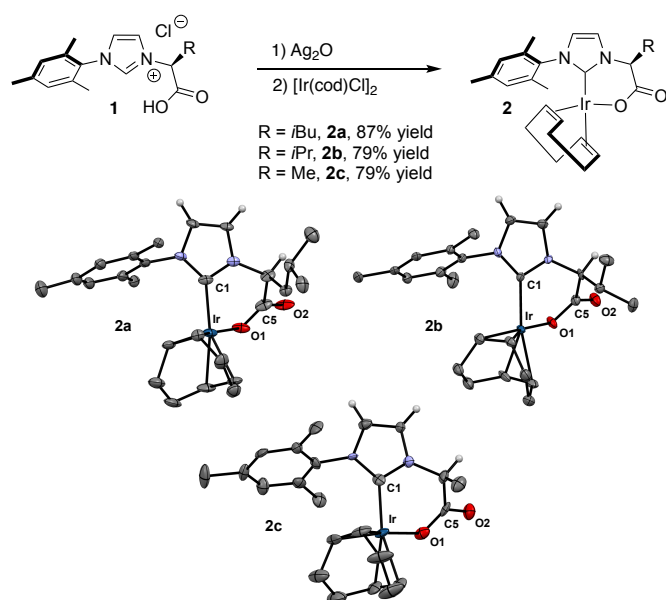
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ligand and the labile 1,5-cyclooctadiene (cod) ligand. To this end, a series of amino acid-based NHC ligand precursors **1** were converted to their corresponding silver-intermediates and subsequently transmetalated to  $[\text{Ir}(\text{cod})\text{Cl}]_2$  to afford the desired (NHC)Ir(cod) complexes in good yields (Figure 2). Complexes **2a**, **2b** and **2c**, respectively derived from *L*-leucine, *L*-valine and *L*-alanine, were fully characterized and their structures could be confirmed by X-ray diffraction analysis. Selected geometrical parameters are shown in Table 1. These three complexes exhibit a slightly distorted square planar geometry without noticeable influence of the substituent at the stereogenic carbon center of the 5-membered cyclometallated NHC-carboxylate “LX type” ligands; as evidenced by the C1-Ir-O1 trigonal angles of 85.5(5)°, 86.27(18)° and 86.2(3)° for **2a**, **2b** and **2c**, respectively. Moreover, the “X-type” ligand nature of the carboxylate arm is attested by the distance between the oxygen atom (O1) that binds to the iridium center and the carboxylate carbon atom (C5) being longer than the bond length of O2-C5, in each case.<sup>10</sup>



**Figure 2.** Synthesis of (NHC)(cod)Ir(I) complexes (top). X-ray crystal structures of **2a** (25% probability ellipsoids) and **2b-c** (50% probability ellipsoids). Most hydrogen atoms are omitted for clarity.

**Table 1.** Selected bond lengths (Å) and angles (degree) for complexes **2a-c**

Bond length (Å)	(S) <b>2a</b>	(S) <b>2b</b>	(S) <b>2c</b>
Ir-C1	2.052(13)	2.054(5)	2.059(10)
Ir-O1	2.069(11)	2.073(4)	2.080(7)
O1-C5	1.26(2)	1.291(7)	1.284(12)
O2-C5	1.24(2)	1.221(7)	1.221(12)
Angle (°)	(S) <b>2a</b>	(S) <b>2a</b>	(S) <b>2a</b>
O1-Ir-C1	85.5(5)	86.27(18)	86.2(3)

With the new complexes in hand, we decided to investigate their catalytic activity in the dehydrogenative silylation of aromatic C–H bonds directed by a pyridine group using a hydrosilane as silylating reagent (Table 2). First, at 120 °C in

**Table 2.** Optimization studies.<sup>[a]</sup>

Entry	Silane	Catalyst	H <sub>2</sub> -acceptor	Solvent	Temp. (°C)	Yield (%) <sup>[b]</sup>
1	Et <sub>3</sub> SiH	<b>2a</b>	norbornene	toluene	120	49 <sup>[c]</sup>
2	Et <sub>3</sub> SiH	<b>2a</b>	-	toluene	120	nd <sup>[d]</sup>
3	Et <sub>3</sub> SiH	-	norbornene	toluene	120	nd <sup>[d]</sup>
4	Et <sub>3</sub> SiH	<b>2a</b>	norbornene	THF	80	14
5	Et <sub>3</sub> SiH	<b>2a</b>	norbornene	2-MeTHF	90	8
6	Et <sub>3</sub> SiH	<b>2a</b>	norbornene	neat	120	36
7	Et <sub>3</sub> SiH	<b>2a</b>	cod	toluene	120	10
8	Et <sub>3</sub> SiH	<b>2a</b>	neohexene <sup>[e]</sup>	toluene	120	40
9	Et <sub>3</sub> SiH	<b>2a</b>	norbornadiene	toluene	120	22
10	Me <sub>2</sub> PhSiH	<b>2a</b>	norbornene	toluene	120	64 <sup>[c]</sup>
11	MePh <sub>2</sub> SiH	<b>2a</b>	norbornene	toluene	120	82
12	Ph <sub>3</sub> SiH	<b>2a</b>	norbornene	toluene	120	74 <sup>[c]</sup>
13	MePh <sub>2</sub> SiH	<b>2b</b>	norbornene	toluene	120	72
14	MePh <sub>2</sub> SiH	<b>2c</b>	norbornene	toluene	120	74
15	MePh <sub>2</sub> SiH	$[\text{Ir}(\text{cod})\text{Cl}]_2$	norbornene	toluene	120	49
16 <sup>[f]</sup>	MePh <sub>2</sub> SiH	(IMes)Ir(cod)Cl	norbornene	toluene	120	16

[a] Reaction conditions: 2-phenylpyridine (**3a**, 0.2 mmol), catalyst (**2**, 0.01 mmol), HSiR<sub>3</sub> (0.6 mmol), H<sub>2</sub> acceptor (0.6 mmol), solvent (1 mL) in preheated oil bath at stated temperature for 16 hours under Ar. [b] %Yield was determined by <sup>1</sup>H NMR using 1,3,5-trimethylbenzene as an internal standard. [c] isolated yields of **4a**, **4b**, and **4d** are 47, 59, and 68%, respectively (See SI). [d] not detected. [e] 3,3-dimethylbut-1-ene. [f] IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene.

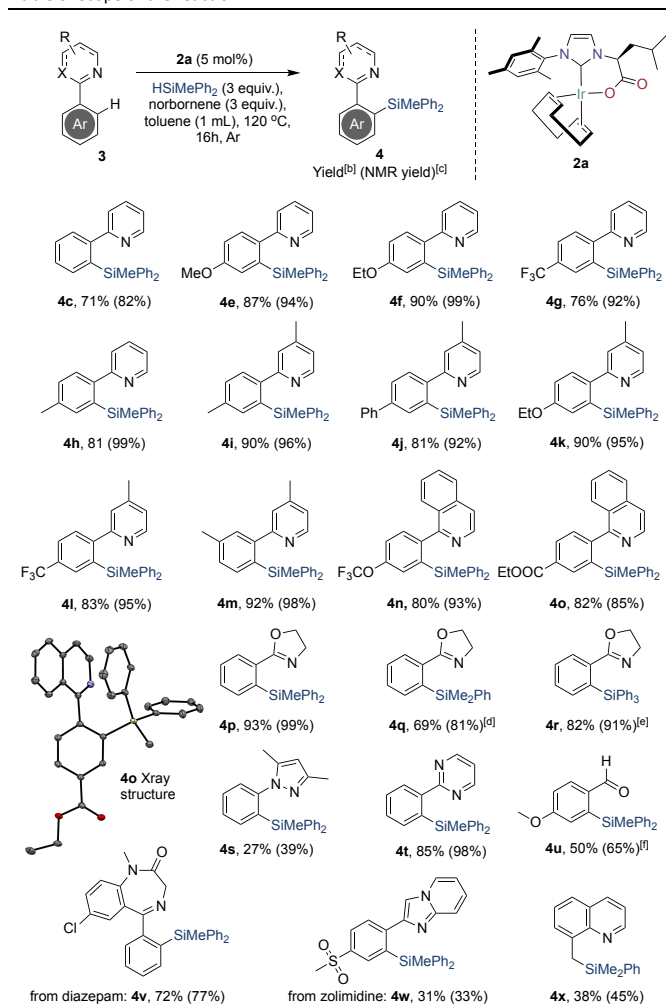
toluene and using norbornene as hydrogen acceptor, complex **2a** bearing the NHC ligand derived from *L*-leucine furnished 40% of the desired *ortho* triethylsilylated product **4a** (entry 1). In the absence of either hydrogen acceptor (entry 2) or iridium catalyst (entry 3) no desired product was detected. When changing the reflux conditions from toluene to THF or 2-MeTHF a significant drop of catalytic activity was observed (entries 4 & 5). The reaction performed well under neat conditions but with reduced yield compared to the use of toluene as solvent (entry 6), whose potential competitive functionalization was not observed.<sup>13</sup> Replacement of norbornene by alternative hydrogen acceptor such as 1,5-cyclooctadiene, neohexene or norbornadiene did not lead to improved catalytic activities (entries 7-9). Interestingly, the use of dimethylphenylsilane as silylating reagent had a beneficial impact on the catalytic process affording 64% yield of the *ortho*-silylated product **4b** (entry 10). A further improved of the silylation process could be achieved with the larger methylphenylsilane coupling partner to reach 82% yield of product **4c**. However, a further increase of the bulkiness of the silylating agent had a detrimental effect on the dehydrogenative coupling process resulting in a reduced yield (entry 12). Under the optimal conditions using

methyldiphenylsilane, the use of complex **2b** or **2c** could not outperform the catalytic activities reached by complex **2a** (entry 13 & 14). Finally, the ligand free [Ir(cod)Cl]<sub>2</sub> and monodentate NHC-based (IMes)Ir(cod)Cl catalysts exhibited modest activities to afford product **4c** in respectively 49% and 16% yield (entries 15 & 16), highlighting the beneficial contribution of the bidentate NHC ligand for the transformation.

To test the viability of this method, we first investigated the scope of the silylation reaction with respect to 2-arylpdridine based substrates (Table 3). Aryl groups bearing a substituent in *para*-position were well tolerated and both electron-poor and electron-rich substrates afforded the desired *ortho*-silylated products (**4e-4h**) in very good yields. Noteworthy is the exclusive *ortho*-selectivity observed in all cases, without detectable competitive C<sub>5</sub>-H bond silylation of the pyridine directing group.<sup>14</sup> Similar excellent results were also obtained when using 4-methylpyridine as directing group, with isolated yields of the *ortho*-silylated products varying from 81 to 92% independently of the electronic nature of the *para*- or *meta*-substituent on the aryl moiety (**4i-4m**). The isoquinoline-group was also amenable to direct the silylation in *ortho*-position of electronically different aryl fragments (**4n-4o**). Furthermore, excellent catalytic activities were achieved when using oxazole as a directing group, affording 93% isolating yield of the coupling product **4p**. Interestingly, dehydrogenative silylation of 2-phenyloxazole with dimethylphenylsilane and triphenylsilane also performed well to produce **4q** and **4r** in 69 and 82% isolated yield, respectively.<sup>15</sup> On the other hand, while the use of 3,5-dimethylpyrazole as a more sterically congested directing group led to a noticeable drop of efficiency providing **4s** in low 27% isolated yield, almost full conversion of 2-phenylpyrimidine was achieved to obtain the corresponding silylated product **4t** in 85% isolated yield. Pleasingly, the reaction also proved compatible with the use of aldimine as removal directing group affording the selective *ortho*-silylated aldehyde **4u** in good 50% isolated yield. In addition, the late-stage silylation of pharmaceuticals attempted on the anxiolytic diazepam,<sup>16</sup> and on the gastroprotective drug zolimidine,<sup>17</sup> led to 72% and 31% isolated yield of the desired silylated drugs **4v** and **4w**, respectively. Finally, silylation of sp<sup>3</sup>C-H bond of 8-methylquinoline could proceed quite satisfactorily with 45% yield to furnish 38% of the corresponding isolated product **4x**.

To gain some insight into the mechanism of the present reaction, we performed a series of stoichiometric reactions in the presence of complex **2a** in *d*<sub>8</sub>-toluene. First, when reacting **2a** with **3a** under increasing temperature (up to 120°C), no cyclometalated intermediate or noticeable decomposition of the NHC-iridium complex could be detected by <sup>1</sup>H NMR spectroscopy.<sup>8</sup> Moreover, the same observation was made in the presence of additional norbornene, demonstrating a total lack of reactivity of complex **2a** in the absence of silylating agent. However, tentatives to isolate or characterize a hydrido-silane based complex resulting from the reaction of **2a** with HSiMePh<sub>2</sub> were also unsuccessful, preventing from identifying transient iridium intermediate species that would be involved in the catalytic C-H silylation process.<sup>7,18</sup> On the other hand, the kinetic profiles for the silylation of **3a** and its pentadeuterated

Table 3. Scope of the reaction.<sup>[a]</sup>



[a] Reaction conditions: **3** (0.2 mmol), **2a** (0.01 mmol), Ph<sub>2</sub>MeSiH (0.6 mmol), norbornene (0.6 mmol), toluene (1 mL) in preheated oil bath at 120°C for 16 hours under Ar. [b] Isolated yield (%). [c] yield (%) determined by <sup>1</sup>H NMR using 1,3,5-trimethylbenzene as an internal standard. [d] PhMe<sub>2</sub>SiH (0.6 mmol). [e] Ph<sub>3</sub>SiH (0.6 mmol). [f] from *N*-(4-methoxybenzylidene)aniline and after hydrolysis (HCl, 3M).

analogue **d<sub>5</sub>-3a** were separately recorded in *d*<sub>8</sub>-toluene and a striking difference was observed. In fact, in the case of **d<sub>5</sub>-3a**, an induction period concomitant with a rapid deuterium-hydrogen exchange at *ortho*-positions was observed before the C-Si bond formation reaction takes place with a rate constant similar to that independently measured for **3a** (Figures 3 & S6-9).<sup>12,19,20</sup> Moreover, we also compared the rates for the functionalization of **3a** using H-SiMePh<sub>2</sub> or D-SiMePh<sub>2</sub> as silylating agent, and a *K<sub>H</sub>/K<sub>D</sub>* value of 2.0 was observed in this case (Figures 3 & S9-S10). Taken together, these results support the reversibility of the *ortho* C-H bond cleavage step and suggest that the Si-H bond breaking, and not the C-H bond, is involved in the rate-determining step.<sup>20,21</sup> Finally, the catalytic silylation of substrate **3a** conducted in the presence of access butylated hydroxytoluene (BHT), TEMPO [2,2,6,6-tetramethylpiperidine-1-oxyl], or mercury metal proceeded without noticeable decrease of activities (Figures S11-12), implying that both the involvement of free radical processes or heterogeneous catalysis are unlikely to be operative.

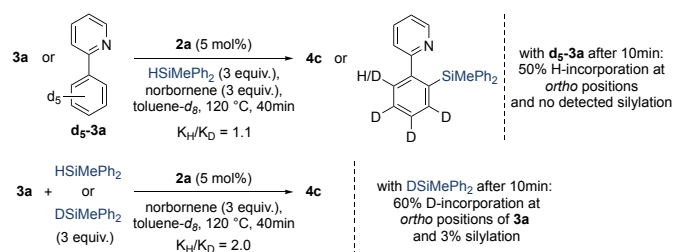


Figure 3. Kinetic isotope effects for parallel reactions

In summary, a series of three new chiral iridium(I) complexes bearing LX-type bidentate NHC-carboxylate ligands derived from amino-acids were synthesized in good yields and fully characterized, including their solid-state structures. These complexes demonstrated excellent catalytic activities in *ortho*-directed dehydrogenative silylation of  $sp^2$  C-H and  $sp^3$  C-H bonds in the presence of norbornene as hydrogen acceptor. Despite the use of bulky aromatic silylating agents, the developed catalytic system allowed for a complete control of the regioselectivity of the silylation reaction and prevents competitive functionalization of both the heterocyclic directing group and the aromatic solvent.

## Author Contributions

RM, MGC, TK, CB, JT, and EB performed experimental investigations; SML realized X-ray diffraction analysis; SY, RC, MM, JBS supervised; OB conceptualized and supervised this work and wrote the article.

## Conflicts of interest

There are no conflicts to declare

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