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# Alkene as Hydrogen Trapper to Control the Regio-Selective Ruthenium(II) Catalyzed *ortho* C-H Silylation of Amides and Anilides

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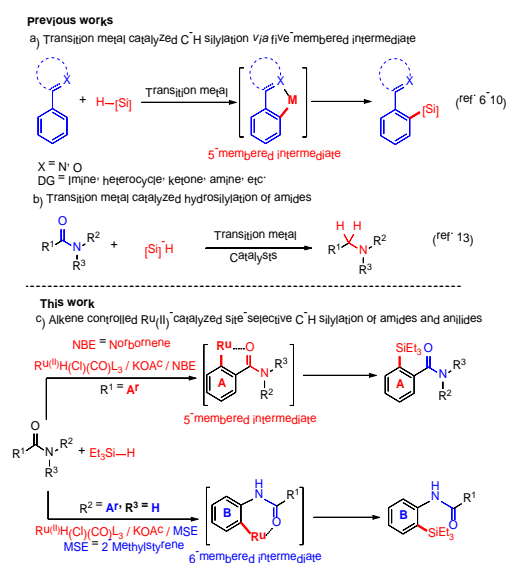
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A convenient and practical pathway to versatile silylated amides and anilides is described via efficient and selective ruthenium(II) catalyzed *ortho* C-H silylation. Both amides and anilides were successfully silylated with good functional group tolerance and high regioselectivity. Different alkenes as the hydrogen acceptors played a crucial role for these two catalytic systems. Unexpectedly, two pathways for RuHCl(CO)(PPh<sub>3</sub>)<sub>2</sub>/KOAc catalyzed C-H silylation involving 5-membered ruthenacycle with arylamides and 6-membered ruthenacycle with arylanilides, take place depending on the nature of the alkene as hydrogen trapper.

Development of efficient regioselective C-H silylation reactions to introduce a reactive silyl group into various organic molecules has an important value because organosilane compounds are important structural units existing in drug development, advanced material,<sup>1</sup> and life sciences.<sup>2</sup> Such silylated derivatives are also valuable key synthetic intermediates for chemical transformations.<sup>3</sup> Recently, there has been a growing interest on the application of organosilicon compounds such as disila-AM580, TMS-phenylalanine, and asparagine mimic in medicinal chemistry.<sup>4</sup> Compared to the classical electrophilic silylation with TMSOTf or TMSCl reagents, direct C-H bond silylation has been shown to be a straightforward method to synthesize functional organosilicon compounds owing to their atom- and step- economy.<sup>5</sup> On the other hand, the direct silylation of C-H bonds is highly useful to afford reactive C-Si bonds allowing important further transformations, such as C-C, C-O, C-N and C-X bond formation, which cannot be obtained directly via classical metal catalyzed C-H bond functionalization.<sup>5b</sup>

In recent years, pioneer examples of transition metal catalyzed *ortho* C-H silylations using oxygen,<sup>6</sup> amine,<sup>7</sup> imine,<sup>8</sup> phosphine<sup>9</sup> and

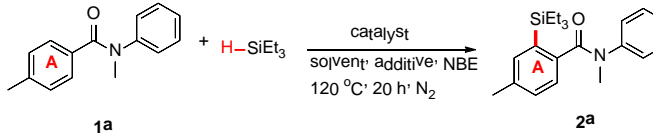
N-containing heterocycles<sup>10</sup> as directing groups have been explored involving a five-membered cyclometallation mechanism (Scheme 1a), which is known to be both kinetically and thermodynamically favored by contrast to its six-membered counter parts.<sup>11</sup> However, only few reports<sup>12</sup> describe the direct regioselective synthesis of silyl-functionalized amides *via* intermolecular *ortho* C-H silylation with amide function as the directing group. Indeed, the C-H silylation of aryl amides is still challenging due to the competition between the C-H silylation of the aryl moiety and the hydrosilylation of amide carbonyl, as amides can be easily reduced to amines using hydrosilane as the reductant with transition metal catalytic system (Scheme 1b).<sup>13</sup> By contrast, the more challenging *ortho* C-H silylation of aryl anilides [ArNHR<sup>1</sup>COR<sup>2</sup>] is expected to take place *via* a six-membered cyclometallation mechanism. In this context, the intermolecular C-H silylation of aryl amides and aryl anilides *via* the controlled formation of five- or six-membered cyclometallate intermediate *via* C-H bond activation has not been demonstrated so far.



**Scheme 1.** Transition metal catalyzed reactions between amides and silanes

Following our previous contributions on Ru(II) catalyzed C-H silylation of *N*-heterocycles,<sup>14</sup> herein, we report an alkene controlled regio-selective aryl *ortho* C-H silylation of (hetero)aryl amides by using a RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>/KOAc catalytic system in the presence of NBE = norbornene, and of (hetero)aryl anilides with the RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>/KOAc catalytic system in the presence of MSE = 2-methylstyrene (Scheme 1c). We show that the nature of the alkene added as a hydrogen acceptor, actually is crucial to perform the reaction, as it differently modifies the initial catalyst species.

**Table 1.** Optimization of Ru(II)-catalyzed *ortho* C-H silylation of amide **1a** [a]

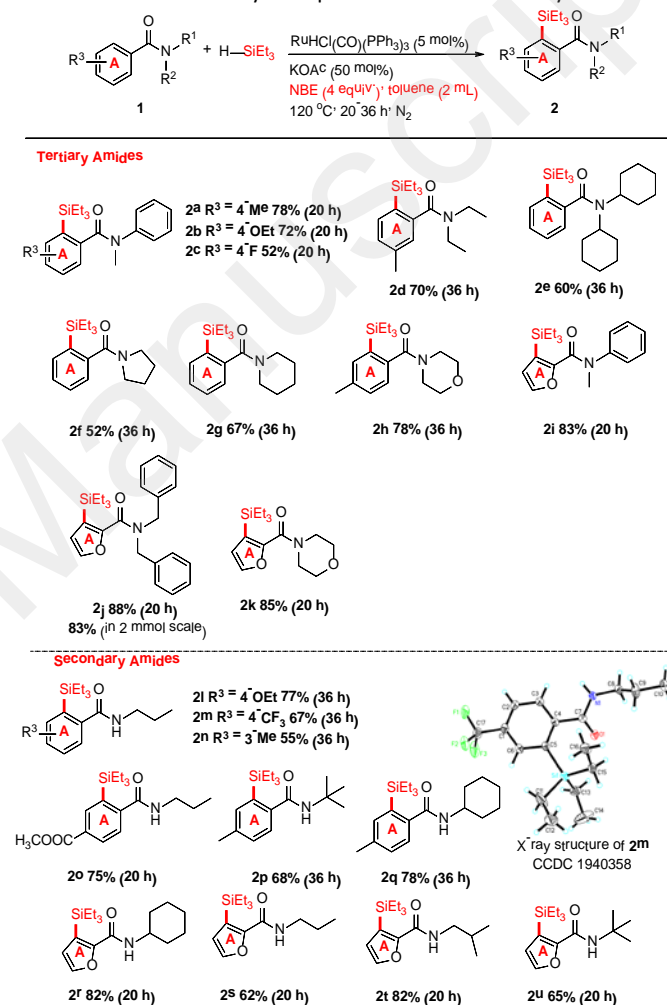


entry	catalyst	additive	solvent	GC-yield (%)
1	[RuCl <sub>2</sub> ( <i>p</i> -cymene)] <sub>2</sub>	KOAc	toluene	-
2	RuCl <sub>2</sub> (2,2'-bipyridyl) <sub>3</sub> ·6H <sub>2</sub> O	KOAc	toluene	-
3	RuCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>3</sub>	KOAc	toluene	43
4	RuH <sub>2</sub> (CO)(PPh <sub>3</sub> ) <sub>3</sub>	KOAc	toluene	21
5	[Ru(COD)Cl <sub>2</sub> ] <sub>n</sub>	KOAc	toluene	-
6	Ru <sub>3</sub> (CO) <sub>12</sub>	KOAc	toluene	-
7	RuHCl(CO)(PPh <sub>3</sub> ) <sub>3</sub>	KOAc	toluene	99(78 <sup>c</sup> )
8	RuHCl(CO)(PPh <sub>3</sub> ) <sub>3</sub>	K <sub>3</sub> PO <sub>4</sub>	toluene	31
9	RuHCl(CO)(PPh <sub>3</sub> ) <sub>3</sub>	KPF <sub>6</sub>	toluene	23
10	RuHCl(CO)(PPh <sub>3</sub> ) <sub>3</sub>	KO <sup>t</sup> Bu	toluene	-
11	RuHCl(CO)(PPh <sub>3</sub> ) <sub>3</sub>	KBF <sub>4</sub>	toluene	33
12	RuHCl(CO)(PPh <sub>3</sub> ) <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> K	toluene	48
13	RuHCl(CO)(PPh <sub>3</sub> ) <sub>3</sub>	KOAc	Xylene	68
14	RuHCl(CO)(PPh <sub>3</sub> ) <sub>3</sub>	KOAc	DMF	-
15	RuHCl(CO)(PPh <sub>3</sub> ) <sub>3</sub>	KOAc	NMP	31
16	RuHCl(CO)(PPh <sub>3</sub> ) <sub>3</sub>	KOAc	THF	--- <sup>b</sup>
17	RuHCl(CO)(PPh <sub>3</sub> ) <sub>3</sub>	KOAc	CH <sub>3</sub> CN	--- <sup>b</sup>
18	RuHCl(CO)(PPh <sub>3</sub> ) <sub>3</sub>	KOAc	toluene	trace <sup>d</sup>
19	RuHCl(CO)(PPh <sub>3</sub> ) <sub>3</sub>	KOAc	toluene	42 <sup>e</sup>
20	RuHCl(CO)(PPh <sub>3</sub> ) <sub>3</sub>	KOAc	toluene	35 <sup>f</sup>

[a] amide **1a** (0.5 mmol), Et<sub>3</sub>SiH (2.0 mmol), Ru catalyst (5 mol%), additive (0.25 mmol), NBE (2.0 mmol), solvent (2 mL), at 120 °C for 20 h, under N<sub>2</sub>. [b] at 80 °C. [c] Isolated yield of **2a**. [d] Without NBE, 18% GC-yield of reduced amine was obtained. [e] Using MSE as the hydrogen acceptor. [f] Using TBE as the hydrogen acceptor.

The positive influence of the acetate ligand on Ru(II) catalyst has first been demonstrated on attempts to perform the direct *ortho* C-H silylation of amide **1a** with Et<sub>3</sub>SiH in the presence of 4 equiv of NBE. (Table 1) Firstly, [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub> catalyst has been shown to be efficient for sp<sup>2</sup> C-H arylation<sup>15</sup> and alkenylation reactions.<sup>16</sup> However, surprisingly, [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub> in the presence of KOAc was not effective for the *ortho* C-H silylation of amide **1a** (Table 1, entry 1). Ruthenium complexes including RuCl<sub>2</sub>(2,2'-bipyridyl)<sub>3</sub>·6H<sub>2</sub>O, [RuCl<sub>2</sub>(COD)]<sub>n</sub>, and Ru<sub>3</sub>(CO)<sub>12</sub> did not favor this C-H silylation of amide (entries 2, 5, 6). When ruthenium catalysts such as RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> or RuH<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>3</sub> with KOAc were used, silylated amide **2a** was generated in 43% and 21% yields, respectively (entries 3 and 4). A full conversion of amide **1a** was finally observed in the presence of RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub> / KOAc catalytic system in toluene (entry 7). Other additives such as K<sub>3</sub>PO<sub>4</sub>, KO<sup>t</sup>Bu, KBF<sub>4</sub>, C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>K (entries 8-12), and solvents including xylene, DMF, NMP,

THF, CH<sub>3</sub>CN (entries 13-17) could not give better results for this C-H silylation of amide. The absence of NBE also disfavours this C-H silylation of amide, but 18% GC-yield of reduced amine was obtained (entry 18 and **Scheme S1**). Other hydrogen trapper such as 2-methylstyrene (MSE) and *tert*-butylethylene (TBE) could not give better results (entries 19 and 20). This result indicated that the addition of NBE is crucial to trap the generated hydrogen for the chemoselectivity of the reaction in order to avoid further reduction of amide and improve the yield of C-H silylation product of amide. No disilylated product was obtained under these reaction conditions, likely because of the decreasing reactivity of another *ortho* C-H bond of the silylated product after the first silylation.



Tertiary amide **1** (0.5 mmol), Et<sub>3</sub>SiH (2.0 mmol), RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub> (0.025 mmol), KOAc (0.25 mmol), NBE (2 mmol), toluene (2 mL), at 120 °C for 20-36 h, under N<sub>2</sub>. Isolated yields.

**Scheme 2.** Ru(II)-OAc catalyzed *ortho* C-H silylation of arylamides.

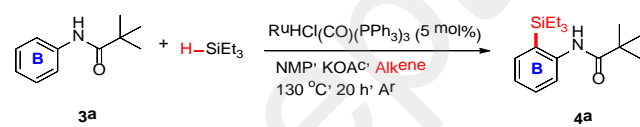
We subsequently investigated the effect of various *tertiary* amides on the efficiency of this *ortho* C-H silylation reaction (Scheme 2). Firstly, *N*-alkyl-*N*-phenyl tertiary amides bearing substituents at *para* position such as -Me, -OEt, -F groups led after 20 h of reaction to the corresponding silylated tertiary amides in good yields (**2a-2c**). *N,N*-Ethyl-3-methylbenzamide was able to give the desired silylated tertiary amides in good yield (70%) but a longer reaction time (36 h) was required (**2d**). Moreover, this catalytic C-H

silylation could also be applied to synthesize silylated *N*-heterocyclic amides (pyrrolidine, piperidine, and morpholine amides) (**2f-2h**), with 52-78% isolated yields. Furthermore, *N*-phenyl-*N*-methyl, *N,N*-dibenzyl, *N*-morpholinyl 2-furoyl tertiary amides showed very good reactivities in the synthesis of silylated furan derivatives (**2i-2k**). Additionally, a **1j** in 2 mmol scale experiment has been performed and the silylated product **2j** was obtained in 83% yield (0.67 g).

We next studied the tolerance and selectivity of the reaction of secondary amide derivatives (Scheme 2). Silylated secondary *N*-alkyl amides could easily be prepared through this RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>/KOAc catalytic system. In particular, the silylated products bearing -Me, -OEt, and -CF<sub>3</sub> substituents in *para* or *meta* position of *N*-*tert*-butyl benzamide, *N*-*n*-propyl benzamide, or *N*-cyclohexyl benzamide, were also produced in 55-80% yields under similar conditions (**2l-2q**). The structure of compound **2m** was confirmed by X-ray crystallography, confirming the regioselectivity of the transformation in *ortho* position of the directing group. Importantly, in the presence of an ester group in *para* position on the aryl ring, the reaction also proceeded selectively as no product resulting from the reduction of ester group was detected (**2o**). Analogously, this C-H silylation also showed excellent reactivity to synthesize functional silylated furans containing secondary amides (**2r-2u**).

The above described catalytic system has then been evaluated for the C-H silylation of anilide **3a** which should proceed *via* a 6-membered ruthenacycle, which is expected to be more difficult to silylate than the corresponding amide with formation of a 5-membered ruthenacycle. However, only slight amount of silylated anilide **4a** was observed. After variations of the hydrogen acceptors (TBE (tert-butylethylene), DTBP (Di-*t*-butyl peroxide), TMBE (2,3,3-trimethylbut-1-ene), NBD (norbornadiene), MSE) (Table 2), ruthenium complexes ([RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub>, RuH<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>3</sub>, RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>), additives (KOAc, KO<sub>i</sub>Piv, PhCOONa, PhCOOH), and solvents (toluene, NMP, DCE, 1,4-dioxane, heptane) (Table S2), the best obtained result was 60% of silylated anilide **4a** when the reaction was conducted in the presence of RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub> (5 mol%), KOAc (50 mol%), MSE (2-methylstyrene) (4 equiv) in NMP at 120 °C for 20 h (Table 2).

**Table 2.** Optimization of RuH(Cl)(CO)L<sub>3</sub> / KOAc / Alkene catalyzed *ortho* C-H silylation of anilide **3a**<sup>a</sup>

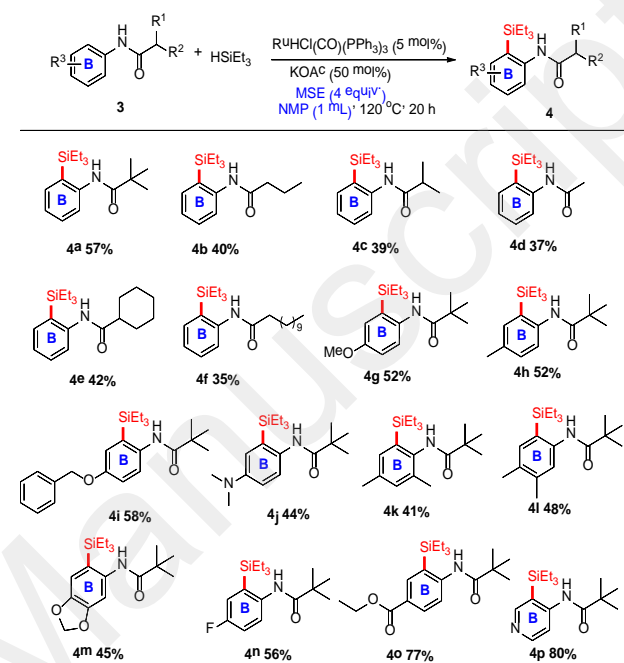


entry	alkene	GC-yield (%)
1	NBE	9
2	TBE	29
3	DTBP	9
4	TMBE	14
5	NBD	5
6	MSE	53
7	MSE	60 <sup>b</sup> (57 <sup>c</sup> )

[a] anilide **3a** (0.25 mmol), Et<sub>3</sub>SiH (1.0 mmol), RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub> (5 mol%), KOAc (0.125 mmol), alkene (1.0 mmol), NMP (0.5 mL), at 130 °C for 20 h, under N<sub>2</sub>. [b] NMP (1 mL), 120 °C. [c] Isolated yield of **4a**.

Importantly, the Ru(II)/KOAc catalytic system in the presence of MSE was broadly applicable and enabled to obtain differently substituted anilides **3** in moderate to good yields by chemo- and regio- selective monosilylations *via* a 6-membered ruthenacycle intermediate (Scheme 3). Thus, different *N*-acyl-anilides **3a-3f**

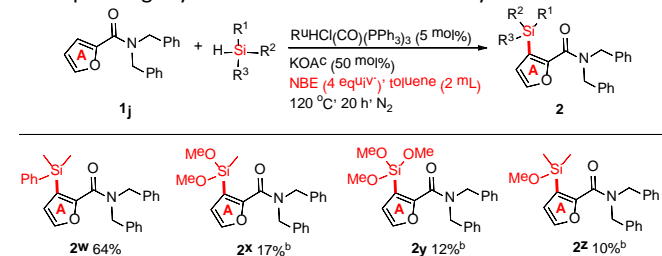
bearing alkyl groups at acyl position led to corresponding *ortho* silylated anilides using the Ru(II)/KOAc/MSE C-H silylation system. Numerous substituents, such as -OMe, -Me, -OBz, -NMe<sub>2</sub>, -F, -COOEt on the anilide ring (**3g-3o**) were tolerated leading to silylated anilides (**4g-4o**) in moderate to good yields. It is noteworthy that this C-H silylation catalytic system exhibited good regio-selectivity (**4l** and **4m** at  $\alpha$ -position) and chemo-selectivity (**4o** without reduction of ester moiety). Furthermore, pyridyl amide derivative **3p** could be easily silylated and **4p** was isolated in 80% yield.



Anilides **3** (0.25 mmol), Et<sub>3</sub>SiH (1.0 mmol), RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub> (0.0125 mmol), KOAc (0.125 mmol), MSE (1 mmol), NMP (1 mL), at 120 °C for 20 h, under N<sub>2</sub>.

**Scheme 3.** Ru(II) catalyzed *ortho* C-H silylation of anilides

Then, several hydrosilanes such as (Me)<sub>2</sub>PhSiH, Me(OMe)<sub>2</sub>SiH, Me<sub>2</sub>(OMe)SiH and (OMe)<sub>3</sub>SiH were evaluated with the tertiary amide **1j** in the presence of 5 mol% of RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>, 50 mol% of KOAc, and 4 equiv of NBE in toluene at 120 °C for 20 h. (Scheme 4) However, only dimethyl(phenyl)silylated amide was obtained **2w** with a rather good isolated 64% yield, other hydrosilanes were not efficient in this catalytic system. Moreover, other hydrosilanes reacted with anilide **3g** and could not give good results to obtain corresponding silylated anilides in the anilide silylation conditions.

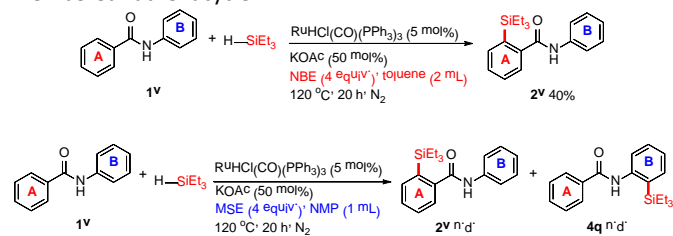


[a] Tertiary amide **1j** (0.5 mmol), hydrosilane (2.0 mmol), RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub> (0.025 mmol), KOAc (0.25 mmol), NBE (2 mmol), toluene (2 mL), at 120 °C for 20 h, under N<sub>2</sub>. Isolated yields. [b] Detected by GC.

**Scheme 4.** Ru(II) catalyzed *ortho* C-H silylation of amide **1j** with different hydrosilanes<sup>[a]</sup>

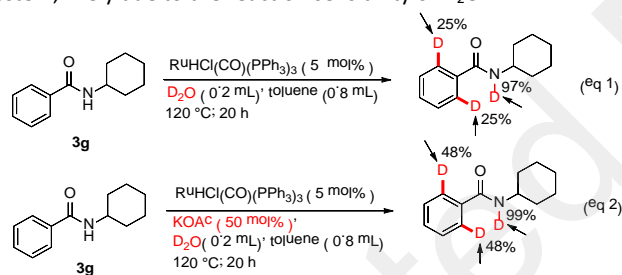
To gain more information on the selectivity of the two catalytic C-H silylation systems, we then performed the C-H silylation of *N*-

phenylbenzamide under two catalytic systems (Scheme 5). 40% yield of silylated amide **2v** was obtained through 5-membered ruthenacycle pathway by using RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>/KOAc/NBE catalytic system. However, no silylated product was obtained with the RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>/KOAc/MSE catalytic system, which is likely due to the competition of C-H bond cleavage between amide ring bearing 5-membered ruthenacycle and anilide ring bearing 5-membered ruthenacycle.



**Scheme 5.** Ru(II) catalyzed *ortho* C-H silylation of *N*-phenylbenzamide

The ease and reversibility of the *ortho* C-H/N-H bond cleavage was studied by H/D exchange experiments. First, the reaction of **3g** in the presence of D<sub>2</sub>O (0.2 mL) was performed at 120 °C for 20 h. 25% *ortho* D-deuterated of *ortho* arene C-H bond and 97% D-deuterated of N-H bond were observed by <sup>1</sup>H NMR. (Scheme 6, eq. 1) However, the addition of 50 mol% of KOAc led to an increase of H/D exchange at the *ortho* position (48%) under similar conditions, (Scheme 6, eq. 2) which indicated that KOAc plays an important role in promoting this C-H cleavage of amides by deprotonation.<sup>15d</sup> However, no positive result was obtained in RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>/KOAc/MSE catalyzed C-H silylation of anilide system, likely due to the reaction sensitivity of D<sub>2</sub>O.

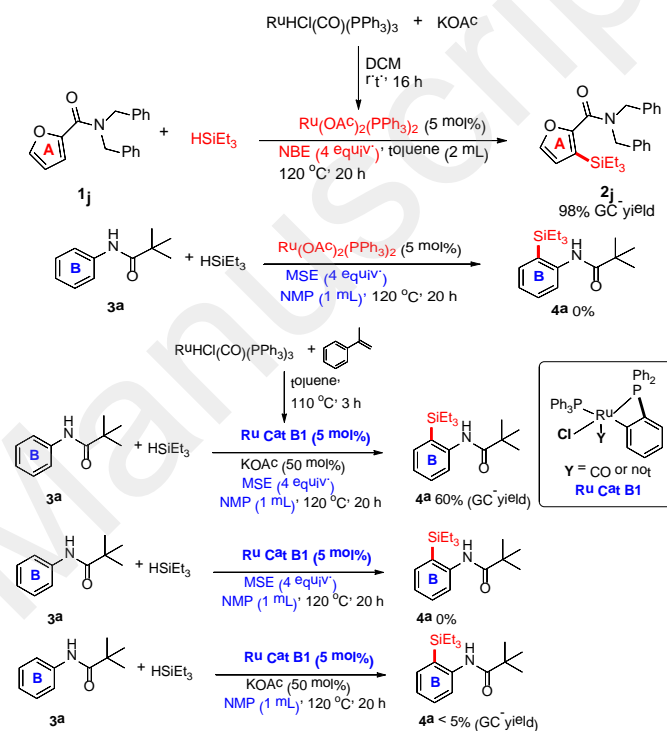


**Scheme 6.** Deuteration experiments.

From a mechanistic point of view, the reaction of RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub> with 2.4 equiv. KOAc in dichloromethane was performed at room temperature for 16 h, and a mixture of complexes Ru(OAc)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (major) and Ru(OAc)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub> (less than 5%) was obtained.<sup>17</sup> Two <sup>31</sup>P NMR signals were observed at 63.1 ppm (s) (major) and 39.1 ppm (s), which are compatible with previous observation by Lynam.<sup>18</sup> On the other hand, tertiary amide **1j** could successfully generate the silylated amide **2j** in 98% GC-yield by using 5 mol% of the generated mixture of complexes Ru(OAc)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and Ru(OAc)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub> in the presence of NBE (Scheme 7). However, no silylated anilide product **4a** was detected in the presence of Ru(OAc)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> as the catalyst with 4 equiv of MSE in NMP at 120 °C for 20 h. These results indicated that the Ru(OAc)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> complex acted as the active ruthenium catalyst only for aryl C-H silylation of amides *via* a 5-membered ruthenacycle pathway and only in the presence of NBE.

Previous work by Murai showed the reaction of RuH<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>3</sub> with trimethylsilane to give the cyclometallate intermediate Ru(H)(*o*-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>(CO).<sup>19</sup> Thus we reacted RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub> with 2-methylstyrene (MSE) under Murai conditions<sup>19</sup> at 110°C for 3

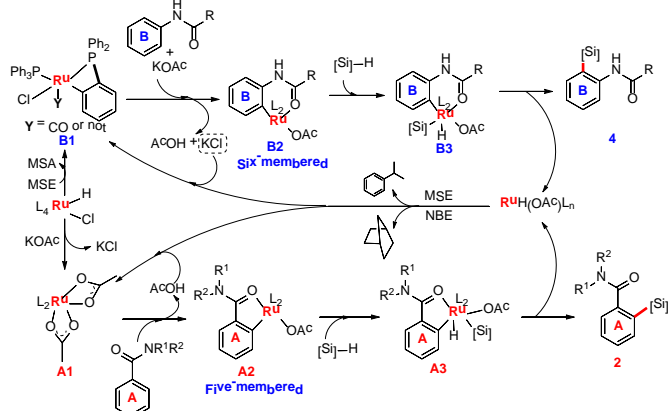
hours and the intermediate **B1** was obtained (Scheme 5). The intermediate **B1** corresponds to a mixture of RuCl(*o*-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)(CO)(PPh<sub>3</sub>) and RuCl(*o*-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)(PPh<sub>3</sub>), which were detected by HR-MS.<sup>20</sup> Then the **B1** intermediate was successfully applied to C-H silylation of anilide **3a** which gave **4a** in similar GC-yield than the ones obtained using RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub> as the catalyst with additional MSE, while less than 5% yield of **4a** was obtained without additional KOAc or MSE. These results indicate that the reaction between RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub> and the sacrificial alkene could be the first step for the C-H silylation of anilide *via* a 6-membered ruthenacycle pathway, and that MSE does not play only the role of hydrogen acceptor but generates the first active species **B1** *via* trapping of hydrogen.



**Scheme 7.** Controlled experiments.

Based on the above results, we propose mechanisms for RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>/KOAc/NBE C-H silylation of amides *via* 5-membered ruthenacycle pathway, and RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>/KOAc/MSE C-H silylation of anilides *via* 6-membered ruthenacycle pathway, as illustrated in Scheme 8. Two different types of active ruthenium species have been shown for the two proposed catalytic pathways for amide and anilide silylations. In the Ru-catalyzed C-H silylation of amide cycle, the active Ru(II)(OAc)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> species **A1** was in situ generated after the release of CO and one PPh<sub>3</sub> from the reaction of RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub> with KOAc. Then the acetate assisted *ortho* C-H bond deprotonation should lead to the five-membered cyclometallate ruthenium intermediate **A2**. Next, following the oxidative addition of hydrosilane, reductive elimination leading to **2** and norbornylene insertion, norbornane elimination and the Ru(OAc)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> active species can be regenerated for the next catalytic cycle. On the other hand, in the Ru-catalyzed C-H silylation of anilide cycle, RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub> reacted with MSE smoothly and led to active Ru species **B1**, which would further generate six-membered intermediate **B2** by acetate assisted *ortho* C-H bond deprotonation. The silylated anilide **4** should be finally obtained by oxidative addition, reductive elimination and MSE insertion, the

corresponding alkane was released and the active Ru species **B1** was regenerated for the next catalytic cycle. It is noteworthy that the MSE plays an important role to generate intermediate **B1** and more faster than the reaction of RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub> with KOAc in NMP, while Ru(OAc)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> species would be first generated in the presence of NBE in toluene.



**Scheme 8.** Proposed mechanism.

## Experimental

**General Remarks.** <sup>1</sup>H NMR spectra were recorded in CDCl<sub>3</sub> at ambient temperature on Bruker AVANCE I 300 or 500 spectrometers at 300.1 MHz or 500.1 MHz, using the solvent as internal standard (7.26 ppm). <sup>13</sup>C NMR spectra were obtained at 75 or 125 MHz and referenced to the internal solvent signals (central peak is 77.2 ppm). Chemical shift ( $\delta$ ) and coupling constants ( $J$ ) are given in ppm and in Hz, respectively. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, and br. for broad. GC analyses were performed with GC-14C (Shimadzu) equipped with a 30-m capillary column (Supelco, SPB-5, fused silica capillary column, 30 M\*0.25 mm\*0.25 mm film thickness), was used with N<sub>2</sub>/air as vector gas. GCMS were measured by GCMS-7890A-5975C (Agilent) with GC-7890A equipped with a 30-m capillary column (HP-5ms, fused silica capillary column, 30 M\*0.25 mm\*0.25 mm film thickness), was used with helium as vector gas. HRMS were measured by MAT 95XP (Termol) (LCMS-IT-TOF).

**General procedure for C-H silylation of amides.** Ru(PPh<sub>3</sub>)<sub>3</sub>(CO)HCl (0.025 mmol, 23.8 mg), amide (0.5 mmol), triethylsilane (2.0 mmol), KOAc (0.25 mmol, 25 mg), norbornylene (2.0 mmol, 188 mg) and toluene (2 mL) were introduced in a tube under N<sub>2</sub>, equipped with magnetic stirring bar and was stirred at 120 °C. After 20 or 36 h, the conversion of the reaction was analyzed by gas chromatography. The solvent was then evaporated under vacuum and the desired product was purified by using a silica gel chromatography column and a mixture of petrol ether/ethyl acetate as eluent.

**General procedure for C-H silylation of anilides.** Ru(PPh<sub>3</sub>)<sub>3</sub>(CO)HCl (0.0125 mmol, 11.9 mg), anilide (0.25 mmol), triethylsilane (1.0 mmol), KOAc (0.125 mmol, 12.5 mg), MSE (1.0 mmol, 130  $\mu$ L) and NMP (1 mL) were introduced in a tube under N<sub>2</sub>, equipped with magnetic stirring bar and was stirred at 120 °C. After 20 h, the conversion of the reaction was analyzed by gas chromatography. The solvent was then evaporated under vacuum and the desired product was purified by using a silica gel chromatography column and a mixture of petrol ether/ethyl

acetate as eluent.

## Conclusion

In conclusion, we have described an efficient and high selective process using RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>/KOAc catalytic system in the presence of sacrificial NBE for the *ortho* C-H silylation of both *secondary* and *tertiary* amides using HSiEt<sub>3</sub> as the silylating reagent *without reduction of amide moiety* via 5-membered ruthenacycle pathway. Furthermore, a regio-selective C-H silylation of anilides was also developed using a catalytic system based on RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub> and KOAc in the presence of MSE as hydrogen acceptor, *via* a 6-membered ruthenacycle pathway. Various silylated amides and anilides bearing numerous tolerated functional groups were successfully synthesized in moderate to excellent yields. Two pathways for these Ru(II) catalyzed C-H silylations were proposed to rationalize the regioselectivity obtained. The "hydrogen acceptor" alkene played an important role to generate the catalytic species in addition to hydrogen acceptor properties for the regio-selective Ru(II) catalyzed C-H silylations of amides and anilides.

## Conflicts of interest

There are no conflicts to declare.

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## Notes and references

CCDC 1940358 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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