

# Cooperative Catalytic Activation of Si-H Bonds by a Polar Ru-S Bond: Regioselective Low-Temperature C-H Silylation of Indoles under Neutral Conditions by a Friedel-Crafts Mechanism

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### Supporting Information

**ABSTRACT:** Merging cooperative Si-H bond activation and electrophilic aromatic substitution paves the way for C-3-selective indole C-H functionalization under electronic and not conventional steric control. The Si-H bond is heterolytically split by the Ru-S bond of a coordinatively unsaturated cationic ruthenium(II) complex, forming a sulfur-stabilized silicon electrophile. The Wheland intermediate of the subsequent Friedel-Crafts-type process is assumed to be deprotonated by the sulfur atom, no added base required. The overall catalysis proceeds without solvent at low temperature, only liberating dihydrogen.

Selective activation of  $C(sp^2)$ -H bonds is a challenge in transition metal catalysis,<sup>1</sup> and the direct transformation of  $C(sp^2)$ -H bonds into  $C(sp^2)$ -Si bonds also receives its share of attention.<sup>2</sup> Several innovative transition metal-catalyzed protocols were disclosed using either Si-H<sup>3-7</sup> or Si-Si<sup>8-10</sup> coupling partners ( $Si = R_3Si$  or RF<sub>2</sub>Si), the former often requiring a sacrificial alkene as a dihydrogen acceptor.<sup>4,5,7</sup> The diverse reaction mechanisms of these catalyses are not fully elucidated in all cases but likely proceed through a step in which the transition metal is involved in the  $C(sp^2)$ -Si bond-forming event.

Our laboratories considered an alternative approach to the transition metal-catalyzed dehydrogenative coupling of a  $C(sp^2)$ —H bond and a Si—H bond that would follow a fundamentally different mechanism,<sup>11</sup> inspired by the unique reactivity of polar M—S bonds (M = late transition metal) in the cooperative heterolysis of dihydrogen<sup>12,13</sup> at low temperature (Scheme 1, upper).<sup>14</sup> We reasoned that the same system could also serve as a reactive site for heterolytic silane activation<sup>15</sup> (Scheme 1, lower), generating a highly electrophilic silicon intermediate.

It was our hope that the thus-formed silicon-substituted sulfonium ion would be sufficiently electrophilic to be susceptible to nucleophilic attack at the silicon atom by an electron-rich heterocycle. This assumption is corroborated by synthetic work from the Simchen laboratory,<sup>16,17</sup> showing that pyrroles and indoles undergo silylation at the C-3 carbon atom with Me<sub>3</sub>SiOTf in the presence of excess base.<sup>18</sup> Pure electronic control in a Friedel– Crafts-type electrophilic aromatic substitution (S<sub>E</sub>Ar)<sup>19</sup> accounts

# Scheme 1. Cooperative Heterolysis of H-H and Si-H Bonds by Polar M-S Bonds

$ \overset{+}{\underset{H^-H}{\overset{H^-SAr}{\Rightarrow}}} \overset{+}{\underset{H^-H}{\overset{H^-SAr}{\Rightarrow}}} \overset{+}{\underset{H^-H^-}{\overset{H^-S}{\Rightarrow}}} \overset{+}{\underset{H^-H^-}{\overset{H^-Ar}{\Rightarrow}}} \overset{+}{\underset{H^-H^-}{\overset{H^-and}{\Rightarrow}}} \overset{+}{\underset{H^-}{\overset{H^-and}{\Rightarrow}}} \overset{+}{\underset{H^-}{\overset{H^-}{\xrightarrow{H^-and}{\Rightarrow}}}} \overset{+}{\underset{H^-}{\overset{H^-and}{\Rightarrow}}} \overset{+}{\underset{H^-}{\overset{H^-and}{\xrightarrow{H^-and}{\xrightarrow{H^-}{\xrightarrow{H^-and}{\Rightarrow}}}}} \overset{+}{\underset{H^-}{\overset{H^-and}{\xrightarrow{H^-}$	Ohki and Tatsumi 2008 (Ref. 12a)
$ \overset{*}{\underset{H^{-}Si}{\overset{H^{-}Si}{\underset{H^{-}Si}{\overset{H^{-}Si}}{\overset{H^{-}Si}}{\overset{H^{-}Si}{\overset{H^{-}Si}}{\overset{H^{-}Si}}{\overset{H^{-}Si}}{\overset{H^{-}Si}}{\overset{H^{-}Si}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}$	proposed activation mode

for the observed C-3 regioselectivity,<sup>17,20</sup> whereas C–H bond activation usually occurs at the C-2 carbon atom.<sup>21</sup> Falck et al.<sup>7</sup> as well as Ishiyama and Miyaura et al.<sup>9b</sup> reported iridium-(I)-catalyzed  $C(sp^2)$ –H silylations of heterocycles at elevated reaction temperatures of 80 and 120 °C, respectively. The inherent C-2 selectivity is steered toward the C-3 position by a large group at the indole nitrogen atom. Methods selectively addressing the C-3 position without the need for a directing group are still elusive, and we describe herein a remarkably mild electrophilic indole C–H functionalization through a cooperative Si–H bond activation mechanism.

We selected the cationic complexes  $1^{12}$  and  $2^{22}$  (Chart 1) introduced by us for the planned Si-H bond heterolysis. The coordinatively unsaturated metal center in 1 and 2 is stabilized by a bulky 2,6-dimesitylphenyl thiolate (SDmp) ligand,<sup>23</sup> which also retards formation of binuclear sulfur-bridged complexes. The polar M-S bond of these (formally) 16-electron complexes combines Lewis acidity at the metal center and Lewis basicity at the adjacent sulfur atom. That electronic situation lends both 1 and 2 the reactivity to heterolytically split dihydrogen.<sup>12,22</sup>

The lability of the thiolate ligand in rhodium(III) complex 1a and iridium(III) complex 1b during the Si-H bond heterolysis results in decomposition.<sup>12c</sup> For that reason, we decided to test ruthenium(II) complex 2 with a tethered thiolate ligand, thereby imparting stability to the Ru-S bond, which was now expected to be retained throughout the catalytic cycle. We were delighted to find that 2 catalyzed the dehydrogenative  $C(sp^2)$ -Si coupling at the indole C-3 carbon atom independent of the nitrogen protective group  $(3-5\rightarrow7a-9a, Table 1, entries 1-3).^{24}$  C-3

Received: December 21, 2010 Published: February 22, 2011 Chart 1. Coordinatively Unsaturated Transition Metal Thiolate Complexes with a Polar M-S Bond [Ar<sup>F</sup> = 3,5-Bis(trifluoromethyl)phenyl]



 Table 1. Indole C-H Bond Functionalization: Protective

 Groups



	in	ıdole				silylated indole		
entry	cmpd	PG	$T[^{\circ}C]$	<i>t</i> [h]	cmpd	C-3:C-2 <sup>b</sup>	yield [%] <sup>c</sup>	
1	3	<i>i</i> -Pr <sub>3</sub> Si	50	6	7a	>99:1	82	
2	4	Bn	50 <sup>d</sup>	2	8a	>99:1	89	
3	5	Me	rt	2	9a	>99:1	92	

<sup>*a*</sup> Conversion was monitored by GLC analysis. <sup>*b*</sup> Ratio of regioisomers was determined by GLC analysis and <sup>1</sup>H NMR spectroscopy prior to purification. <sup>*c*</sup> Yield refers to analytically pure product isolated after purification by flash chromatography on silica gel. <sup>*d*</sup> The reaction temperature corresponds to the melting point of the indole.

over C-2 selectivity was of course obtained for *i*-Pr<sub>3</sub>Si (in 3) and Bn (in 4) protection, but electronic control also secured the same superb site-selectivity for the Me group (in 5). The catalyses neither required solvent<sup>25</sup> nor base<sup>18</sup> nor a hydrogen acceptor<sup>4,5,7</sup> to maintain turnover, and catalyst loadings as low as 0.1 mol % still promoted the above coupling of 5, yet at reduced reaction rate. Complex 2 retained its reactivity after consumption of the reactants, and  $\geq$  10 reuses were possible at similar reaction rates, with unchanged regioselectivity.

Having established the new catalytic system, we next focused on the silane scope in the C-H silylation of structurally unbiased **5** (Table 2). A comparison of representative triorganosilanes **6a**-**6e** revealed that steric factors override electronic effects, that is the Lewis acidity of the silicon atom. Nonhindered silanes **6a**-**6c** reacted with expected reaction rates in the order MePh<sub>2</sub>SiH > Me<sub>2</sub>PhSiH > Et<sub>3</sub>SiH (Table 2, entries 1-3). Larger silanes **6d** (with three Ph groups) and **6e** (with one *t*-Bu group) cannot accommodate the congested environment around the Ru-S bond in **2** (Table 2, entries 4 and 5).<sup>26</sup>

The pronounced electronic preference for C–H bond functionalization in the indole C-3 position was further probed in the reaction of indole 10 with C-3 blocked by a Me group, which completely thwarted the dehydrogenative coupling  $(10\rightarrow11a,$ Scheme 2), clearly supporting a Friedel–Crafts mechanism.

We next examined the scope of the indole motif (Table 3). Our survey included examples of 2-substituted indoles (12 and 13, Table 3, entries 1 and 2) and several indoles substituted on the benzene ring (14–18, Table 3, entries 3–7). Both





		silane	silylated ind				dole	
entry	cmpd	Si-H	T [°C]	<i>t</i> [h]	conv. [%] <sup><i>a</i></sup>	cmpd	yield [%] <sup>c</sup>	
1	6a	Me <sub>2</sub> PhSi-H	rt	1/3	>95	9a	96	
2	6b	MePh <sub>2</sub> Si-H	rt	1/8	>95	9b	93	
3	6c	Et <sub>3</sub> Si-H	90	4	>95	9c	89	
4	6d	Ph <sub>3</sub> Si-H	90	24	0	9d	_	
5	6e	t-BuMe <sub>2</sub> Si-H	90	24	0	9e	_	

<sup>*a,b,c*</sup> For footnotes *a*-*c*, see Table 1. <sup>*d*</sup> Too high viscosity toward full silane consumption is avoided by using excess indole. Reaction rates increase: cf. Table 1, entry 3 vs Table 2, entry 1.





electron-donating and withdrawing groups were tolerated, and the reaction rates were in the same order of magnitude irrespective of the electronic nature of the substituent. The reaction temperature was determined by the melting point of the indole rather than lack of reactivity. The C-3:C-2 ratio was flawless in all cases.

On the basis of current spectroscopic and experimental observations, we suggest a catalytic cycle (Scheme 3) that consists of (i) a cooperative silane activation step (cf. Scheme 1)<sup>12</sup> and (ii) an  $S_EAr$  reaction. (i) Initial coordination of the Si-H bond to the vacant ruthenium(II) site merges into the reversible heterolytic Si-H bond cleavage by the polar Ru-S bond  $(2\rightarrow 26)$ . A <sup>1</sup>H/<sup>2</sup>H scrambling experiment at room temperature employing  $[^{2}H]$ -6a and  $[^{1}H]$ -6b in the absence of a nucleophile demonstrated their reversible interaction with complex 2. Mass spectrometric analysis of the isotopic distribution showed complete scrambling  $({}^{1}\text{H}/{}^{2}\text{H} \approx 50.50)$  for  $[{}^{1}\text{H}/{}^{2}\text{H}]$ -6a and  $[^{1}H/^{2}H]$ -6b. One- and two-dimensional NMR measurements of **26** (using excess silane in the absence of indole) are consistent with our hypothesis. At room temperature, dynamic processes including reversibility result in line-broadening, while in turn, a clearly resolved doublet with no  ${}^{1}J_{Si-H}$  satellites at  $\delta = -8.25$  $(^{2}J_{P-H} = 48.7 \text{ Hz}) \text{ ppm} [^{1}\text{H NMR} (500 \text{ MHz}) \text{ in } 1,2\text{-}Cl_{2}C_{6}D_{4}]$ at -10 °C provided unambiguous evidence for a phosphinecoordinated Ru-H. The corresponding doublet is seen in the <sup>31</sup>P NMR (202 MHz) spectrum at  $\delta$  = 39.8 (<sup>2</sup>J<sub>P-H</sub> = 48.4 Hz) ppm while a singlet appears at  $\delta = 23.2$  ppm for 2. (ii) The assumed sulfur-stabilized trivalent silicon cation (silicon-substituted sulfonium ion<sup>27</sup>) in **26** is then transferred onto nucleophilic indole 5, yielding Ru–H complex 27 (26 $\rightarrow$ 27) and  $\sigma$ -complex 28 (5 $\rightarrow$ 28). The fate of Wheland intermediate 28 could either be reduction to the indoline followed by oxidation to 9 mediated by 2 (not shown) or proton abstraction from 28 facilitated by





<sup>*a*</sup> All reactions were conducted according to the general procedure (for details, see Supporting Information): indicated indole (1.0 equiv) and silane **6a** (1.0 equiv) in the presence of **2** (1 mol %) at the indicated reaction temperature. <sup>*b*</sup> C-3:C-2 > 99:1. <sup>*c*</sup> Yield refers to analytically pure product isolated after purification by flash chromatography on silica gel. <sup>*d*</sup> The reaction temperature corresponds to the melting point of the indole.

the weakly basic sulfur atom in 27  $(28\rightarrow 9)$ .<sup>28</sup> Complex 2 is indeed capable of indoline-to-indole dehydrogenation, though at elevated temperature. An independent experiment using a deuterated silane ruled out that pathway; no deuterium incorporation into the indole was detected ([<sup>2</sup>H]-6a $\rightarrow$ 9a, Scheme 4). The deprotonation of 28 by 27 affords 29, which is known to immediately release dihydrogen  $(27\rightarrow 29\rightarrow 2)$ ;<sup>22</sup> a related iridium complex, generated from 1b and dihydrogen, was crystallographically characterized.<sup>12a</sup> The proposed dual role of the sulfur atom of 2 is remarkable as it is vital in both steps (i) and (ii).

To gain additional insight into these steps, we probed the reversible Si-H bond activation  $(2\rightarrow 26)$  as well as the intermolecular transfer of the trivalent silicon group  $(26\rightarrow 27)$  with a silicon-stereogenic silane (experimental data are detailed in the Supporting Information). By this, we established that the former (in the absence of indole) proceeds with partial racemization at extended reaction times (not shown), whereas the latter (in the presence of indole) proceeds with complete racemization  $[({}^{Si}R)-6f\rightarrow rac-9f$ , Scheme 5]. We interpret these findings as additional evidence in support of an S<sub>E</sub>Ar mechanism, involving cationic silicon intermediates. Aside from the configurational lability of the silicon in a sulfur-stabilized silicon cation, several events might account for the observed racemization, e.g., shuffling of the silicon moiety between the reactants (silane and indole), particularly at those high concentrations without solvent.

The above mechanistic picture will still require further verification but a conventional Lewis acid-mediated Si-H

Scheme 3. Proposed Catalytic Cycle: Cooperative Ru–S-Catalyzed Si–H Bond Activation Followed by Regioselective Friedel–Crafts-Type Indole C–H Bond Functionalization  $(Bar_{4}^{F})$  Omitted for Clarity)



Scheme 4. Control Experiment with Deuterated Silane



Scheme 5. Control Experiment with Silicon-Stereogenic Silane



bond activation by cationic complex **2** is unlikely.<sup>29</sup> Examples of that in carbonyl reduction are known though.<sup>29b,c</sup> As opposed to our proposal, no ligand at the ruthenium atom is directly participating in that process.<sup>29c</sup> Its mechanism is likely related to the  $B(C_6F_5)_3$ -catalyzed silane activation,<sup>30</sup> and clean inversion of the configuration at the silicon atom is observed.<sup>31</sup> Indoles are, in fact, reduced to indolines under these conditions.<sup>32</sup>

To recap, we disclosed a perfectly regioselective and mild indole C–H functionalization. The catalysis proceeds neat at room temperature, not requiring a base or a hydrogen acceptor. The regioselectivity is now C-3 and not C-2 at the indole core. We think that these unique features are made possible by combining cooperative Si–H bond activation and Friedel– Crafts-type S<sub>E</sub>Ar. The ruthenium-coordinated sulfur atom in catalyst **2** is believed to be decisive in both steps, stabilizing a trivalent silicon cation and later facilitating proton abstraction. Our laboratories are currently extending this strategy to related heterocycles along with an in-depth mechanistic investigation.

# ASSOCIATED CONTENT

**Supporting Information.** Experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) Donor solvents deactivate **2**, whereas non-nucleophilic solvents, i.e., hydrocarbons such as *n*-hexane, are tolerated.

(26) A color change from green (complex 2) to yellow (silane adduct 26) visualizes successful Si-H bond activation. No color change was observed with 6d or 6e.

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