

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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S Supporting Information

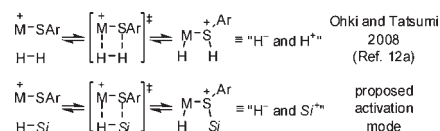
ABSTRACT: Merging cooperative Si–H bond activation and electrophilic aromatic substitution paves the way for C-3-selective indole C–H functionalization under electronic and not conventional steric control. The Si–H bond is heterolytically split by the Ru–S bond of a coordinatively unsaturated cationic 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(sp²)–H bonds is a challenge in transition metal catalysis,¹ and the direct transformation of C(sp²)–H bonds into C(sp²)–Si bonds also receives its share of attention.² Several innovative transition metal-catalyzed protocols were disclosed using either Si–H^{3–7} or Si–Si^{8–10} coupling partners (Si = R₃Si or RF₂Si), the former often requiring a sacrificial alkene as a dihydrogen acceptor.^{4,5,7} 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(sp²)–Si bond-forming event.

Our laboratories considered an alternative approach to the transition metal-catalyzed dehydrogenative coupling of a C(sp²)–H bond and a Si–H bond that would follow a fundamentally different mechanism,¹¹ inspired by the unique reactivity of polar M–S bonds (M = late transition metal) in the cooperative heterolysis of dihydrogen^{12,13} at low temperature (Scheme 1, upper).¹⁴ We reasoned that the same system could also serve as a reactive site for heterolytic silane activation¹⁵ (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,^{16,17} showing that pyrroles and indoles undergo silylation at the C-3 carbon atom with Me₃SiOTf in the presence of excess base.¹⁸ Pure electronic control in a Friedel–Crafts-type electrophilic aromatic substitution (S_EAr)¹⁹ accounts

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



for the observed C-3 regioselectivity,^{17,20} whereas C–H bond activation usually occurs at the C-2 carbon atom.²¹ Falck et al.⁷ as well as Ishiyama and Miyaura et al.^{9b} reported iridium(I)-catalyzed C(sp²)–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,²³ 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.^{12,22}

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.^{12c} 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(sp²)–Si coupling at the indole C-3 carbon atom independent of the nitrogen protective group (3–5→7a–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^F = 3,5-Bis(trifluoromethyl)phenyl]

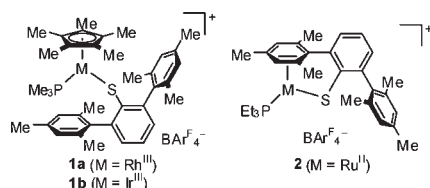
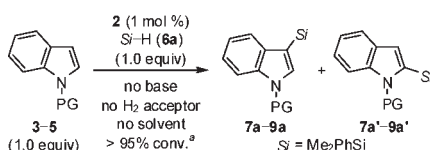


Table 1. Indole C–H Bond Functionalization: Protective Groups



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

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

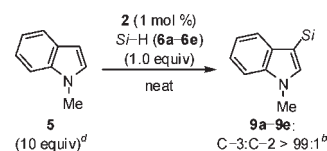
over C-2 selectivity was of course obtained for *i*-Pr₃Si (in 3) and Bn (in 4) protection, but electronic control also secured the same superb site-selectivity for the Me group (in 5). The catalyses neither required solvent²⁵ nor base¹⁸ nor a hydrogen acceptor^{4,5,7} to maintain turnover, and catalyst 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 ≥ 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 MePh₂SiH > Me₂PhSiH > Et₃SiH (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).²⁶

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→11a, 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

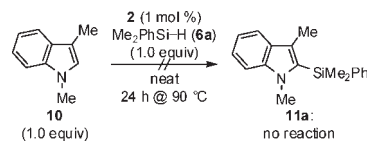
Table 2. Indole C–H Bond Functionalization: Silanes^{a,b,c}



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

^{a,b,c} For footnotes a–c, see Table 1. ^d 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.















Scheme 2. C-3 Selectivity Put to the Test



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)¹² 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→26). A ¹H/²H scrambling experiment at room temperature employing [²H]-6a and [¹H]-6b in the absence of a nucleophile demonstrated their reversible interaction with complex 2. Mass spectrometric analysis of the isotopic distribution showed complete scrambling (¹H/²H ≈ 50:50) for [¹H/²H]-6a and [¹H/²H]-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 ¹J_{Si–H} satellites at δ = –8.25 (²J_{P–H} = 48.7 Hz) ppm [¹H NMR (500 MHz) in 1,2-Cl₂C₆D₄] at –10 °C provided unambiguous evidence for a phosphine-coordinated Ru–H. The corresponding doublet is seen in the ³¹P NMR (202 MHz) spectrum at δ = 39.8 (²J_{P–H} = 48.4 Hz) ppm while a singlet appears at δ = 23.2 ppm for 2. (ii) The assumed sulfur-stabilized trivalent silicon cation (silicon-substituted sulfonium ion²⁷) in 26 is then transferred onto nucleophilic indole 5, yielding Ru–H complex 27 (26→27) and σ-complex 28 (5→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

Table 3. Indole C–H Bond Functionalization: Indoles^a

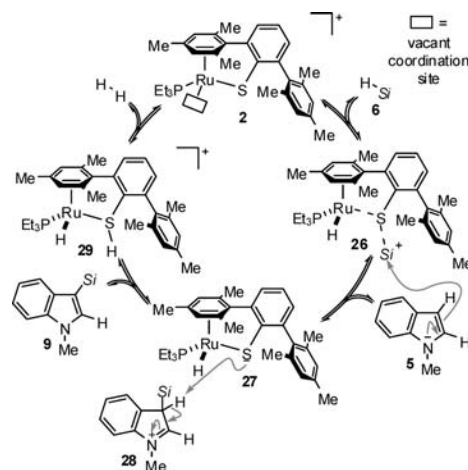
entry	indole	T [°C]	t [h]	silylated indole ^b	yield [%] ^c
1	 12	50 ^d	2	 19a	95
2	 13	90 ^d	4	 20a	81
3	 14	rt	2	 21a	94
4	 15	40 ^d	4	 22a	91
5	 16	40 ^d	4	 23a	93
6	 17	rt	6	 24a	91
7	 18	rt	6	 25a	89

^a 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. ^b C-3:C-2 > 99:1. ^c Yield refers to analytically pure product isolated after purification by flash chromatography on silica gel. ^d The reaction temperature corresponds to the melting point of the indole.

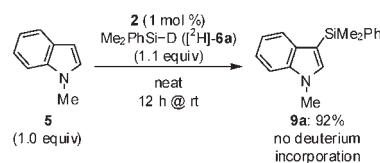
the weakly basic sulfur atom in **27** (**28**→**9**).²⁸ Complex **2** is indeed capable of indoline-to-indole dehydrogenation, though at elevated temperature. An independent experiment using a deuterated silane ruled out that pathway; no deuterium incorporation into the indole was detected (²H]-**6a**→**9a**, Scheme 4). The deprotonation of **28** by **27** affords **29**, which is known to immediately release dihydrogen (**27**→**29**→**2**);²² a related iridium complex, generated from **1b** and dihydrogen, was crystallographically characterized.^{12a} 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**→**26**) as well as the intermolecular transfer of the trivalent silicon group (**26**→**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**→*rac*-**9f**, Scheme 5]. We interpret these findings as additional evidence in support of an S_EAr 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.

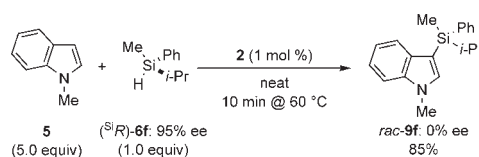
The above mechanistic picture will still require further verification but a conventional Lewis acid-mediated Si–H

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^F₄[−] 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.²⁹ Examples of that in carbonyl reduction are known though.^{29b,c} As opposed to our proposal, no ligand at the ruthenium atom is directly participating in that process.^{29c} Its mechanism is likely related to the B(C₆F₅)₃-catalyzed silane activation,³⁰ and clean inversion of the configuration at the silicon atom is observed.³¹ Indoles are, in fact, reduced to indolines under these conditions.³²

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_EAr. 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

S 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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ACKNOWLEDGMENT

This research was supported by the Deutsche Forschungsgemeinschaft (International Research Training Group Münster–Nagoya, GRK 1143 with a predoctoral fellowship to H.F.T.K., 2007–2010), the G-COE program in chemistry (Nagoya), and a Grant-in-Aid for Scientific Research (No. 18GS0207) from the Ministry of Education, Culture, Sports, Science and Technology, Japan. We acknowledge Dr. Christian Kesenheimer (Nagoya) for a preliminary experiment, Dr. Klaus Bergander (Münster) for expert advice with the NMR spectroscopic measurements, and Barbara Hildmann (Münster) for her skillful technical assistance.

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