Si–C Activation

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Cascade Activation of Si–H, C–H, and Si–C Bonds at a Rhodium β-Diiminate Complex**

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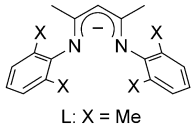
Silyl groups are versatile moieties in organic synthesis.[1] They can be introduced by nucleophilic or electrophilic substitution as well as by addition (of Si–H) to multiple bonds.[2] Once introduced, they are inert enough to survive a variety of transformations, but at the same time reactive enough to be removed or replaced when desired. Thus, they are often used as protective groups.[3] While Si–C_{alkyl} bonds are rather poor donor groups,[4] the Si–H bond is a good σ-donor for many transition metals,[2,5] and can be used to anchor a silyl-bearing substrate to a metal, inducing further reactions. This idea has been exploited by Hartwig and co-workers,[6] who used an Ir fragment to effect C–H activation with regioselectivity dictated by initial SiH coordination to Ir.

While Si–H bonds are quite reactive, reactions involving Si–C bond cleavage are less common. This observation has led to the common view of trialkylsilyl groups as "inert" entities that can be transferred or removed, but cannot readily be modified.[7] Strategies to modify silyl groups 'in place' could add significantly to their usefulness in organic synthesis. However, only a handful of examples of Si–C(sp^3) cleavage reactions at metal centers have been reported,[8] and none of these led to the formation of a new Si–C(sp^3) bond in the product. Turculet and co-workers[9] recently described the reversible breaking of Si–C(sp^2) and Si–C(sp^3) bonds in PSiP pincer ligands bound to Ni and Pd. Herein, we report the cascade breaking and forming of Si–H, C(sp^3)–H, and Si–C(sp^3) bonds at a rhodium center, resulting in replacement of one of the alkyl groups of trialkyl silanes by a benzyl group that is part of a β-diiminate ligand (Scheme 1).



L: X = Me

Scheme 1. β-Diiminate ligands.

Reaction of [LRh(COE)(N_2)][10] (COE = cyclooctene) with excess $HSiEt_3$ leads to a complex with the stoichiometry [LRh($HSiEt_3$)$_2$] (**1**), which was studied in detail by NMR spectroscopy and X-ray diffraction. It is reminiscent of [Cp*Rh($HSiEt_3$)$_2$], reported in 1984 by Koetzle and co-workers,[11] in that it contains two nonequivalent $HSiEt_3$ moieties in the solid state (Figure 1 A), one being further along the Si–H oxidative addition pathway than the other. DFT studies confirm this structural preference. However, in solution, complex **1** is highly fluxional with two equivalent silyl groups, two equivalent hydrides, and four equal Si–H couplings ($\delta_H = -14.73$ ppm, $J_{RhH} = 21.2$ Hz, $J_{SiH} = 8.8$ Hz,

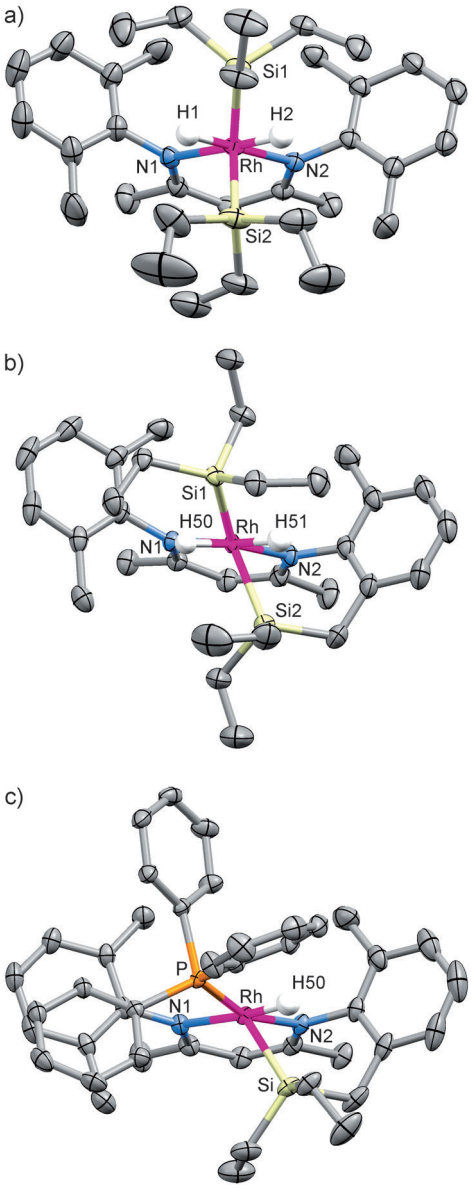


Figure 1. X-ray structures of complexes **1** (a),[12] **2** (b),[13] and **3** (c),[14] showing thermal ellipsoids at 25% probability. All hydrogen atoms except hydrides omitted for clarity.

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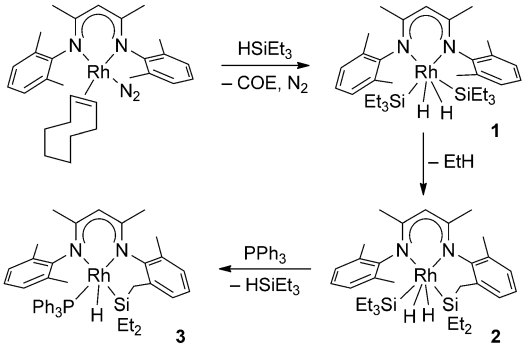
$J_{RhSi} = 20.0$ Hz). Exchange with free $HSiEt_3$ is slow on the NMR timescale, thus indicating that the two silane moieties are held closely to Rh by the Si–H coordination.

Complex **1** is stable in the solid state, but in cyclohexane solution it slowly and quantitatively transforms into compound **2**, which contains two nonequivalent (and nonexchanging) hydrides, two nonequivalent silicon atoms, and only five ethyl groups, with concomitant formation of free ethane. Although this new complex is extremely soluble even in pentane, a few crystals suitable for X-ray diffraction could be obtained by cooling a concentrated pentane solution to −35 °C. The structure (Figure 1 B) shows that one of the $HSiEt_3$ moieties has lost an Et group and is bound to a benzylic carbon atom of the diiminate ligand (Scheme 2). Interestingly, when the transformation of **1** to **2** was carried

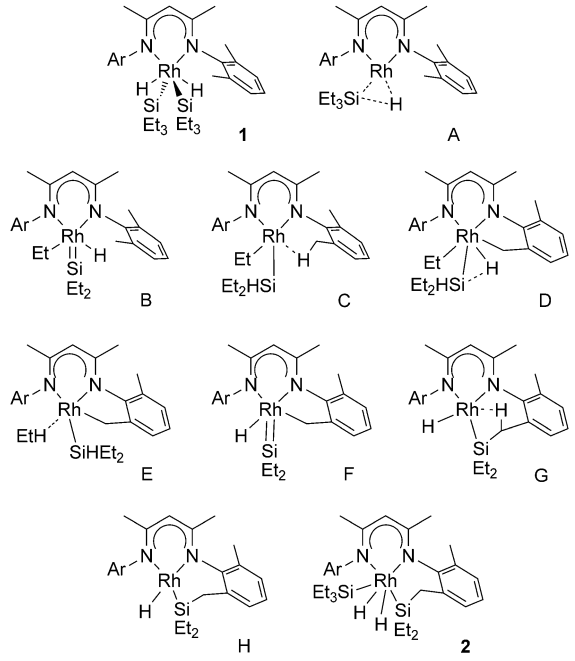


Scheme 2. Formation and rearrangement of **1**.

out in [D_8]THF, deuterium was incorporated at the hydride positions of **2** ([d_0]-**2**:[d_1]-**2**:[d_2]-**2** ≈ 58:37:5) as well as in the Et(Si) groups, thus indicating that at some stage of the reaction, intermolecular C(sp^3)–D bond activation of [D_8]THF occurs as well. The reaction in [D_8]THF is about three times as fast as in C_6D_{12}, but it is also somewhat less clean.

The intact $HSiEt_3$ fragment in **2** can be replaced by PPh_3, leading to the more easily purified complex **3**. The modified ligand skeleton of **2** is retained in **3**, as confirmed by single-crystal X-ray diffraction (Figure 1 C). Interestingly, Geier and Stephan have proposed an intermediate similar to **3** (except for the intramolecular diiminate–silane linkage) in the activation of P–P bonds at a Rh(β-diiminate) center;[15] isolation of complex **3** thus provides support for his proposed mechanism.

From the nature of the reactant (**1**) and the product (**2**), it is clear that this reaction involves breaking a C(sp^3)–H bond and forming an Si–C(sp^3) bond. Several paths can be envisaged for the transformation of **1** to **2**, differing mainly in the order in which the various Si–H, C–H, and Si–C cleavage reactions occur. Based on extensive DFT studies[16] we propose the mechanism depicted in Scheme 3 as the most likely one. The first step involves dissociation of one molecule of $HSiEt_3$ from **1** to produce 14-e intermediate **A**.[17] This step is followed by Si–C bond cleavage to give species **B**, which is best described as a hydride/ethyl/silylene complex. Remark-



Scheme 3. Proposed intermediates for conversion of **1** to **2**.

ably, the barrier for this step is rather modest (15.8 kcal mol^{-1}). Next, a virtually barrierless transfer of the hydride back to the silylene moiety, accompanied by coordination of a benzylic C–H bond to Rh, gives **C**. This benzylic C–H bond is then cleaved, and its hydrogen atom is transferred to a position close to the silicon atom (**D**). In a separate step, this hydrogen atom is transferred to the ethyl group, generating in the rate-limiting step complex **E**, which contains a weakly coordinated ethane molecule. Dissociation of ethane gives hydride/benzyl/silylene complex **F**, which goes on to form the new Si–C bond (**G**,**H**). Recapture of the dissociated $HSiEt_3$ molecule produces the final product **2**. The free energy profile for this path is shown in Figure 2. In accordance with this profile, no intermediates of this rearrangement could be detected when following the reaction by ^{1}H NMR spectroscopy.

Perhaps the most interesting aspect of the proposed path is that the Si–C bond cleavage appears to be induced by initial coordination and cleavage of the Si–H bond, leading to a silylene intermediate. While there are no examples of

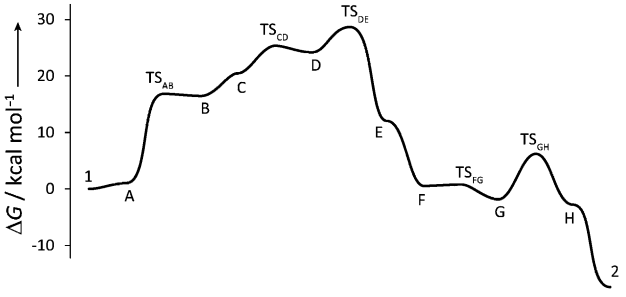


Figure 2. Calculated free-energy profile (b-p/TZVP) for the conversion of **1** to **2** via the path shown in Scheme 3.

structurally characterized Rh/silylene complexes, Tilley and co-workers have isolated several examples of Ir/silylene complexes.[18] The intermediacy of Rh/silylene complexes in hydrosilation of ketones has been proposed by Gade[19] and Herrmann[20] and their respective co-workers based on computational studies. Furthermore, computational work by Eisenstein and co-workers indicates that silylene complexes, and structures intermediate between silyl and silylene moieties, are often comparable in energy to the more common silyl groups.[21] However, in both Tilley's work and that of Gade and Herrmann, the silylene complexes were formed by consecutive cleavage of two Si–H bonds; in the present case, the second bond to break is a much more inert Si–C_{Et} bond. Attempts to locate Si–C cleavage transition states that do not involve such silylene complexes led to significantly higher barriers. In contrast, silylene formation is not even the rate-limiting step of the proposed mechanism.

Alternative paths involving coupling of the β-diiminate ligand to an $SiEt_3$ group before breaking an Si–Et bond were also found to be higher in energy. In these paths, either H_2 and ethene are released in separate steps (instead of together as the more favorable ethane), or one of these two small molecules is retained for a while, leading to less unsaturated and hence less reactive intermediates. Three such paths are discussed in the Supporting Information.

Exchange with [D_8]THF probably occurs through reversible addition of a C–D bond to **A**, and incorporation of deuterium into the Et(Si) groups may then proceed through reversible β-elimination from **B**. The precise details of the activation of THF and its rate-enhancing effect are still under investigation.

Both the present work and that of Turculet[9] suggest that "anchoring" the Si fragment to the metal (by phosphine donor groups in Turculet's work, or by the Si–H bond in complex **1**) is the key to activation of the rather inert Si–C bond. Si–H bonds are usually much more reactive than Si–C bonds, so it comes as a surprise that in the rearrangement of **1** to **2**, the Si–H bond acts mainly as an anchor, while the Si–C_{Et} bond is irreversibly broken.

Complex **2** contains a rare example of a highly asymmetric, formally dianionic NNSi ligand. With a plausible mechanism established for the rearrangement, we began exploring the scope of the reaction, which could be conveniently monitored by ^{1}H NMR spectroscopy. While the aliphatic and aromatic regions of the spectrum are very often cluttered and difficult to interpret, both the ligand backbone H3 region (4.5–5.5 ppm) and the hydride region (−10–−20 ppm) are quite characteristic (for details see the Supporting Information). The results are summarized in Table 1. It appears that steric hindrance is a crucial factor in this chemistry. Increasing the steric bulk of the ligand results in faster rearrangement (entry 3 vs. 1). However, increasing the steric bulk even more blocks the formation of the silane complex altogether (entries 4 and 5). Use of a less-hindered ligand produces a bis(silane) complex that is so stable that it does not even rearrange on heating (entry 2). However, slow H/D exchange between the hydrides and [D_8]THF could be observed by ^{1}H NMR spectroscopy for this system. The Si–C activation is not limited to ethyl groups: tris(*n*-octyl) silane undergoes a similar rearrangement to a single asymmetric product. In contrast, dimethyl octadecyl silane produces two rearranged products in a ratio close to 1:1, most likely diastereomers formed by activation of Si–Me bonds (entry 7); the reaction with dimethyl cyclohexyl silane proceeds with higher selectivity (about 1:2, entry 8). With dimethyl phenyl silane, the initial bis(silane) adduct is formed, but heating does not lead to the expected rearrangement product, giving instead a mixture of various mono(hydride) complexes; we tentatively ascribe this to arene coordination to Rh.[22] Tris(isopropyl)silane appears to be too hindered to form a silane complex. Triethylgermane is more reactive than triethylsilane; it does form a bis(germane) complex with the 2,6-Me_2-substituted ligand and appears to rearrange to the analog of **2**, but the reaction is not as clean as for **1**; use of the less-hindered 2,6-$(OMe)_2$ ligand results in formation of a stable, nonrearranging bis(germane) complex.

Table 1: Reactivity of β-diiminate complexes with silanes.

Entry	Ar substituents[a]	Silane	Result
1	2,6-Me_2	$HSiEt_3$	rearrangement (days)[b]
2	2,6-$(OMe)_2$	$HSiEt_3$	stable complex[c]
3	2-Me-6-*i*Pr	$HSiEt_3$	rearrangement (hours)[b] two isomers 76:24[e]
4	2,6-$(iPr)_2$	$HSiEt_3$	no reaction[d]
5	2-Me-6-*t*Bu	$HSiEt_3$	no reaction[d]
6	2,6-Me_2	$HSi(n\text{-}C_8H_{17})_3$	rearrangement (days)[b]
7	2,6-Me_2	$HSi(n\text{-}C_{18}H_{37})Me_2$	rearrangement (days)[b] two isomers 56:44[f]
8	2,6-Me_2	$HSi(cy\text{-}C_6H_{11})Me_2$	rearrangement (days)[b] two isomers 64:36[f]
9	2,6-Me_2	$HSiPhMe_2$	bis(silane) complex decomposes on heating
10	2,6-Me_2	$HSi(iPr)_3$	no reaction[d]
11	2,6-Me_2	$HGeEt_3$	rearrangement (hours)[b]
12	2,6-$(OMe)_2$	$HGeEt_3$	stable complex[c]

[a] Groups X in Scheme 1. [b] Bis(silane) complex formed, rearranges to analogue of **2**. [c] Bis(silane) complex formed and stable. [d] No silane complexes formed. [e] Assigned as complexes of *rac* and *meso* ligands. [f] Assigned as diastereomers differing in configuration at Si.

In summary, we reported coupling of $HSiEt_3$ and related silanes to β-diiminate ligands through a series of reversible Si–H, C–H, and Si–C(sp^3) cleavage reactions under mild conditions, as well as evidence for related intermolecular C–H activation. A key factor that facilitates Si–C bond cleavage appears to be anchoring of the trialkylsilane to the metal center through coordination of the Si–H bond. Efforts to use these findings in catalytic chemistry are underway.

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[12] Complex **1**: Monoclinic $P2_1/n$, $a = 10.523(3)$, $b = 29.791(11)$, $c = 11.205(3)$ Å, $\beta = 91.766(13)°$, $Z = 4$, R $(F_o > 4\sigma(F_o)) = 0.0386$. Selected bond distances [Å] and angles [deg]: Rh–N1 2.1146(18), Rh–N2 2.1172(16), Rh–Si2 2.3428(9), Rh–Si1 2.3591(9), Rh–H1 1.55(3), Rh–H2 1.45(3); N1-Rh-N2 88.77(6), N1-Rh-Si2 112.72(5), N2-Rh-Si2 109.97(5), N1-Rh-Si1 122.36(5), N2-Rh-Si1 121.60(5), Si2-Rh-H1 71.5(9), Si1-Rh-H1 58.5(10), Si2-Rh-H2 73.0(10), Si1-Rh-H2 58.1(12), H1-Rh-H2 95.5(15). CCDC 6886571 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[13] Complex **2**: Monoclinic $P2_1/n$, $a = 10.531(2)$, $b = 27.213(6)$, $c = 11.749(4)$ Å, $\beta = 98.581(8)°$, $Z = 4$, R $(F_o > 4\sigma(F_o)) = 0.0325$. Selected bond distances [Å] and angles [deg]: Rh–N1 2.0922(15), Rh–N2 2.0453(15), Rh–Si2 2.2984(9), Rh–Si1 2.3890(7), Rh–H50 1.6339, Rh–H51 1.5030, Si1–H50 1.8353; N2-Rh-N1 88.90(6), N2-Rh-Si2 85.08(5), N1-Rh-Si2 122.34(5), N2-Rh-Si1 136.89(5), Si2-Rh-Si1 111.98(3), Si2-Rh-H50 88.0, Si1-Rh-H50 50.1, Si2-Rh-H51 62.7, Si1-Rh-H51 68.6, H50-Rh-H50 93.0. CCDC 886570 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[14] Complex 3: Monoclinic $P2_1/n$, $a = 10.676(3)$, $b = 32.477(10)$, $c = 11.320(3)$ Å, $\beta = 96.525(6)°$, $Z = 4$, R $(F_o > 4\sigma(F_o)) = 0.0305$. Selected bond distances [Å] and angles [deg]: Rh–N2 2.0537(4), Rh–N1 2.1482(14), Rh–P 2.2677(7), Rh–Si 2.3111(6), Rh–H50 1.38(3); N2-Rh-N1 88.56(5), N2-Rh-P 160.73(4), N1-Rh-P 102.06(4), N2-Rh-Si 86.50(4), N1-Rh-Si 124.88(4), P-Rh-Si 100.04(2), N2-Rh-H50 86.7(10), N1-Rh-H50 171.7(10), P-Rh-H50 80.7(9), Si-Rh-H50 61.7(9). CCDC 886569 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[17] Indeed, addition of $HSiEt_3$ inhibits the conversion of **1** to **2**.

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