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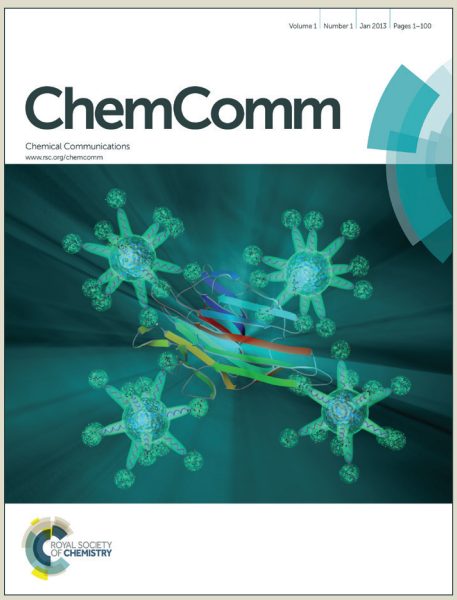

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Si–H Activation by means of Metal Ligand Cooperation in a Methandiide Derived Carbene Complex

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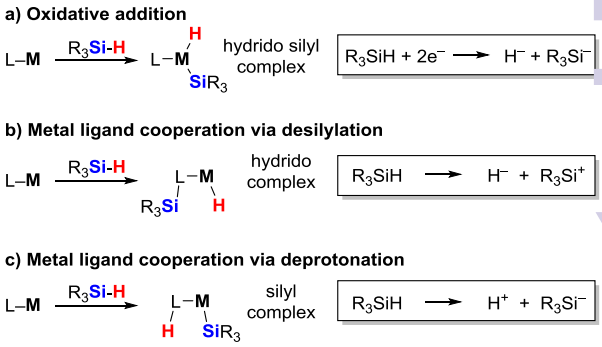
Si–H bond activation of a number of silanes via metal ligand cooperation in a carbene complex is reported. Thereby, the electronic flexibility of the carbene ligand allows for the activation via a unique mechanism with oxidative addition to an 18e species without a formal change in the number of valence electrons.

Activation of Si–H bonds by transition metal complexes is a fundamental step in many stoichiometric and catalytic transformations of organosilanes.[1] These include reactions of academic as well as industrial interest, such as hydrosilylation,[2] silane polymerization[3] or Si–C coupling reactions.[4] Comparable to other E–H bond activation reactions, the activation of the Si–H bond usually proceeds via its oxidative addition onto a metal centre resulting in the formation of hydrido silyl complexes (Scheme 1a). This has been studied in detail with a variety of different metal complexes.[5] An alternative, yet much less explored strategy for bond activation reactions is the use of metal ligand cooperation. This method has been applied for the cleavage of a series of E–E and E–H bonds and their catalytic transformations.[6] However, only very few examples have been reported for the activation of Si–H bonds. This limitation is probably due to the fact that metal ligand cooperation often relies on the propensity of the ligand to act as internal proton acceptor, such as in the Noyori[7] and Milstein[8] systems. This reactivity however, is in contradiction to the polarity of the Si–H bond and its hydridic character. Accordingly, cooperative Si–H bond activation reactions proceed via desilylation and the formation of a hydrido complex (Scheme 1b). This has for example been demonstrated by the addition of silanes to polar M–S (M = Ru, Ir)[9] and Re=O bonds,[10] which led to the application of the hydrido complex in hydrosilylation and silylation reactions, respectively. The reverse Si–H activation via deprotonative bond cleavage (Scheme 1c) through metal-ligand cooperation has only been observed once by Stradiotto and coworkers by means of a zwitterionic complex.[11]



Scheme 1. Methods for the activation of Si–H bonds.

As part of our research program on carbene complexes derived from methandiides we have focused on the exploration of the non-innocent behavior of these ligands and their use in cooperative bond activation reactions.[12,13] This has allowed for the activation of polar E–H bonds as well as the H–H bond in dihydrogen.[14] Yet, so far only the activation of protic compounds, such as alcohols and amines, has been achieved.[15] Due to the strong nucleophilicity of the carbene moiety, we assumed that Si–H cleavage would proceed with the reverse selectivity than observed for protic E–H bonds, i.e. formation of a hydrido complex via desilylation by the carbene ligand. Here, we show that cooperative Si–H activation of a series of silanes selectively occurs against the polarity of the M=C bond and that this is due to the unique reaction mechanism and the unusual non-innocent behavior of the carbene ligand.

The activation of Si–H bonds by carbene complex **1** was investigated by $^{31}P\{^{1}H\}$ NMR spectroscopy (for experimental details see the ESI). Treatment of a purple solution of **1** in toluene at room temperature with an excess of phenylsilane, $PhSiH_3$, instantaneously resulted in the selective formation of a single new product characterized by a singlet at δ_P = 65.2 ppm (δ_P = 67.1 ppm for **1**) and a distinct color change to orange.[16] However, no formation of the expected hydrido complex was observed, but selective transformation to the silyl complex **2a**, which could be isolated as orange solid in 79% yield (Scheme 2). **2a** is unequivocally characterized by the signal of the methanide hydrogen atom, which appears as doublet at δ_H = 3.71 ppm with a coupling constant of $^{2}J_{PH}$ = 9.40 Hz. The diastereotopic

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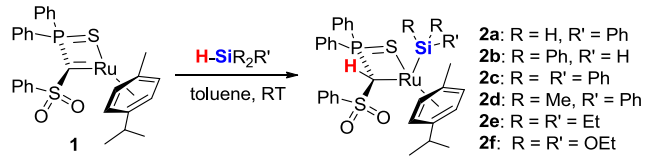
Electronic Supplementary Information (ESI) available: Experimental procedures, characterization data, crystallographic and computational details. See DOI: 10.1039/x0xx00000x



Scheme 2. Cooperative Si–H activation with ruthenium carbene complex 1.

SiH_2 protons appear as AB system at δ_H = 4.39 and 4.80 ppm (J_{AB} ≈ 5 Hz). No signal indicating the formation of a hydrido species or any other product was observed. The silicon resonance appears as doublet at δ_{Si} = –0.99 ppm ($^3J_{PSi}$ = 7.68 Hz) in the $^{29}Si\{^1H\}$ NMR spectrum. Thus, in total Si–H activation cleanly occurred across the M=C double bond with transfer of the hydridic hydrogen to the nucleophilic carbon centre.

The same reactivity was observed for a series of other secondary and tertiary silanes with aromatic and aliphatic substituents independent of the steric demand (Scheme 2). Even the often employed reducing agents, Et_3SiH and $(EtO)_3SiH$, underwent selective Si–H activation to the corresponding silyl complexes **2** without formation of any by-products (see ESI). In the case of Et_3SiH the Si–H activation resulted in the formation of an equilibrium between carbene complex **1** and silyl complex **2e**. Thereby, quantitative activation could only be observed by using an excess of silane. Dissolving of the formed addition product **2e** immediately resulted in the re-formation of **1** and the free silane. This reversibility was studied by VT-NMR spectroscopy, which only showed a small temperature dependency of the equilibrium. However, the reversibility of the Si-H activation of Et_3SiH was unambiguously confirmed via an exchange experiment. Treatment of the silyl complex **2e** with Ph_2SiH_2 resulted in the consumption of **2e** and the formation of the activation product **2b** (see ESI for NMR spectra). Only few examples of reversible, cooperative Si–H activations have been described before.[9,10] Due to this equilibrium, silyl complex **2e** could not be obtained in pure form. However, all other silyl complexes **2** could be isolated at room temperature as yellow to orange solids in good to excellent yields (see ESI).

The activation products **2a, 2b** and **2c** were additionally characterized by single-crystal X-ray diffraction analysis (Figure 1 and the ESI). The structures confirm the constitution of the silyl complexes and exhibit a *cis*-arrangement of the hydrogen and the silyl moiety relative to the former M=C bond. In solid as well as in solution only these *cis*-isomers were found. This diastereoselectivity suggests that the addition reaction selectively proceeds in a *cis*-manner. Upon Si–H addition the M–C bond elongates from 1.965(2) Å in the carbene complex **1** to 2.194(2) Å in **2a** and 2.210(2) Å in **2c**. This is in line with a change from a M=C double to a M–C single bond. The Ru–Si bonds are in the range of known ruthenium silyl complexes.[17]

The reactivity of carbene complex **1** towards silanes is remarkable, above all the observed selectivity, which clearly disagrees with the strong nucleophilicity of the carbene moiety and the polarity of the Si–H bond. Thus, DFT calculations were performed to provide further insight into the reaction mechanism (see the ESI for details). Optimizations were conducted on a methyl substituted model system of **1** with $PhSiH_3$ and Me_3SiH (Figure 2). For both silanes, the reaction was found to be exergonic. Thereby, the energy gain is higher for $PhSiH_3$ (ΔG = –93 kJ·mol^{-1}) than for Me_3SiH (ΔG = –[illegible] kJ·mol^{-1}), thus being in line with the reversibility observed for Et_3Si[illegible] in experiment.[18] The hypothetic hydrido complexes turned out t[illegible] be considerably less stable than the silyl complexes. Interestingly, no concerted reaction mechanism via simple 1,2-addition of th[illegible] Si–H bond across the M=C bond was found to be operative. Instead, Si–H activation proceeds via two reaction steps: (i) oxidative addition of the Si–H bond onto the ruthenium centre followed by (ii) hydrogen transfer to the ligand. This is in contrast to O–H and H–H activation reactions with complex **1**, which both proceed via 1,2-addition reactions.[14] However, for the Si–H activation reactions no transition state for such a concerted 1,2-addition of the Si–H bond across the M=C bond to form the silyl complexes **2** could be located. All optimizations resulted in the oxidative addition of the Si–H bond to the ruthenium centre. This addition showed a barrier of only 79 and 85 kJ·mol^{-1}, respectively, which corroborates with the fast reaction process observed in experiment. It is noteworthy that the intermediate hydrido silyl complex (**Int1**) is higher in energy than the carbene complex **1**. Yet, the final hydrogen transfer from ruthenium to carbon requires almost no energy. This low activation barrier suggests that the hydrogen transfer proceeds smoothly and presumably faster than any conformational changes in **Int1**. This might be the reason for the observed diastereoselectivity of the activation reaction.

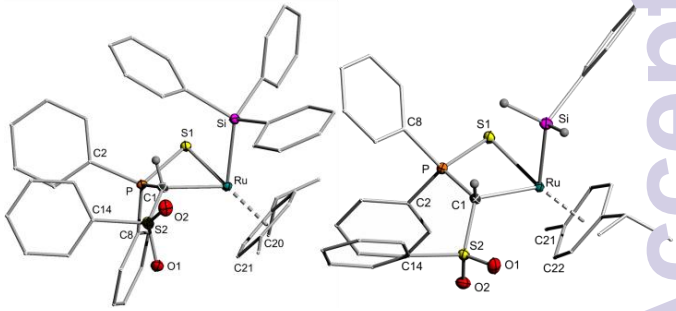


Figure 1. Molecular structures of the activation products (left) **2c** and (right) **2a**. All hydrogen atoms except for the H atoms at C1 and Si have been omitted for clarity. Displacement ellipsoids drawn at the 50% probability level. For the molecular structure of **2b** see the SI. Selected bond lengths [Å] and angles [°]: **2a**: Ru–C1 2.194(2), Ru–Si 2.4168(7), Ru–S1 2.445(1), S1–P 2.0091(8), S2–O1 1.4417(17), S2–O2 1.4478(17), S2–[illegible] 1.750(2), P–C1 1.788(2), C1–Ru–Si 86.89(6), C1–Ru–S1 75.3(1), S2–C1–P 125.73(13), S2–C1–Ru 121.64(12), P–C1–Ru 90.9(1). **2c**: Ru–C1 2.2101(15), Ru–Si 2.3547(5), Ru–S1 2.4237(4), S1–P 2.006(1), P1–C1 1.8006(16), C1–S2 1.762(2), O1–S2 1.440(1), S2–O2 1.439(1), C1–Ru–Si 84.70(4), C1–Ru–S1 79.34(4).

Overall, the cooperative Si–H activation results from an oxidative addition of the Si–H bond to the metal centre and the H transfer to the ligand. Thus, the selective transfer of the hydridic hydrogen of the silane to the nucleophilc carbon atom of the carbene ligand originates from the higher migration ability of hydrogen compared to the silyl group. Accordingly, silyl transfer to the ligand (from **Int1**) showed a higher activation barrier ($\Delta G^{\ddagger}$ = 84 kJ·mol^{-1} for Me_3SiH). The same holds true for the concerted 1,2-addition of the Si–H bond across the M=C bond ($\Delta G^{\ddagger}$ = 100 kJ·mol^{-1} for Me_3SiH) to yield the hypothetical hydrido complex. The facile and high-yielding Si–H activation with complex **1** is remarkable and can be attributed to the unique metal carbon interaction in methandiide based carbene complexes. Contrary to "classical" alkylidene complexes, the [illegible] substituents in **1** allow for an efficient delocalization of the π-

electron density either to the metal or into the ligand backbone. This results in an extremely flexible metal carbon interaction and its adjustment to the electronic situation at the metal.[19] Table 1 shows the Wiberg bond indices (WBI) and the NBO charges in the complex during the activation process, which reflect the flexible bonding situation. While the WBI of the Ru–Si bond continuously increases during the silyl complex formation, the index of the Ru–C bond decreases, thus being well in line with the change from the M=C double to the M–C single bond. This is connected with an increase of the negative charge at carbon, which is stabilized by the positive charges of the thiosphosphinoyl and sulfonyl moiety (see SI). According to the calculations, the metal carbon double character is already lost as a result of the interaction of the Si–H bond with the ruthenium centre (**TS1**). It is interesting to note, that the "free" coordination site at the metal for oxidative addition is solely generated by the flexibility of the M–C bond. The Ru–S bond remains intact during the whole activation process (c.f. $WBI_{Ru–S}$). This suggests, that the ligand does not only serve as proton acceptor. Instead, its electronic flexibility also enables the shuttling of electrons to the metal and back. This flexibility allows for the oxidative addition of the Si–H bond to the 18e species **1**, while keeping the 18 valence electrons of the metal (c.f. **1** and **Int1**).

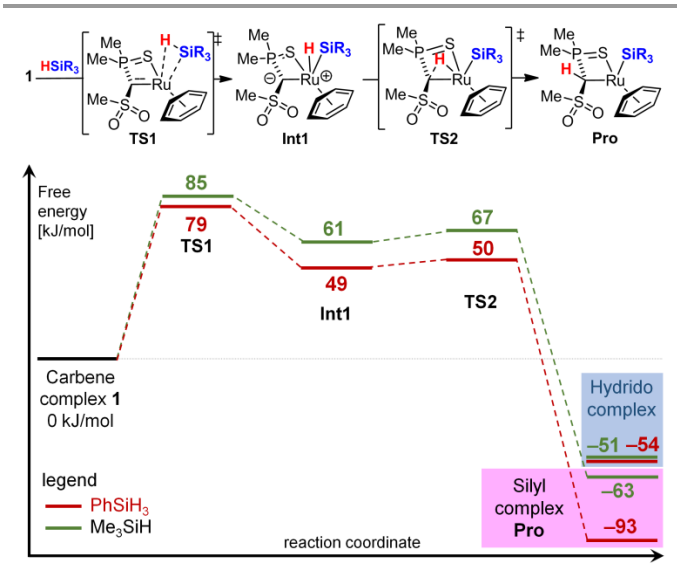


Figure 2. Calculated mechanism and reaction profile for the Si–H activation of $PhSiH_3$ and Me_3SiH with a methyl substituted model system of complex 1 [M062X//6-311+G(d,p)/LANL2TZ(f)].

Table 1. Wiberg bond indices and NBO charges of the complex **1** during Si–H bond activation.

	1	**TS1**	**Int1**	**TS2**	**Pro**
$WBI_{Ru–C}$	1.26	0.77	0.78	0.70	0.58
$WBI_{Ru–Si}$	–	0.23	0.55	0.57	0.71
$WBI_{Ru–H}$	–	0.34	0.55	0.44	0.02
$WBI_{Ru–S}$	0.59	0.74	0.76	0.76	0.65
q_C	–0.93	–1.13	–1.08	–1.11	–1.00
q_{Ru}	–0.19	–0.55	–0.83	–0.87	–0.80
q_S	–0.39	–0.33	–0.22	–0.24	–0.29
q_H	–0.15	–0.02	0.22	0.29	0.27

The ease of the Si–H activation by carbene complex **1** and the observed reversibility led us to explore a possible transfer of the activated silane to organic substrates. Due to its importance in academia as well as industry we chose the hydrosilylation as first test reaction. Treatment of a toluene solution of the Ph_2SiH_2 activation product **2b** with norbornene at 60 °C resulted in the consumption of the complex (as evidenced by ^{31}P NMR spectroscopy). GC/MS analysis of the product mixture showed the formation of the hydrosilylation product (see ESI), yet only in small quantities due to the preferred ring-opening metathesis polymerization of the alkene.[20] Thus, all attempts to establish catalytic hydrosilylation based on complex **1** failed so far. It is interesting to note, that Grubbs-type ruthenium complexes were found to be active in hydrosilylation reactions.[21] Recent studies, however, led to the conclusion that the initial stage of the catalytic cycle involves direct σ-bond metathesis between the silane Si–H bond and the Ru–Cl bond of the catalyst and no Si–H addition across the Ru=C bond. The alkylidene ligand was thus proposed to solely act as spectator ligand.[22] Despite the fact that methanediide derived carbene complexes are electronically different from prototypical alkylidene ligands, also for these complexes a mechanism via ligand assisted Si–H activation at the metal (Figure 2) might be operative.

In conclusion, we reported the efficient Si–H activation of a number of silanes via metal ligand cooperation in a methandiide based carbene complex. The activation proceeds selectively via transfer of the hydridic hydrogen to the nucleophilic carbon atom of the carbene ligand. DFT calculations show that the activation does not proceed via a concerted 1,2-addition across the M=C bond, but in a step-wise fashion via oxidative addition to the metal centre and hydrogen transfer to the carbene ligand. Thereby, the ligand enables the activation by its electronic flexibility as well as its function as Brønsted base. These properties allow for the oxidative addition of the Si–H bond to the metal centre, while keeping its 18 valence electrons.

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