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Mechanism of the cooperative Si–H bond activation at Ru–S bonds†

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The nature of the hydrosilane activation mediated by ruthenium(II) thiolate complexes of type [(R,P)Ru(SDmp)][BARF] is elucidated by an in-depth experimental and theoretical study. The combination of various ruthenium(II) thiolate complexes and tertiary hydrosilanes under variation of the phosphine ligand and the substitution pattern at the silicon atom is investigated, providing detailed insight into the activation mode. The mechanism of action involves reversible heterolytic splitting of the Si–H bond across the polar Ru–S bond without changing the oxidation state of the metal, generating a ruthenium(II) hydride and sulfur-stabilized silicon cations, i.e. metallasilysulfonium ions. These stable yet highly reactive adducts, which serve as potent silicon electrophiles in various catalytic transformations, are fully characterized by systematic multinuclear NMR spectroscopy. The structural assignment is further verified by successful isolation and crystallographic characterization of these key intermediates. Quantum-chemical analyses of diverse bonding scenarios are in excellent agreement with the experimental findings. Moreover, the calculations reveal that formation of the hydrosilane adducts proceeds via barrierless electrophilic activation of the hydrosilane by sterically controlled η2 (side-on) or η3 (end-on) coordination of the Si–H bond to the Lewis acidic metal center, followed by heterolytic cleavage of the Si–H bond through a concerted four-membered transition state. The Ru–S bond remains virtually intact during the Si–H bond activation event and also preserves appreciable bonding character in the hydrosilane adducts. The overall Si–H bond activation process is exergonic with ΔG° ranging from ~20 to ~40 kJ mol−1, proceeding instantly already at low temperatures.

Introduction

Neutral tetracoordinate hydrosilanes do generally not undergo spontaneous reaction with organic substrates and require the activation of the Si–H bond. Among the diverse modes that are known for hydrosilane activation,1 protocols using transition metal complexes clearly prevail. Numerous transition metal hydrosilane complexes were structurally characterized and identified as key intermediates in various catalytic processes.2 The diverse bonding motifs in these structures reveal a continuum along the Si–H bond activation pathway, ranging from several nonclassical (three-center-two-electron) interactions to full homolytic cleavage of the Si–H bond (I→IV, Scheme 1A).3 Since oxidative addition typically leads to an increase of both the formal oxidation state and coordination number of the metal (cf. IV), this mechanism is usually invoked with low-valent, electron-rich transition metal complexes, particularly those of groups 9 and 10. Alternatively, the Si–H bond is heterolytically split without change in the oxidation state of the metal to formally generate a hydride (H−) and a silylium ion (R3Si+).4 This event is favored with electrophilic (cationsic) metal centers and requires assistance of a Lewis base. By coordination to the Lewis acidic metal center, through either binding modes I, II, and III, the silicon atom is rendered sufficiently electrophilic to react with a wide variety of nucleophiles. In the absence of any externally added Lewis base, heterolytic cleavage of the Si–H bond is also facilitated by cooperative metal–ligand interactions where the ancillary ligand serves as an internal Lewis-basic site and is directly involved in the Si–H bond activation process.5 In this case, a mechanism following a [2+2]-type cycloaddition (Scheme 1B) or a σ-bond metathesis (Scheme 1C) is generally postulated.6 In the former scenario, well-defined addition of the Si–H bond across a metal–ligand multiple bond results in the formation of a metal hydride complex in which the silyl group is incorporated (cf. V). In the latter, the product distribution strongly depends on the nature of the metal–ligand combination. While σ-bond metathesis via concerted transition state TS-VI (Scheme 1C, upper) leads to a metal silyl complex VII with release of side product VIII (typically

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Chem. Sci., 2015, 6, 1-11 | 1
dihydrogen or methane), reaction via TS-IX (Scheme 1C, lower) produces a metal hydride X with concomitant dissociation of silylated ligand XI (typically a silyl ether or silyl amine).

\[
\begin{align*}
\text{A} & \quad \text{Si-H} \rightarrow \text{Si-H} - [M] \\
\eta^1-MH(Si) & \quad \eta^1-MH(Si) \\
\alpha\text{-complex} & \quad \alpha\text{-agostic, IHI, SISHA, (A)SOAP} \\
\text{IV} & \quad \text{M}(SiH) \\
\text{SIIH} & \quad \text{classical silyl hydride}
\end{align*}
\]

\[
\begin{align*}
\text{B} & \quad \text{Si-H} + X \rightarrow \text{Si-H} + X \\
\text{X} = \text{NR, O, S} & \quad \text{[2+2] addition}
\end{align*}
\]

\[
\begin{align*}
\text{C} & \quad \text{Si-H} + [M]^n - L \rightarrow [M]^n - L_2 \\
\text{typically} \ L = \text{H or Me} & \quad \text{TS-VI} \\
\text{VII} & \quad \text{VIII} \\
\text{Si-H} + [M]^n - L \rightarrow [M]^n - L_2 \\
\text{typically} \ L = \text{OR or NR}_2 & \quad \text{TS-IX} \\
\text{X} & \quad \text{XI}
\end{align*}
\]

Scheme 1 Diverse bonding scenarios in the Si-H bond activation by transition metal complexes [IHI = interligand hypervalent interactions, SISHA = secondary interactions between a silicon and a hydrogen atom, (A)SOAP = (a)symmetric oxidative addition products, and SI = RI SI = trionorganoyl].

Compared to the classical oxidative addition pathway commonly proposed, heterolytic Si-H bond activation with transition metals is less well-established and was initially postulated by Luo and Crabtree in the iridium(III)-catalyzed alcoholysis of hydrosilanes.7 Since this report, several transition metal mediated heterolyses of Si-H bonds have been documented.8 In most cases, however, a highly reactive silicon electrophile was generated through coordination to a cationic metal center and subsequently trapped in a less controlled manner by intermolecular reaction with adventitious water, the solvent (e.g. CH2Cl2), or counteranion (e.g. OTf, SbF6 or BF4). A few examples of intramolecular cooperative Si-H bond activation were shown where the Si-H bond is preferentially split across a polar M=X double bond (cf. Scheme 1b with X = NR, O, S), using early or middle transition metals in high oxidation states where oxidative addition is not possible or unlikely (e.g. Ti(IV), Ta(V), Re(V)).9 However, this activation mode allowed for the isolation and crystallographic characterization of unique hydrosilane adducts, as specified by complex V, its synthetic use and application to catalytic processes is still out of the ordinary and mainly restricted to hydrodefluorination reactions.8

As part of our ongoing research endeavors of exploring new approaches to the generation of silicon electrophiles, we introduced the cationic ruthenium(II) thiolate complexes 1 (with Ar1 = 3,5-(triﬂuoromethyl)phenyl, Scheme 2, top right).8 The tethered bulky 2,6-dimethylphenyl thiolate (SDmp) ligand stabilizes the coordinately unsaturated metal center in 1 and also prevents formation of binuclear sulfur-bridged complexes. The polar Ru–S bond of these (formally) 16-electron complexes combines Lewis acidity at the metal center and Lewis basicity at the adjacent sulfur atom. We reasoned that this motif could be considered as a transition metal frustrated Lewis pair (FLP)10 mediates the heterolytic cleavage of Si–H bonds, generating a metal hydride and a sulfur-stabilized silicon cation (Scheme 2, top left).11 This assumption was corroborated by a related study of Stradiotto and co-workers, reporting the addition of the Si-H bond of Ph2SiH2 and PhSiH3 across the M-S bond of cationic [CP*M(κ2-3-PPr3-2-S-indene)]2[B(C6F5)4] complexes (with M = Rh and Ir).12 Compared to harder nitrogen or oxygen donors, the interaction with the soft sulfur atom was expected to give a more reactive silicon electrophile.11b,13 In addition, weak stabilization ought to favor reversible coordination, thereby facilitating R2Si- transfer and securing turnover in catalytic processes. The rationally designed complexes 1 indeed proved to serve as potent catalysts for the facile activation not only of Si-H but also H-H and B-H15 bonds. Since our initial report on Si-H bond activation,14c we have disclosed a number of catalytic transformations, including dehydrogenative silylations,14d chemoselective hydrosilylations,14f as well as hydrodefluorination reactions14e (Scheme 2, bottom). It is interesting that Stradiotto and co-workers had been able to apply their rhodium(III) thiolate complex in ketone hydrosilylation (not shown)12 where we later observed dehydrogenative silyl enol ether formation with our system.14b All catalyses proceeded already at room temperature, neither requiring a hydrogen acceptor nor an added base for the catalytic cycle to close.

1 with 2

Hydrodefluorination of CF3-Substituted Anilines (Ref. 14g)

Hydroxylation of CO2 (Ref. 14f)

N-Silylation of Heterocycles and Anilines (Ref. 14d)

1,4-Hydroxylation of Pyridines (Ref. 14e)
Encouraged by the broad spectrum of catalytic reactions that were accomplished by using a single catalyst, we pursued an in-depth analysis of the Si–H bond activation event by ruthenium(II) thiolate complexes 1. Since the activation mode naturally impacts the course and outcome of a reaction, its mechanistic understanding is of vital importance and provides useful insights for the future design and development of more efficient catalysts.

All proposed mechanistic assumptions have so far relied on the heterolytic splitting of the Si–H bond at the polar Ru–S bond in 1 (cf. Scheme 2, top left) and have been primarily based on the interpretation of experimental observations. In view of the fact that the ruthenium(II) metal center is coordinately unsaturated and in low oxidation state several possibilities of Si–H bond activation exist (Chart 1). Aside from the proposed cooperative activation mode (cf. 3 in Chart 1), addition of the Si–H bond across the Ru–S bond with reversed regioselectivity might occur, leading to metal silyl complex 4 (cf. Scheme 1C). Since tetracoordinate silicon readily expands its coordination sphere, activation of the hydrosilane through coordination to the Lewis basic sulfur atom as in 5 needs to be considered. Moreover, pathways without participation of the sulfur atom are another option. These could proceed via electrophilic activation of the Si–H bond either by η^1 (side-on) or η^2 (end-on) coordination (cf. 6 and 6’, respectively), followed by heterolytic cleavage of the Si–H bond by an externally added nucleophile. Likewise, full homolytic cleavage of the hydrosilane via classical oxidative addition affording metal silyl hydride 7 cannot be ignored. Therefore, several mechanistic questions have remained, including the role of the thiolate ligand.

Results and discussion

From our previous studies, we already knew that Si–H bond activation with cationic ruthenium(II) thiolate complexes 1 is remarkable facile, proceeding instantly at room temperature. The tethered coordination mode of the SDmp ligand proved to be crucial: While the lability of a monodentate thiolate ligand in related rhodium(III) and iridium(III) complexes resulted in decomposition and formation of various metal hydride species in the presence of hydrosilanes, the two-point binding mode in 1 imparts increased stability to the Ru–S bond. In addition, this motif leads to structural rigidity and improved steric accessibility of the Ru–S bond, as seen in the molecular structure of these complexes.

Elucidation of the Si–H bond activation with NMR spectroscopy

To gain deeper insight into the Si–H bond activation, we performed a detailed NMR study using one- and two-dimensional multinuclear NMR measurements. In an initial investigation, monitoring the reaction of ruthenium(II) thiolate complex 1a (R=Et) with hydrosilanes under typical catalysis conditions (room temperature, excess hydrosilane) emerged as difficult since dynamic processes led to significant line-broadening in the NMR spectra. However, we identified the combination of complex 1b where the ruthenium atom is coordinated by a para-fluorinated aryl phosphine and MePh,SiH (2a) to be particularly suitable for NMR studies. Treatment of 1b with two equivalents of MePh,SiH (2a) at ambient temperature resulted in an immediate color change from green to yellow, “visualizing” successful Si–H bond activation. Clearly resolved spectra, obtained in both CCl4 and CD2Cl2 (with slightly better resolution in CD2Cl2, see the ESI for details) were consistent with formation of hydrosilane adduct 3ba (1b → 3ba, Scheme 3).

The reaction proceeded cleanly, and resonance signals of unsaturated ruthenium(II) thiolate complex 1b were no longer detectable. Instead, a doublet at −7.5 ppm in the 1H NMR...
spectrum (Figure 1) provided unambiguous evidence for a phosphine-ligated ruthenium hydride (ruling out intermediates 4 and 5). The absence of any $^{1}J_{CS}$ satellites, typically observed for $\eta^1$ and $\eta^2$ hydrosilane complexes, further supported complete Si–H bond cleavage (making 6 and 6* unlikely). The coupling constant of 47 Hz is in the typical range for $^{1}J_{CH}$ coupling and was also identified in the $^{29}$P NMR spectrum at 48.5 ppm whereas a singlet is observed at 30.0 ppm for complex 1b. While the latter is C$_2$ symmetric, the additional hydride ligand creates a chiral center at the ruthenium atom in 3ba. This is also reflected in the $^{1}$H NMR spectrum that shows six rather than four singlets for the methyl groups and four rather than two signals for the meta-CH groups of the SDmp ligand (Figure 1).

Using a $^{1}$H,$^{29}$Si HMBC experiment, a $^{29}$Si NMR resonance signal was detected at 20.1 ppm, significant downfield shifted ($\Delta \delta = 37.6$ ppm) relative to free MePh$_2$SiH (2a, $\delta = 17.5$ ppm). This is an indication for the generation of an electrophilic silicon species and is in accordance with postulated intermediate 3ba. For comparison, the corresponding neutral silyl thioether Ph$_2$MeSiSDmp (for its preparation and characterization, see the ESI) that features an S–Si linkage without an adjacent metal center is characterized by a $^{29}$Si NMR chemical shift of 2.9 ppm ($\Delta \delta = 20.4$ ppm relative to MePh$_2$SiH (2a)). The substantial deshielding of the silicon nucleus in hydrosilane adduct 3ba reveals a strong influence of the metal center on its Lewis acidity that is expected to be higher compared to Ph$_2$MeSiDmp. The latter is in fact not a potent silyl transfer agent.

All NMR signal assignments were also confirmed by our state-of-the-art relativistic calculations of NMR chemical shifts at the four-component matrix Dirac–Kohn–Sham (mDKS) level (cf. Table 1 and Table S2 in the ESI for detailed data). Spin-orbit (SO) effects were found to have a sizeable shielding contribution to both $^{1}$H (up to $\sim$3.1 ppm) and $^{31}$P (up to $\sim$35 ppm) NMR chemical shifts, owing to the large involvement of both ruthenium 4d-orbitals and ligand s-orbitals in metal–ligand binding.

The analysis of the NMR spectroscopic data, including further 2D NMR measurements (see the ESI for details), clearly supports the structural assignment of adduct 3ba. Evidence for the intact Ru–S bond is provided by a $^{3}J_{CH}$ coupling in the $^{1}$H,$^{13}$C HMBC NMR spectrum between the quaternary sulfur-substituted carbon atom of the SDmp ligand and the ruthenium hydride. However, unambiguous information about the existence of an S–Si linkage and the reversibility of the Si–H bond activation step was still elusive. A $^{1}$H,$^{1}$H EXSY NMR then shed light on this problem: Cross peaks revealed chemical exchange between the hydrides of Ru–H and MePh$_2$Si–H on the NMR time scale (Figure 2, upper), further exchange effects were found in the alkyl and aryl range (Figure 2, lower).

The two phenyl groups at the silicon atom are chemically inequivalent, showing chemical exchange between each other and the phenyl group of the free hydrosilane ([m,n,Ph$_2$Si]). Surprisingly, chemical exchange is also observed for the “half-sites” of the SDmp ligand. These findings can be rationalized by cooperative Si–H bond activation. Heterolytic splitting of the Si–H bond across the polar Ru–S bond not only generates a stereogenic metal center but also stereogenicity at the sulfur atom. By reversible syn-addition from either side (front or back), the resulting enantiomers of 3ba are in equilibrium, and this is exactly what is observed as chemical exchange between the diastereotopic protons of [a,e], [b,d], [f,k], and [g,j] (Scheme 4). The syn-selectivity of the activation step was secured by the absence of any detectable diastereomers of 3ba.
The role of the phosphine ligand and the substitution pattern at the silicon atom

Having elucidated a cooperative hydrosilane activation mode, we next examined the reaction of hydrosilanes 2a–e with complexes 1a and 1b. In all cases, successful Si–H bond heterolysis was monitored by NMR spectroscopy. The characteristic $^1$H, $^{29}$Si, and $^{31}$P NMR chemical shifts of the various hydrosilane adducts 3 as well as the corresponding free hydrosilanes 2 and thiolate complexes 1 are collected in Table 1. While the resonance signals for mixtures of ruthenium complex 1a, decorated with a Et$_3$P ligand, and hydrosilanes 2a and 2b were too broad to be observed at 300 K, better resolved NMR resonances are obtained at 250 K (entries 1 and 2). The $^1$H NMR spectra of adducts 3 each feature two signature resonances, one corresponding to the Si–H group of excess hydrosilane 2 (3.7–4.8 ppm) and one upfield-shifted doublet for the ruthenium hydride either at around ~8.2 (for 3aa–3ad, entries 1–4) or ~7.6 ppm (for 3ba–3bc and 3be, entries 5–8). The $^{29}$Si NMR resonances of adducts 3 (18.2–41.6 ppm) are shifted to higher frequencies relative to 2 (~17.5–0.6 ppm), indicating decreased electron density at the silicon atom. Although this is an oversimplified argument (for instance, a rather poor correlation, if any, between $^{29}$Si NMR chemical shifts and atomic charges on the silicon atom in ferrocene-stabilized silylium ions was found in our previous study$^{20}$), the more electrophilic nature of the silicon atom in hydrosilane adducts 3 as compared to the starting hydrosilanes 2 is also evident from NPA charge analysis (cf. Table S4 in the ESI). As expected, the $^{31}$P NMR chemical shifts are sensitive towards the substituents at the silicon atom, and the highest downfield shifts of 3 are observed for trialkysilanes 2c and 2d (entries 3, 4, and 7). The $^{31}$P NMR chemical shifts are static again, and a resonance at 40 ppm is characteristic for 3aa–3ad (entries 1–4), whereas a chemical shift at 48 ppm is indicative for 3ba–3bc and 3be (entries 5–8). The overall trends in the NMR spectroscopic data reveal that the phosphine ligand mainly influences the electronic nature of the ruthenium hydride while the Lewis acidity of the silicon electrophile is largely controlled by the substitution pattern at the silicon atom.

Table 1 Experimental and calculated $^1$H, $^{29}$Si, and $^{31}$P NMR chemical shifts of hydrosilane adducts 3

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reaction</th>
<th>$^1$H NMR</th>
<th>$^{29}$Si NMR</th>
<th>$^{31}$P NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\delta$(Si–H)</td>
<td>$\delta$(Ru–H)</td>
<td>$\delta$(Si–H)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[ppm]</td>
<td>[ppm]</td>
<td>[ppm]</td>
</tr>
<tr>
<td>1$^a$</td>
<td>1a + MePh$_2$SiH (2a) $\rightarrow$ 3aa</td>
<td>4.8</td>
<td>-8.2 ($-7.8)^b$</td>
<td>-13.0</td>
</tr>
<tr>
<td>2$^a$</td>
<td>1a + Me$_2$PHSiH (2b) $\rightarrow$ 3ab</td>
<td>4.4</td>
<td>-8.3 ($-7.9)^b$</td>
<td>-12.7</td>
</tr>
<tr>
<td>3$^a$</td>
<td>1a + Et$_2$SiH (2c) $\rightarrow$ 3ac</td>
<td>3.7</td>
<td>-8.0</td>
<td>-11.7</td>
</tr>
<tr>
<td>4$^a$</td>
<td>1a + EtMe$_2$SiH (2d) $\rightarrow$ 3ad</td>
<td>3.7</td>
<td>-8.1 ($-7.8)^b$</td>
<td>-11.8</td>
</tr>
<tr>
<td>5$^a$</td>
<td>1b + MePh$_2$SiH (2a) $\rightarrow$ 3ba</td>
<td>4.8</td>
<td>-7.5 ($-7.6)^b$</td>
<td>-12.3</td>
</tr>
<tr>
<td>6$^a$</td>
<td>1b + Me$_2$PHSiH (2b) $\rightarrow$ 3bb</td>
<td>4.4</td>
<td>-7.7 ($-7.5)^b$</td>
<td>-12.1</td>
</tr>
<tr>
<td>7$^a$</td>
<td>1b + Et$_2$SiH (2c) $\rightarrow$ 3bc</td>
<td>3.7</td>
<td>-7.6</td>
<td>-11.3</td>
</tr>
<tr>
<td>8$^a$</td>
<td>1b + iPrMePHSiH (2e) $\rightarrow$ 3be</td>
<td>4.3</td>
<td>-7.7</td>
<td>-12.0</td>
</tr>
</tbody>
</table>

$^a$All reactions were performed in an NMR tube using ruthenium(II) thiolate complex 1a or 1b (1.0 equiv, 20 mM) and the corresponding hydrosilane 2 (2.0 equiv). $^b$In parentheses, NMR chemical shifts calculated at the four-component m0Ks level using the PBE functional and the GIAO method in conjunction with Dyall’s VDZ basis set on Ru and fully uncontracted IGLO-II basis sets on the ligand atoms (cf. Computational Details and Table S2 in the ESI). $^c$$^1$H,$^{29}$Si HMOC NMR spectroscopy optimized for $f = 8$ Hz. $^d$The resonance appears as a doublet with a coupling constant of 47–50 Hz. $^e\Delta\delta$(H) = $\delta$(Ru–H) – $\delta$(Si–H). $^f\Delta\delta$(Si) = $\delta$(5–Si) – $\delta$(Si–H). $^g\Delta\delta$(P) = $\delta$(P) – $\delta$(1) $^h$In CD$_2$Cl$_2$ at 250 K. $^i$In CD$_2$Cl$_2$ at 300 K.
Mechanistic control experiments with deuterium-labeled and silicon-stereogenic hydrosilanes

To further probe the Si–H bond activation step, control experiments employing deuterium-labeled MePh₂SiD (2a–d₁) were performed. As expected, reaction of ruthenium(II) thiolate complex 1b with two equivalents of deuterolsilane 2b–d₁ in CD₂Cl₂ at room temperature resulted in complete incorporation of deuterium into adduct 2ba–d₁. In ¹H/²H scrambling experiments, deuterium-labeled Me₂Ph₂SiD (2b–d₁) was treated with non-deuterated MePh₂SiH (2a) in the presence of catalytic amounts of either complex 1a or 1b at room temperature (Scheme 5). Whereas ¹H/²H exchange was fast and complete with ruthenium(II) thiolate complex 1a, no scrambling was observed with 1b even after 3 h.

The pronounced differences in reactivity of both complexes led us to investigate the role of the phosphine ligand (Et₃P in 1a versus (p-FC₆H₄)₂P) in 1b) in more detail. Since electron-rich Et₃P is a stronger σ-donor than the electron-deficient para-fluorinated aryl phosphine, the ruthenium hydride in hydrosilane adduct 3a is expected to be a better hydride donor than in 3b. On the other hand, 3b is likely to be a better R₂Si⁻ transfer reagent compared to 3a. Both of these properties will contribute to the ¹H/²H exchange, depending on whether this process proceeds through a σ-bond metathesis solely involving the metal hydride (TS-XII, Scheme 6, left)¹⁴ or through formation of hydronium ions 9 ([Si-H-Si⁺])¹⁵ by R₂Si⁻ transfer to a free hydrosilane (Scheme 6, right).

The use of a silicon-stereogenic hydrosilane as a stereochemical probe finally allowed to distinguish between these two mechanisms: Enantioenriched hydrosilane (R(Si)-2e) was reisolated with complete retention of configuration at the silicon atom after treatment with complex 1b (Scheme 7). On the basis of this result, the generation of hydronium ions is highly unlikely, as this pathway would result in racemization. The better hydride donor strength of 3a thus is likely to account for the ¹H/²H exchange.

Isolation and crystallographic characterization of hydrosilane adducts 3ab and 3ad

To provide unambiguous evidence for the generation of silylthioruthenium hydride intermediates, we pursued the crystallization of hydrosilane adducts 3. Single crystals suitable for X-ray diffraction were obtained for 3ab as well as 3ad at −30 °C from a solution of complex 1a in neat hydrosilane, either Me₂Ph₂SiH (2b) or EtMe₂SiH (2d). Compared to the Ru–S bond in coordinatively unsaturated complex 1a (2.21 Å), the molecular structure of 3ab shows a slightly elongated (about 8%) yet intact Ru–S bond (2.39 Å, Figure 3). The Si–H bond is completely broken and an interatomic Si–H distance of 3.17 Å indicates no interaction of the silicon with the hydrogen atom. While the hydride is bound to the ruthenium center with a bond length of 1.58 Å, the silicon atom is connected to the sulfur atom with a distance of 2.24 Å. This S–Si distance is slightly elongated (about 6–7%) compared to structurally related neutral ruthenium(II) silylthiolate complexes (2.11 Å² and 2.09 Å¹⁸). The average C–Si–C angle of 110.5° reflects a tetrahedral (silylated sulfonium ion) rather than a trigonal planar (sulfur-stabilized silicon cation) coordination around the silicon atom. All selected bond lengths and angles of the EtMe₂SiH adduct 3ad are comparable to those of 3ab and are in excellent agreement with the DFT optimized structures (see the ESI for detailed data).

Scheme 7 Control experiment with a silicon-stereogenic hydrosilane: No support for the intermediacy of hydronium ions.

Chem. Sci., 2015, 6, 1-11 | 6

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Isolation and characterization of \([\text{R}_3\text{POSiR}']_2\text{BAR}^{+}_2\text{BAR}^{+}\] (10)

During our NMR spectroscopy studies, we noticed the presence of minor amounts of another species next to hydrosilane adduct 3 in the majority of the measurements. This observation became apparent by a second high-frequency-shifted signal in both the \(^{29}\text{Si}\) NMR and \(^{31}\text{P}\) NMR spectra. For instance, when ruthenium(II) thiolate complex 1a was treated with \(\text{MePh}_2\text{SiH}\) (2a) to generate 3aa, an additional minor peak was observed at 8.8 ppm in the \(^{29}\text{Si}\) NMR spectrum and at 92.9 ppm in the \(^{31}\text{P}\) NMR spectrum (later assigned to 10aa; for a tabulated summary of all combinations of 1 and 2 to form 8, see Table S1 in the ESI). While the structure determination solely on the basis of NMR spectroscopy failed, the calculated mass for \([\text{p-FC}_6\text{H}_{14}]\text{POSiMePh}_3]^+ (10ba)\] was found by ESI mass spectrometry. We were then able to crystallize the related silyloxyphosphonium salt \([\text{Et}_3\text{POSiMe}_2\text{Ph}]\text{BAR}^{+}_2\text{BAR}^{+}\] (10ab), providing conclusive evidence for our structural assignment (Figure 4). Single crystals of 10ab suitable for X-ray diffraction were obtained from a solution of ruthenium(II) thiolate complex 1a and excess hydrosilane 1b in toluene layered by n-hexane at \(-30^\circ\text{C}\).

To further probe the structure and reactivity of the silyloxyphosphonium salts, we independently prepared \([\text{Et}_3\text{POSiMePh}_2]\text{BAR}^{+}_2\text{BAR}^{+}\] (10aa) by treatment of in-situ generated silylthioruthenium hydride intermediate 3ba with stoichiometric amounts of \(\text{Et}_3\text{PO}\) (11a) in \(\text{C}_6\text{D}_6\) (Scheme 8). Beside the expected chemical shift for ruthenium hydride complex 8b at 53.5 ppm, a resonance signal at 91.3 ppm was seen in the \(^{31}\text{P}\) NMR spectrum, matching with the observed side product found in the above-described preparation of hydrosilane adduct 3aa (cf. Table S1, entry 1).

To test the ability of the silyloxyphosphonium salts to act as silyl transfer reagents, acetophenone was added to the independently prepared mixture of 10aa and 8b. No reaction was observed even at prolonged reaction times, thereby ruling out 10aa as an active species in our catalyses. \(^{13}\)b The source of oxygen, however, remains unclear but traces of dioxygen cannot be fully excluded given the high reactivity of intermediate 3. Water is unlikely since this would result in immediate silanol or disiloxane formation, and neither various equivalents of the hydrosilane nor a change of the solvent had an effect on the proportion of 10ab.

DFT calculations

To gain deeper insight into the nature of the Si–H bond activation step and to identify possible intermediates, quantum-chemical calculations at the B3LYP-D3(BJ)/ECP/6-31+G(d,p) level including an atom-pairwise correction of Grimme’s D3 model with Becke-Johnson (BJ) damping for dispersion forces and using an SMD solvation model to account for bulk solvent effects (benzene as a solvent) were performed (cf. Computational Details in the ESI). Combination of various triaryl- and trialkylyphosphine ligands and hydrosilanes \([\text{MePh}_2\text{SiH}] (2a), \text{Me}_2\text{PhSiH} (2b), \text{EtMe}_2\text{SiH} (2d), \text{tBuMe}_2\text{SiH})\] were examined computationally. The free-energy profile together with the optimized structures of relevant intermediates and transition states for the reaction of ruthenium(II) thiolate complex 1a\(^+\) with \(\text{Me}_2\text{PhSiH} (2b)\) is shown in Figure 5 (selected structural parameters and thermodynamic data for the entire series of complexes studied in this work are collected in Table S3 in the ESI).

Cooperative heterolysis of the Si–H bond commences with coordination of the hydrosilane to the unsaturated 16-electron \([\text{R}_3\text{P}](\text{Ru} \text{SDmp}))^+ complex 1\(^+\), filling the ruthenium(II) vacant...
coordination site by forming a stable \( \eta^1 \)- or \( \eta^2 \)-hydrosilane complex (\textit{cf.} 6 or 6' in Chart 1). The coordination of the hydrosilane to ruthenium(II) thiolate complex 1 was revealed as barrierless on the electronic energy surface, albeit the counteranion might affect the reaction barrier when ion-pair dissociation/formation takes place. The reaction is in most cases exergonic, with exception of the hydrosilane decorated with a bulky tert-butyl group, where the \( \Delta G^\circ \) is slightly positive (\textit{cf.} Table S3). The bonding situation in the hydrosilane adducts 3 depends on the nature of the phosphine ligand as well as on the hydrosilane (\textit{cf.} Figure 6). For instance, the sterically least demanding complex bearing a Me\(_3\)P ligand prefers side-on \( \eta^2 \)-coordination of Me\(_2\)PhSiH (2b) with a somewhat more elongated Si–H bond (1.794 Å) and a more acute \( \alpha(\text{Ru}…\text{H}…\text{Si}) \) angle (99°) as compared to the \( \eta^1 \)-hydrosilane complex of 1a (with Et\(_3\)P instead of Me\(_3\)P) and Me\(_2\)PhSiH, featuring a Si–H bond distance of 1.627 Å and \( \alpha(\text{Ru}…\text{H}…\text{Si}) \) angle of 120°. While the end-on \( \eta^1 \)-hydrosilane coordination appears to be driven mainly by steric hindrance (changing the electron-donating/-withdrawing substituents in the Ar\(_3\)P ligand does not have any significant influence on the structural preference), the preference for a \( \eta^2 \)-H(Si) binding mode may be recovered by introducing a second phenyl group at the silicon atom (\textit{cf.} Si–H bond distances in Table S3). In spite of some structural and NMR spectroscopic differences between the \( \eta^1 \)- and \( \eta^2 \)-hydrosilane complexes (\textit{cf.} Tables S2 and S3 for computed properties), the \( \Delta G^\circ \) of their formation are very similar (\textit{cf.} Table S3), indicating a rather weak stabilization energy due to Ru–Si interaction in the side-on adduct. These observations are fully consistent with some of the previous findings of Brookhart and co-workers on iridium(III) hydrosilane complexes.\(^{24}\)

**Fig. 5** Calculated relative free energies \( \Delta G^\circ \) together with the structure of relevant intermediates and transition states for the Si–H bond activation of Me\(_2\)PhSiH (2b) by ruthenium(II) thiolate complex 1a (results obtained at the B3LYP-D3(BJ)/ECP/6-31+G** level of theory using an SMD solvation model). All C–H hydrogen atoms are omitted for clarity. Bond lengths are in Å. Computed and experimental \(^1\)H NMR shifts of intermediates are reported in ppm (with respect to TMS). Wiberg bond indices (WBI) of selected bonds are also indicated.

In analogy to our previous study on iridium pincer complexes,\(^{25}\) we attempted to detect any intermediate experimentally by using NMR spectroscopy at low temperatures (note that the hydrosilane complexes 6 and 6' are predicted to display a characteristic \(^1\)H hydride resonance shifted to lower frequencies by ca. ~3 to ~5 ppm as compared to those of the observed adducts 3; \textit{cf.} Figure 5 and Table S2 in the ESI). Those attempts were, however, not successful, most likely due to the high reactivity of these species (\textit{vide infra}). Irrespective of the hydrosilane binding mode (\( \eta^1 \) or \( \eta^2 \)), the
Ru–S bond length in these complexes is much longer (2.39–2.40 Å) than in the starting complex 1 (2.24 Å; cf. Table S3 in the ESI). Nevertheless, various bonding analyses including Wiberg bond indices (WBI, cf. Table S4 in the ESI) and the electron localizability indicator (ELI-D; cf. Figure 6, lower left) show the remaining partial Ru–S bonding character.

While a classical oxidative addition pathway (cf. 7 in Chart 1) could not be located by the calculations, two different pathways for the heterolytic Si–H bond cleavage based on hydrosilane complexes 6′ or 6″ have been investigated. These include either migration of the silyl group or the hydrogen atom to the sulfur atom of the SDmp ligand. The hydrogen transfer has been found to be energetically disfavored by more than 30 kJ mol⁻¹ in both the transition state energy and in the free energy of the products when compared to the transfer of a silylum ion. This coincides with the experimental ESI observations that a ruthenium silyl complex (a silylium ion. This coincides with the experimental free energy of the products when compared to the transfer of a silylum ion. This coincides with the experimental free energy of the products when compared to the transfer of a silyl group onto the sulfur atom of the SDmp ligand. The transition states are computed to lie at ΔG°* ranging from ca. –20 to –40 kJ mol⁻¹. Nevertheless, the higher reaction barrier in the case of rBuMe₂SiH would explain why hydrosilanes decorated with bulky groups do not react with ruthenium(II) thiolate complexes 1 although the overall free reaction energy is negative. Notably, the catalytically active cation in 1 may also form ion pairs with the sterically demanding BArF⁺ counterion (particularly in organic solvents with low polarity), and that could additionally hamper the interaction of 1 with bulky substrates.

During the formation of complexes 6′ or 6″, the Ru–S bond remains virtually intact and also preserves some bonding character in the hydrosilane adducts 3′. Attempts to locate a possible intermediate corresponding to the activation of the hydrosilane through coordination to the Lewis basic sulfur atom failed (cf. 5 in Chart 1). This may be ascribed to a partial positive charge located on the sulfur atom in complex 1′, reducing its electron-donating ability. Upon binding of the hydrosilane, the positive charge at the sulfur atom diminishes, which enhances its Lewis basic properties (cf. Figure 7 for MEP and Table S4 in the ESI).

**Conclusions**

In the light of the reactivity of ruthenium(II) thiolate complexes of type [(R₅P)Ru(SDmp)]⁺[BARF₂⁺] (1) in the activation of E–H bonds, e.g. H–H²⁺, Si–H¹⁴ and B–H¹⁵ bonds, detailed mechanistic insight into the hydrosilane activation mode have been disclosed. A combined experimental, spectroscopic, crystallographic, and theoretical investigation provided conclusive evidence for a heterolytic Si–H bond activation pathway involving metal–ligand cooperativity. The principal results are summarized as follows:

1. The quantum-chemical analyses reveal that the hydrosilane is initially activated by coordination of the Si–H bond to the Lewis acidic metal center rather than Lewis base activation through the Lewis basic thiolate ligand, as often proposed for...
metal–alkoxide and –oxo complexes (cf. 6 or 6′ vs. 5 in Chart 1). In accordance with previous studies, the exact coordination mode, either \( \eta^1 \) (side-on) or \( \eta^2 \) (end-on), is driven by the steric demand of the phosphate ligand as well as the substituents at the silicon atom. While the \( \eta^1 \)-complexes can be considered as a more potent source of electrophilic silicon, the energy differences are very small, indicating a rather weak stabilization energy due to ruthenium to \( \sigma^* \)(Si–H) backbonding. Both coordination modes are barrierless on the electronic energy surface and could not be detected spectroscopically.

(2) After electrophilic activation, the Si–H bond is heterolytically split at the polar Ru–S bond via a concerted four-membered transition state (cf. 3ab\(^{-}\)TS in Figure 5). The \( \sigma \)-bond metathesis results in formation of a cationic silolithio ruthenium hydride intermediate (cf. 3 in Chart 1), combining a ruthenium(II) hydride and a sulfur-stabilized silicon cation, i.e. metallasilsulfonium ion, in one molecule.\(^{12} \)

(3) Addition of the Si–H bond across the Ru–S bond with reversed regioselectivity, affording a ruthenium silyl complex, represents a rare system of heterolytic bond activation (5) The overall Si–H bond activation process is reversible and exergonic with \( \Delta G\(^{\circ} \) \) ranging from \( -20 \) to \( -40 \) kJ mol\(^{-1} \), proceeding instantly already at low temperatures.

(6) The spectroscopic and computational characterization of the stable yet reactive cationic silolithio ruthenium hydride intermediates is reported. Unambiguous proof for the structural assignment was provided by the successful isolation of intermediates (“snapshots” along the reaction coordinate

Notes and references


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The heterolytic splitting of hydrosilanes by ruthenium(II) thiolates is illuminated by a combined spectroscopic, crystallographic, and computational analysis.