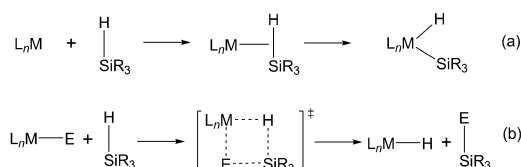


An Yttrium Hydride–Silane Complex as a Structural Model for a σ -Bond Metathesis Transition State**

Jiliang Zhou, Jiexiang Chu, Yanyan Zhang, Guang Yang, Xuebing Leng, and Yaofeng Chen*

The transition-metal-promoted Si–H bond cleavage is a pivotal step in several important catalytic processes, such as hydrosilylation, hydrosilane dehydropolymerization, and dehydrogenative silylation.^[1–4] There are two different mechanisms for the metal-mediated Si–H bond cleavage: a) oxidative addition of Si–H bond toward a low-valent electron-rich metal, in which a σ -complex is believed to be the key intermediate; and b) σ -bond metathesis of Si–H and M–E bonds (E = C, N, H, etc.) via a four-center transition state (Scheme 1).^[5] As evidence for the oxidative addition mech-



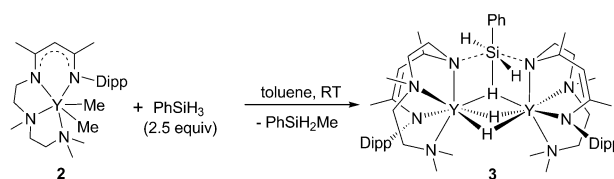
Scheme 1. Two commonly accepted mechanisms for Si–H bond cleavage: a) oxidative addition through an intermediate σ -silane–metal complex, and b) σ -bond metathesis via a four-center transition state.

anism, σ -silane transition-metal complexes have been well documented.^[5] For d^0 -transition-metal complexes, the oxidative addition is impossible, and the Si–H bond cleavage proceeds through the σ -bond metathesis mechanism. However, to the best of our knowledge, there has been no report of such a d^0 -transition-metal complex, which can be considered as a model for the σ -bond metathesis transition state. On the other hand, β -agostic interactions between metal ions and Si–H bonds are commonly observed in the coordinative unsaturated d^0 -transition-metal complexes.^[6]

Rare-earth-metal hydrides attract intense interest because of their fascinating structural features and high reactivity.^[7] Recently, we have developed a β -diketiminato-

based tetradentate ligand, which can stabilize a scandium complex with the terminal imido group.^[8] To explore further applications of this powerful multidentate ligand, we sought to synthesize an yttrium dihydride supported by this ligand. During this study, we obtained an unprecedented yttrium hydride–PhSiH₃ complex, which represents the first structural model for the σ -bond metathesis transition state of a Si–H bond cleavage mediated by a d^0 transition metal. Further studies showed that the coordinated PhSiH₃ molecule in the complex can be either retained or released during the reactions with other substrates.

A salt elimination of LiL (L = [MeC(N(Dipp))CH–C(Me)NCH₂CH₂N(Me)CH₂CH₂NMe₂][–], Dipp = 2,6-(*i*Pr)₂–C₆H₃) with anhydrous YCl₃ in toluene gave an yttrium dichloride [LYCl₂] (**1**) in 88% yield. This yttrium dichloride was treated with two equivalents of MeLi in toluene to afford an yttrium dimethyl complex [LYMe₂] (**2**) in 68% yield. The ¹H NMR spectrum of **2** in C₆D₆ clearly shows two signals at δ = –0.43 and –0.98 ppm for two unequal Y–Me groups. Complex **2** (shown in the Supporting Information, Figure S1). is a monomer, in which the yttrium center adopts a distorted octahedral geometry with three nitrogen atoms of L and a methyl ligand forming the equatorial plane, and the remaining nitrogen atom of L and the other methyl ligand occupying the axial positions. The reaction of **2** with two equivalents of PhSiH₃ was monitored by ¹H NMR spectroscopy in C₆D₆ at room temperature, showing the formation of a complicated mixture of products and PhSiH₂Me. Surprisingly, when the amount of PhSiH₃ was increased to three equivalents, complex **2** was nearly quantitatively converted into complex **3** with some unreacted PhSiH₃. Subsequently, the reaction of **2** with three equivalents of PhSiH₃ was scaled up in toluene, the unreacted PhSiH₃ was removed under vacuum after the reaction was completed, and **3** was isolated as a pale yellow solid in 77% yield (Scheme 2). The NMR spectral data of **3** in C₆D₆ were intriguing and inconsistent with what we expected for an yttrium dihydride [LYH₂]₂. For example, the ¹H NMR spectrum of **3** shows a distinct triplet at δ = 5.37 ppm with a ¹J_{Y–H} coupling constant of 21.2 Hz for the Y–H–Y unit of the complex, but this triplet integrates for 3H atoms rather than 4H atoms; in addition, an unexpected



Scheme 2. Synthesis of complex **3**.

[*] J. L. Zhou, J. X. Chu, Dr. X. B. Leng, Prof. Dr. Y. F. Chen
State Key Laboratory of Organometallic Chemistry, Shanghai
Institute of Organic Chemistry, Chinese Academy of Sciences
345 Lingling Road, Shanghai 200032 (P.R. China)
E-mail: yaofengchen@mail.sioc.ac.cn

Y. Y. Zhang, G. Yang
Shanghai Key Laboratory of Magnetic Resonance
Department of Physics, East China Normal University
3663 North Zhongshan Road, Shanghai 200062 (P.R. China)

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doublet was observed at $\delta = 8.17$ ppm (d, $^3J_{\text{HH}} = 6.8$ Hz). The proton-coupled ^{29}Si DEPT 45 spectrum of **3** shows a triplet at $\delta = -124.8$ ppm with a $^1J_{\text{Si-H}}$ coupling constant of 220 Hz, which is very different from that of PhSiH_3 ($\delta = -59.5$ ppm, q , $^1J_{\text{Si-H}} = 200$ Hz).

The single-crystal structure of the yttrium hydride- PhSiH_3 complex **3** was determined and the high-quality data set allowed us to locate the H atoms on Y/Si, H1M to H5M, from the Fourier map. Complex **3** has some rather remarkable structural features (Figure 1). The tetradentate monoanionic

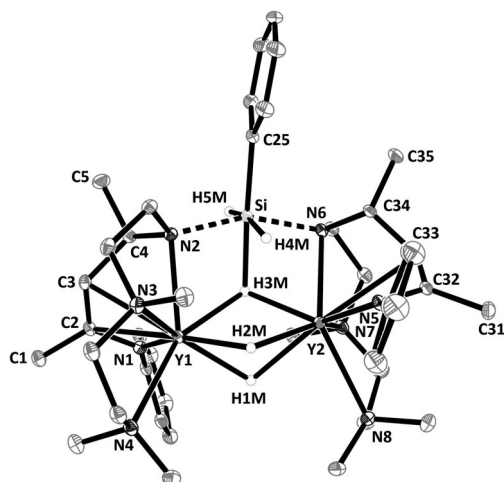
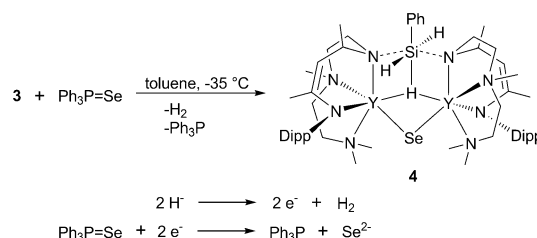


Figure 1. Molecular structure of **3** with thermal ellipsoids set at 30% probability level. Isopropyl groups of Dipp and hydrogen atoms (except those bound to yttrium and silicon) have been omitted for clarity.

ligand **L** in **2** was converted into a dianionic ligand **L'** by addition of the Y-H bond of the initially formed yttrium hydride to the C=N bond of the β -diketiminato backbone. The most intriguing structural features are related to the PhSiH_3 moiety, which coordinates to a $[\text{L}'\text{YH}]_2$ dimer through Y-H (Y1-H3M, Y2-H3M) and Si-N (Si-N2, Si-N6) interactions. The distances from the yttrium centers to the H3M atom (both 2.09(2) Å) are close to those from the yttrium centers to the H1M and H2M atoms (2.12(3)–2.24(3) Å), and fall in the range of 2.00 to 2.30 Å observed for the Y-H bonds in reported dimeric yttrium- μ -hydrido complexes.^[7] The Si-N distances, 1.916(2) and 1.925(2) Å, are longer than normally observed for Si-N single bonds in aminosilyl complexes (1.70–1.78 Å),^[6b] but significantly shorter than the sum of their van der Waals radius (3.65 Å; the van der Waals radius of Si is 2.10 Å, and that of N is 1.55 Å).^[9] The Si-H3M bond (1.82(2) Å) is about 0.4 Å longer than the Si-H4M and Si-H5M bonds (1.47(2) and 1.42(2) Å) and the Si-H bond in hydrosilanes (1.425 Å in average),^[5d] indicating that the Si-H3M bond is apparently activated. The elongation of the Si-H3M bond is also supported by the solution NMR spectrum. The ^1H - ^{29}Si HSQC experiment with $J = 200$ Hz only shows the coupling of Si with H4M and H5M. The coupling of Si with H3M was observed in the experiment with $J = 7$ Hz. The INEPT experiment is unable to give a coupling constant of Si with H3M (see the Supporting Information). The interaction

can be viewed as a coordination of the H3M atom to the Lewis acidic Y ion and the Si atom to the electronegative N, which causes a polarization and weakening of the Si-H3M bond. It is also noteworthy that, in comparison with the Y-N1 and Y-N5 bonds (2.367(2) and 2.389(2) Å), the Y-N2 and Y-N6 bonds are slightly stretched (2.420(2) and 2.416(2) Å). A fast exchange of H3M with H1M and H2M was observed in the room-temperature ^1H NMR spectrum, which shows a triplet at $\delta = 5.37$ ppm for these three hydrogen atoms. Lowering the temperature to -90°C only led to a broadened resonance and the resonance decoalescence did not occur, thus indicating a very small energy barrier for the observed hydride exchange in solution. Although complex **3** may be racemic or have meso forms, only the racemic form that minimizes steric interactions between the bulky Dipp substituents is observed.

We also examined the reactivity of the complex **3**. The reaction of **3** with triphenylphosphine selenide ($\text{Ph}_3\text{P}=\text{Se}$) gave an yttrium selenide- PhSiH_3 complex **4** (Scheme 3).



Scheme 3. Reaction of **3** with $\text{Ph}_3\text{P}=\text{Se}$.

Consistent with the formation of **4**, monitoring of the reaction in C_6D_6 by NMR spectroscopy showed a release of H_2 (4.47 ppm in the ^1H NMR spectrum) and Ph_3P (−5.4 ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum). Therefore, the reaction is a hydride-based reduction.^[10] During the reaction, two H^- ligands in **3** are oxidatively coupled to form an H_2 molecule and reduce $\text{Ph}_3\text{P}=\text{Se}$ to Se^{2-} and Ph_3P . It is noteworthy that only two of Y-bound H atoms in the Y_2H_3 moiety take part in the reaction, while the other one stays intact. The molecular structure of **4** is shown in Figure 2. The H atoms on Y/Si, H1M to H3M, were also located from the Fourier map. In **4**, the two yttrium centers are bridged by a $\mu\text{-Se}^{2-}$ ligand. Y1-Se and Y2-Se bond lengths are 2.7584(4) and 2.7260(4) Å, respectively. The PhSiH_3 moiety was retained during the reaction, and the Y-N-Si-H four-membered rings were retained in **4**, with only minor deviations of structural parameters from the parent complex **3**. In the ^1H NMR spectrum of **4**, the Si-H-Y signal displays as a triplet of triplets at $\delta = 6.90$ ppm ($^1J_{\text{YH}} = 12.4$ Hz, $^2J_{\text{HH}} = 4.4$ Hz, 1 H), the $^2J_{\text{HH}}$ value is remarkably smaller than that reported for the two diastereotopic hydrogen atoms of the Ti-N-SiH₂Ph unit in the titanium complex $[\text{Cp}^*\text{Ti}\{\text{MeC}(\text{N}i\text{Pr})_2\}(\text{H})\{\text{N}(\text{NMe}_2)\text{SiH}_2\text{Ph}\}]$ (8.0 Hz).^[11] As for **3**, the ^1H - ^{29}Si HSQC experiment with $J = 7$ Hz shows coupling of Si with H1M-H3M, whereas that with $J = 200$ Hz only shows the coupling of Si with H2M and H3M. The INEPT experiment also shows that the coupling of Si with H1M is very small, so that its value was not determined. In

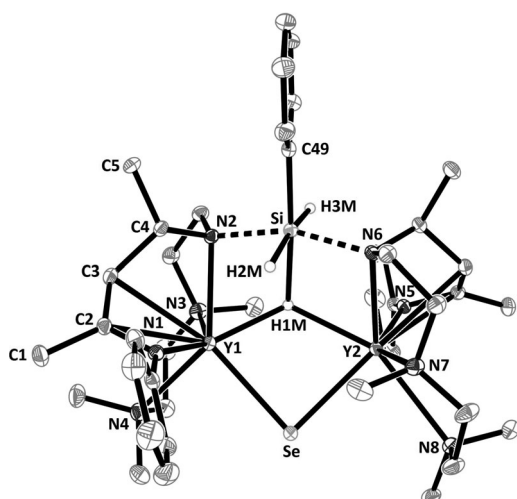
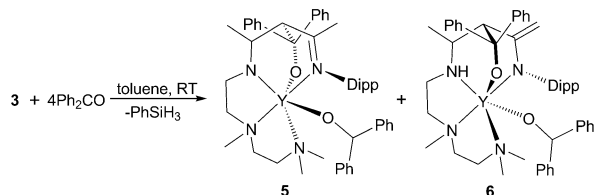


Figure 2. Molecular structure of **4** with thermal ellipsoids set at 30% probability level. Isopropyl groups of Dipp and hydrogen atoms (except those bound to yttrium and silicon) have been omitted for clarity.

accord with ^1H – ^{29}Si HSQC and INEPT spectra, the ^{29}Si NMR spectrum of **4** shows a triplet at $\delta = -120.4$ ppm with a $^1J_{\text{Si-H}}$ coupling constant of 217 Hz as a result of the coupling of Si with H2M and H3M.

From the reaction of **3** with four equivalents of benzo-phenone (Ph_2CO), two yttrium alkoxo isomers **5** and **6** were isolated in 56% and 26% yield, respectively (Scheme 4).



Scheme 4. Reaction of **3** with Ph_2CO .

Both **5** and **6** were fully characterized by ^1H and ^{13}C NMR spectroscopy, elemental analysis, and single crystal X-ray diffraction (Figure 3 and Figure S2 in the Supporting Information).^[12] Apparently, the formation of **5** and **6** involves not only the insertion of the C=O double bond into the Y–H bond but also the nucleophilic attack of the C3 atom of the tetradentate ligand at the carbonyl carbon atom of Ph_2CO . Notably, the PhSiH_3 molecule is released during the reaction, which was evidenced by a ^1H NMR spectral monitoring of the reaction in C_6D_6 (4.23 ppm in ^1H NMR spectrum). The X-ray structural data clearly show the difference between the multidentate ligands in the two isomers. In **5**, the C1–C2 bond (1.516(5) Å) is a single bond and the C2–N1 bond (1.283(4) Å) is a double bond, whereas in **6** the C1–C2 bond (1.353(3) Å) is a double bond and the C2–N1 bond (1.392(3) Å) shows single-bond character. Attempts to obtain the intermediate with only one inserted molecule of

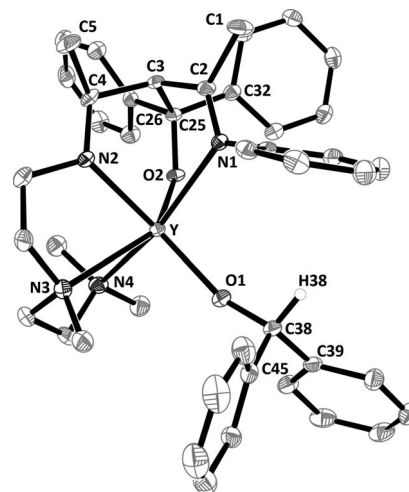


Figure 3. Molecular structure of **5** with thermal ellipsoids set at 30% probability level. Isopropyl groups of Dipp and hydrogen atoms (except H38) have been omitted for clarity.

Ph_2CO by controlling using a molar ratio of 2:1 of Ph_2CO :**3** were unsuccessful; the reaction gave a mixture of **5** and **6** with some unreacted **3**.

In summary, an yttrium hydride– PhSiH_3 complex **3** has been obtained and structurally characterized by single-crystal X-ray diffraction and solution NMR spectroscopy. Complex **3** shows interactions between Y–N and Si–H bonds, which represents the first structural model for σ -bond metathesis transition state between Si–H and M–E (M: d^0 transition metal). Further reactions of **3** have also been investigated and, depending on substrates, the PhSiH_3 moiety can be either retained or released during the reactions.

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