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Author(s)	Nakatani, Naoki; Hasegawa, Jun-ya; Sunada, Yusuke; Nagashima, Hideo
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Platinum-catalyzed reduction of amides with hydrosilanes bearing dual Si-H groups: a theoretical study of the reaction mechanism

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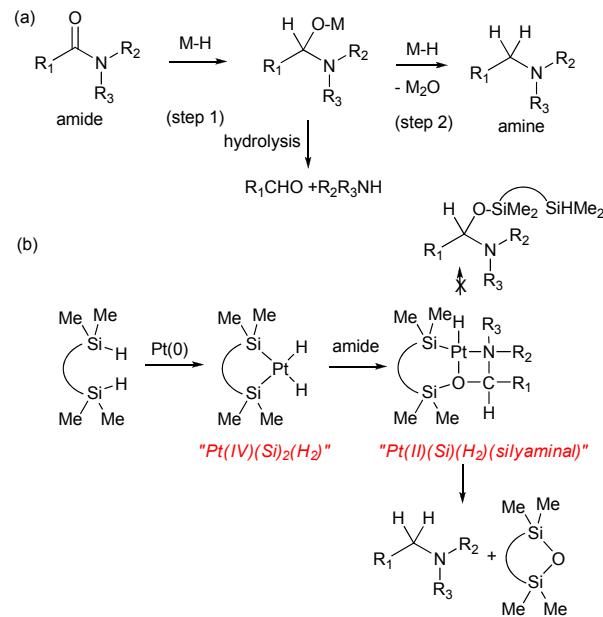
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Naoki Nakatani,^{a*} Jun-ya Hasegawa,^{a,b} Yusuke Sunada,^b and Hideo Nagashima^{b,c}

A platinum-catalyzed amide reduction through hydrosilylation with 1,2-bis(dimethylsilyl)benzene (BDSB) was investigated on a theoretical basis. While the platinum-catalyzed hydrosilylation of alkenes is well known, that of carbonyl groups rarely occurs. The only exception involves the use of bifunctional hydrosilanes having dual, closely located Si-H groups, which accelerates the hydrosilylation of carbonyl groups, leading to successful reduction of amides to amines under mild conditions. In the present study, we determined through density functional theory calculations that the platinum-catalyzed hydrosilylation of the C=O bond proceeds via a Pt(IV)-disilyl-dihydride intermediate with the associated activation energy of 29.6 kcal/mol. Although it was believed that the hydrosilylation of carbonyl groups does not occur via the classical Chalk-Harrod cycle, the computational results support a mechanism involving the insertion of the amide C=O bond into a Pt-H bond. This insertion readily occurs because a Pt-H bond in the Pt(IV)-disilyl-dihydride intermediate is highly activated due to the strong σ -donating interaction of the silyl groups. The modified Chalk-Harrod mechanism that occurs preferentially in rhodium-catalyzed hydrosilylation as well as the ionic outer sphere mechanism associated with iridium-catalyzed amide reduction were both safely ruled out as mechanisms for this platinum-catalyzed amide reduction, because of the unexpectedly large activation barrier (> 40 kcal/mol) for the Si-O bond formation.

Introduction

The hydrosilylation of unsaturated molecules is one of the most important reactions in the synthesis of organosilicon compounds.¹ The hydrosilylation of alkenes is an industrially important process used to make silane coupling reagents and silicones,² while the reaction of ketones has received attention from synthetic organic chemists as a method for the reduction of carbon-oxygen double bonds.³ A wide variety of transition metal compounds show catalytic activity toward hydrosilylation reactions. Among them, metal compounds, which include rhodium,³ ruthenium,⁴ and iridium complexes,⁵ more ubiquitous iron, copper, zinc, and manganese compounds,⁶ as well as molybdenum and rhenium oxides⁷ have been investigated as catalysts for the reduction of ketones.³ Progress in research of the hydrosilylation of carbonyl compounds led to increase of the range of substrates from aldehydes and ketones to carboxylic acid derivatives,⁸ which are typically difficult to reduce by standard reduction reactions.⁹ Of interest is catalytic properties of platinum compounds, which are the most commonly used catalysts for



Scheme 1. (a) A general scheme for hydride reduction of amides. (b) A scheme for platinum-catalyzed hydrosilane reduction of amides with bifunctional hydrosilanes.

^a Catalysis Research Center, Hokkaido University, Kita 21 Nishi 10, Sapporo, Hokkaido 001-0021, Japan.

^b Institute for Materials Chemistry and Engineering, Kyushu University, Kasuga, Fukuoka 816-8580, Japan.

^c CREST, JST, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan.

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the reactions of alkenes,² but showed poor catalytic activity towards the hydrosilane reduction of carbonyl compounds.

We have recently discovered the platinum-catalyzed reduction of tertiary amides with certain hydrosilanes, which offers a practical means of inducing reduction for the

preparation of tertiary amines.¹⁰ It is well known that reduction of amides is the most difficult reaction by metal hydrides, and this discovery opened a practical access to amines from amides with commercially available and easy-to-handle hydrosilanes and a catalytic amount of platinum compounds. It is also important that this is a rare example of the successful platinum-catalyzed reduction of carbonyl compounds with hydrosilanes,¹¹ and a key discovery with regard to accomplishing this reaction is the use of the bifunctional hydrosilanes $\text{Me}_2\text{HSiOSiHMe}_2$ (TMDS) and 1,2-bis(dimethylsilyl)benzene (BDSB) for the hydrosilylation reaction. In fact, it was observed that the reaction did not proceed when using monohydrosilanes such as PhMe_2SiH and EtMe_2SiH or with di- or trihydrosilanes.

As shown in Scheme 1a, reduction of tertiary amides with metal hydrides (M-H) is generally explained by two elementary steps, addition of a M-H species to a C=O bond of the amide (step 1) and reductive deoxygenation of the intermediary metallated hemiaminal to the amine (step 2).⁹ Step 1 and step 2 are usually continuous to give amines from amides; however, step 2 can be suppressed with appropriate reducing reagents under optimized conditions to give the hemiaminal intermediate, of which hydrolysis gives aldehydes. One of the clues for understanding the facile reduction of amides by platinum catalysts is the effectiveness of TMDS and BDSB for step 1, which was ascribed to a proximity effect arising from the two Si-H groups that accelerates the catalytic hydrosilylation of carbonyl compounds in conjunction with various rhodium, ruthenium, and iron catalysts.¹² Studies to isolate metal-silyl complexes which are closely related compounds to active species in the catalytic cycle, suggest the involvement of double oxidative addition of BDSB to the metal complexes to form disilametallacycles. However, detailed mechanisms of the proximate effect, i.e. why two closely located Si-H groups accelerate the hydrosilylation, needed further investigation. Mechanisms of the catalytic hydrosilylation reactions have been studied both experimentally and theoretically, which include the conventional Chalk-Harrod and modified Chalk Harrod cycles as well as outer sphere mechanisms recently proposed (as briefly introduced later on).¹³⁻²¹ These provided us the basis to discuss the proximity effect in the platinum-catalyzed hydrosilylation, as summarized in the first part of Results and Discussion. In contrast, mechanisms of the catalytic deoxygenative reduction (step 2), in which two proximate Si-H groups may facilitate the reaction, have totally been unexplored.

In this paper, we report the results of density functional theory (DFT) calculations for the platinum-catalyzed reduction of amides with BDSB. Our results clearly suggest that the reaction proceeds via the intermediate species including Pt(IV)- dihydride-disilyl species, " $\text{H}_2\text{Pt}^{\text{IV}}\text{Si}_2$ ", and that the catalytic cycle is initiated by the facile insertion of the C=O bond of the amide into the Pt-H bond (Chalk-Harrod mechanism). The insertion of the C=O bond into the Pt-Si bond (modified Chalk-Harrod mechanism) was ruled out. In the course of the study, we discovered a mononuclear Pt(II)

intermediate, " $\text{HPt}^{\text{II}}(\text{Si})(\eta^2\text{-Si-H})$ ", in which one of the Si-H bonds in BDSB is oxidatively added to the platinum center, while the other is coordinated to the metal center of the resulting H-Pt-Si moiety in an $\eta^2\text{-Si-H}$ fashion. Although this $\eta^2\text{-Si-H}$ species coordinated to the Pt(II) center may be involved in the nucleophilic attack by carbonyl oxygen to the $\eta^2\text{-Si-H}$ moiety (outer sphere mechanism), a detailed study suggests that it only contributes to the formation of an $\text{H}_2\text{Pt}(\text{IV})(\text{disilyl})_2$ intermediate by oxidative addition to the Pt(II) center. These results provide the first evidence supporting the involvement of the double oxidative addition of two Si-H groups to the metal center to produce a highly reactive metal hydride intermediate that promotes the reaction of carbonyl compounds, and in which the conventional Chalk-Harrod mechanism is adopted for the catalytic hydrosilylation of carbonyl compounds. Further study revealed mechanisms of the reductive deoxygenation, in which the reductive deoxygenation did not proceed through the silyl heminal intermediate but *via* a Pt(II)-hydride-silyl intermediate having a characteristic bicyclic structure (Scheme 1b).

Computational Details

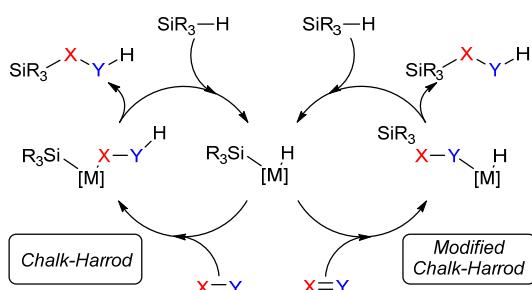
All geometry optimizations and energy calculations were performed on the basis of DFT. We initially performed simple assessments of functional dependency.[†] In these initial studies, we examined geometries and energies using several common functionals, such as B3LYP, B3PW91, B97D, M06, and PBE0, and concluded that the functional dependency in the present system is very small. Hence, we simply used the B3LYP functional²² because it has been most commonly employed for the theoretical investigations of transition metal complexes including 4d and 5d series and tends to generate results that agree well with experimental findings, especially for ground state reactions. We employed the Stuttgart/Dresden (611111/22111/411) basis sets^{23a} for the valence electrons of Pt atoms and the 60 core electrons were replaced by the effective core potentials (ECP60MWB).^{23b} The valence triple-zeta basis sets plus polarization functions, namely 6-311G(d, p), were employed for H, C, and Si atoms,²⁴ and these sets plus diffuse functions, namely 6-311+G(d, p), were employed for anionic atoms such as N, O, and S.²⁴ For the energies discussed in the following sections, a free energy correction²⁵ was taken into account and solvation effects were evaluated using a polarized continuum model (PCM)²⁶ with a dielectric constant value of $\epsilon = 7.4257$ for tetrahydrofuran (THF). The Gaussian 09 package (revision number B-01) was employed for all calculations.²⁷

Results and Discussion

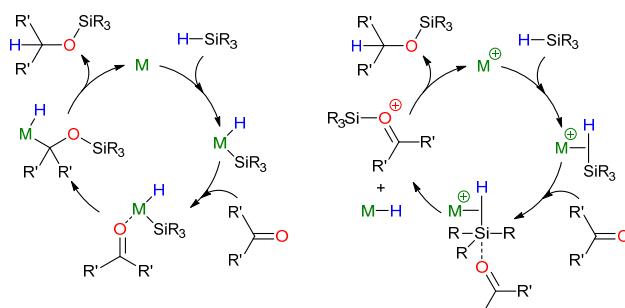
Mechanisms of hydrosilylation in the literature.

A short review of the catalytic hydrosilylations of a C=C bond and a C=O bond. It is necessary for the following discussion to summarize the proposed mechanisms of hydrosilylation reactions in the literature. The Chalk-Harrod mechanism¹³

proposed for the platinum-catalyzed hydrosilylation of alkenes in the 1960s includes the oxidative addition of a Si-H bond to a metal center to form an intermediate including a H-M-Si



Scheme 2. Chalk-Harrod and modified Chalk-Harrod cycles.



Scheme 3. Ojima's modified Chalk-Harrod mechanism (left) and ionic outer sphere mechanism (right) for the hydrosilylation of ketons.

moiety, followed by the insertion of the C=C bond into the resulting H-M bond and subsequent reductive elimination of the adduct, as shown in Scheme 2 (left). In the case of cobalt and rhodium-catalyzed processes, a modified Chalk-Harrod mechanism (Scheme 2, right),¹⁴ in which the insertion of the C=C bond into the M-Si bond of a H-M-Si species takes place, has been proposed.

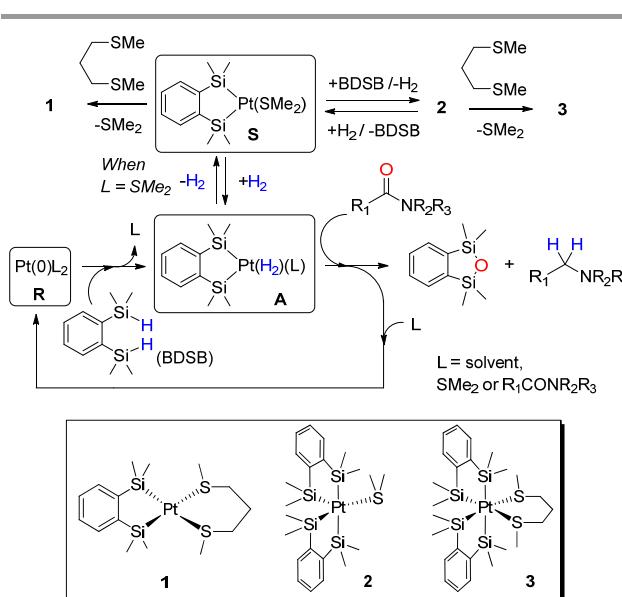
The hydrosilylation of carbonyl groups has a different mechanistic aspect due to the strong affinity of silicon for oxygen. Ojima and co-workers reported that the modified Chalk-Harrod mechanism better explains the rhodium-catalyzed hydrosilylation of ketones compared to the Chalk-Harrod cycle (Scheme 3, left).¹⁵ In addition, a notable proposal has recently appeared in which the hydrosilylation does not involve any oxidative additions but rather proceeds through an η^2 -R₃Si-H species. In this newly-proposed, so-called outer sphere mechanism, Si-O bond formation occurs via the direct attack of the oxygen atom of the carbonyl group on the silicon atom of the η^2 -R₃Si-H species. Typical examples include the hydrosilylation of ketones by cationic iridium or ruthenium complexes, in which a carbonyl group (O=CR₂) attacks the Si atom of an (η^2 -R₃Si-H)^{M+} species through this mechanism. In this process, Si-O bond formation produces a five-coordinate silicone species, R₂C=O-SiR₃-H⁺ \cdots M⁺, which is followed by the generation of a silylum ion-activated carbonyl group, R₃Si-O⁺=CR₂, and M-H. The hydride transfer from M-H to the carbon

atom of the activated carbonyl group gives the product shown in Scheme 3 (right).^{16,17} In this case, a silylum ion, R₃Si⁺, activates the oxygen atom of a carbonyl group to produce a siloxycarbenium ion that subsequently undergoes attack by a hydride at the carbon atom.^{20,21} These possible mechanisms were examined one by one to elucidate the platinum-catalyzed hydrosilane reduction of amides to amines with BDSB in the following study.

Isolation of disilaplatinacyclopentanes related to catalytic hydrosilane reduction of amides and a proposed mechanism.

It should be noted that three disilaplatinacyclopentanes, **1** to **3**, bearing Me₂S or MeS(CH₂)₃SMe ligands, were synthesized and characterized as reported in our previous paper.^{28a} All of these compounds showed catalytic activity for the hydrosilane reduction of amides with BDSB comparable to that observed in reactions catalyzed by the Pt(0) catalyst precursor Pt(db_a)₂ (db_a = dibenzylideneacetone). The Me₂S or MeS(CH₂)₃SMe ligands were weakly coordinated to the platinum center, thus stabilizing compounds **1** to **3** without disturbing the catalytic reaction. These complexes were not directly involved in the catalytic cycle, but were instead closely related to the actual catalytic intermediates.

In considering the mechanism of the hydrosilane reduction of amides by BDSB, three intermediates, **R**, **A**, and **S** are important (Scheme 4). The double oxidative addition of BDSB to a Pt(0) intermediate such as [Pt(0)(L)₂] (**R**) occurs, followed by the dissociation of L to form the disilaplatina(IV) intermediate "*H₂Pt^{IV}Si₂(L)*" (**A**), where L is a solvent molecule, substrate, or weakly coordinated ligand such as Me₂S. When L is Me₂S, the elimination of H₂ gave an intermediate, "*Pt^{II}Si₂(SMe₂)*" (**S**), that is a precursor of **1**, **2**, and **3** previously isolated. The ligand exchange of **S** with MeS(CH₂)₃SMe gives **1**, whereas the oxidative addition of BDSB and subsequent elimination of H₂ and ligand substitution explains the formation of **2** and **3** from **S**. These processes suggest that **A** is a key intermediate in the hydrosilane reduction of the amide during this catalytic cycle. In this context, it is helpful to first consider in detail the mechanistic aspects of the reactions



Scheme 4. Three key intermediates (**R**, **A**, and **S**) in this study and three isolated complexes (**1**, **2**, and **3**) closely related to the intermediates in the catalytic cycle in our previous study.

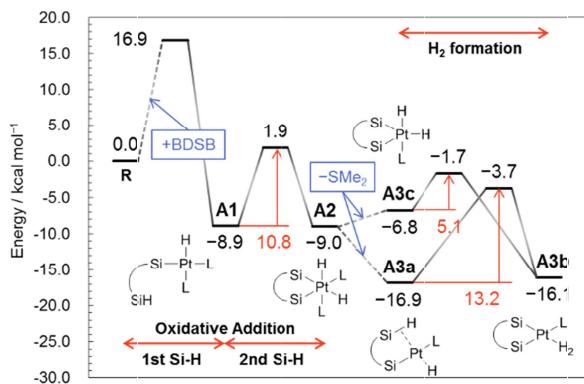


Figure 1. Energy diagram from **R** to **A**. Numbers in the diagram are Gibbs free energy in THF solution in kcal/mol.

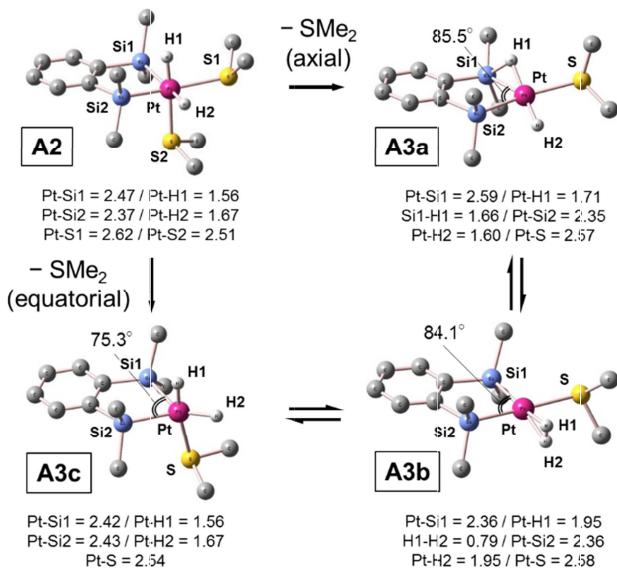


Figure 2. Optimized geometries of intermediates **A2**, **A3a**, **A3b**, and **A3c**. Important bond lengths are shown in Å.

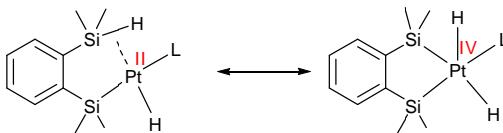
going from **R** to **A** and from **A** to complex **2** via **S**, that involve the double oxidative additions of BDSB to Pt(0) and Pt(II) species, respectively. In the following subsections, we first investigated the oxidative additions of BDSB to the Pt(0) intermediate **R** to **A**, which led to the formation of **1**, **2**, and **3** via **S**, and then, investigated possible catalytic cycles of the hydrosilane reduction of amides via the Chalk-Harrod, the modified Chalk-Harrod, and the ionic outer-sphere pathways.

Double Oxidative Additions of BDSB to Afford Active Species.

The reaction from **R to **A**.** Figure 1 summarizes the energy profile of this reaction process. Calculations suggest that the oxidative addition of one of the Si-H bonds in BDSB to a Pt(0) species $[\text{Pt}(0)(\text{SMe}_2)_2]$ (**R**, L = SME₂) readily occurs to form the “ $\text{H}\text{Pt}^{\text{IV}}\text{Si}_2(\text{SMe}_2)_2$ ” intermediate **A1**. The reaction energy of this first oxidative addition was computed to be exothermic by 8.9 kcal/mol, and the estimated activation energy of this

process is 16.9 kcal/mol. The oxidative addition of the remaining Si-H group occurs to form the six-coordinate “ $\text{Pt}^{\text{IV}}\text{Si}_2(\text{SMe}_2)_2$ ” species **A2**. The activation energy of this second oxidative addition was estimated to be 10.8 kcal/mol and so **A2** was predicted to be slightly more stable than **A1** by 0.1 kcal/mol. The optimized geometry of **A2** showed a typical octahedral structure reflecting the d⁶ electron configuration of Pt(IV) (Figure 2). The two hydrides occupy cis positions, where one hydride occupies the axial position and the other is located equatorially. Due to the strong trans-influence of the silyl group, the computed Pt-H length of the equatorial hydride (1.67 Å) trans to the silyl group was somewhat longer than that of the axial hydride (1.56 Å) trans to the SME₂ ligand.

Elimination of a Me₂S ligand from **A2** produces three species, **A3a**, **A3b**, and **A3c**, that correspond to the intermediate **A** shown in Scheme 4. Dissociation of the axial SME₂ ligand forms the stable four-coordinate “ $\text{H}\text{Pt}^{\text{II}}\text{Si}(\eta^2\text{-Si-H})(\text{SMe}_2)$ ” complex **A3a** (Figure 2), and this complex was computed to be 7.9 kcal/mol more stable than **A2**. With regard to **A3a**, it is of considerable interest that one Si-H group is regenerated by the reductive elimination between the axial hydride and one silyl moiety of **A2**, with no associated energy barrier. The resulting Si-H moiety remains in the coordination sphere of platinum to give **A3a**, with η²-coordination to the Pt center. The Si-H bond length of the η²-Si-H moiety was computed to be 1.66 Å, which is clearly longer than the 1.49 Å value in free BDSB, and a value of 2.59 Å was determined for the Pt-Si length, which is also longer than the other Pt-Si bond (2.35 Å). These geometrical features clearly indicate that a strong agostic interaction exists between the η²-Si-H moiety and the Pt center, which can also be understood as a resonance structure between Pt(II) and Pt(IV) species.



In contrast, dissociation of the equatorial SME₂ ligand from **A2** gives the five-coordinate “ $\text{H}_2\text{Pt}^{\text{IV}}\text{Si}_2(\text{SMe}_2)$ ” complex **A3c**, predicted to be 10.1 kcal/mol less stable than **A3a**. Thus, **A3c** was found to be a meta-stable intermediate. It should be noted that the equatorial SME₂ ligand dissociates more readily than the axial ligand because of the strong trans-influence of the silyl groups. Therefore, the formation of **A3c** is kinetically favorable whereas the formation of **A3a** is thermodynamically favorable.

Oxidative addition of the η²-Si-H group of **A3a** occurs with concomitant H-H bond formation, resulting in the four-coordinate “ $\text{Pt}^{\text{II}}\text{Si}_2(\eta^2\text{-H}_2)(\text{SMe}_2)$ ” complex **A3b** (Figures 2), with an activation energy of 13.2 kcal/mol. It should be noted that **A3b** can also be formed by the reductive elimination of the two hydrides of **A3c**, with an associated activation energy of 5.1 kcal/mol. **A3b** was computed to be slightly less stable than **A3a** by 0.8 kcal/mol and somewhat more stable than **A3c** by 9.3 kcal/mol. In this regard, we considered these three intermediates, **A3a** to **A3c**, as candidates for the active species

in the catalytic hydrosilylation reaction, as discussed in the addition of the remaining Si-H group and the simultaneous

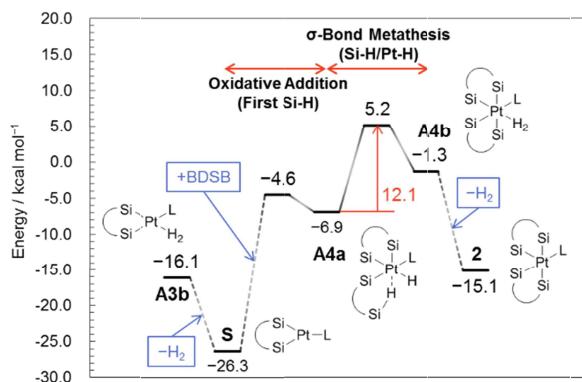


Figure 3. Energy diagram from **A** to **2**. Numbers in the diagram are Gibbs free energy in THF solution in kcal/mol.

later subsections.

The reaction from A to 2 via S. Additional reactions from intermediate **A** to form the experimentally isolated complex “ $\text{Pt}^{\text{IV}}\text{Si}_4(\text{SMe}_2)_2$ ” (**2**) were considered. Figure 3 summarizes the calculated energy profile of this reaction process. The elimination of a H_2 molecule from **A3b** to form the three-coordinate intermediate **S** was determined to be an exothermic process with an estimated energy of 10.2 kcal/mol. Thus, the catalytically active intermediates **A3a** to **A3c** and **S** are basically interchangeable.²⁹ These results indicate that the isolated complex **1** can be formed by the ligand exchange of **S** with $\text{MeS}(\text{CH}_2)_3\text{SMe}$.

The oxidative addition of one of the two Si-H bonds in another BDSB molecule to **S** was found to form the six-coordinate “ $\text{HPt}^{\text{IV}}\text{Si}_3(\eta^2\text{-Si-H})(\text{SMe}_2)$ ” intermediate **A4a**, which is somewhat less stable than **S** by 19.4 kcal/mol and has an estimated activation energy of 21.7 kcal/mol. The oxidative

Scheme 5. The Chalk-Harrod and the modified Chalk-Harrod mechanisms for the platinum-catalyzed hydrosilane reduction of amides.

formation of H_2 occur to afford the six-coordinate “ $\text{Pt}^{\text{IV}}\text{Si}_4(\eta^2\text{-H}_2)(\text{SMe}_2)$ ” complex **A4b** with an associated energy barrier of 12.1 kcal/mol. This step can be understood as the σ -bond metathesis reaction of the Pt-H and Si-H bonds. **A4b** was found to be 5.6 kcal/mol less stable than **A4a**. Once **A4b** is formed, a H_2 molecule readily dissociates to form the isolated complex **2**, determined to be 13.8 kcal/mol more stable than **A4b**. In addition, the activation energy for the reverse reaction from **2** to **S** via **A4a** was estimated to be 20.2 kcal/mol. These results suggest that **2** and **S** are also interchangeable and the isolated complex **3** can be formed by the ligand exchange of **2** with $\text{MeS}(\text{CH}_2)_3\text{SMe}$. Consequently, the isolated complex **2** can show catalytic activity because it is interchangeable with the catalytically active intermediates **A3a** to **A3c** via **S** in the presence of H_2 molecules. These computational results are consistent with our previous experiments that the isolated complexes **1** to **3** exhibit catalytic activity.^{28a}

Amide Reduction with BDSB.

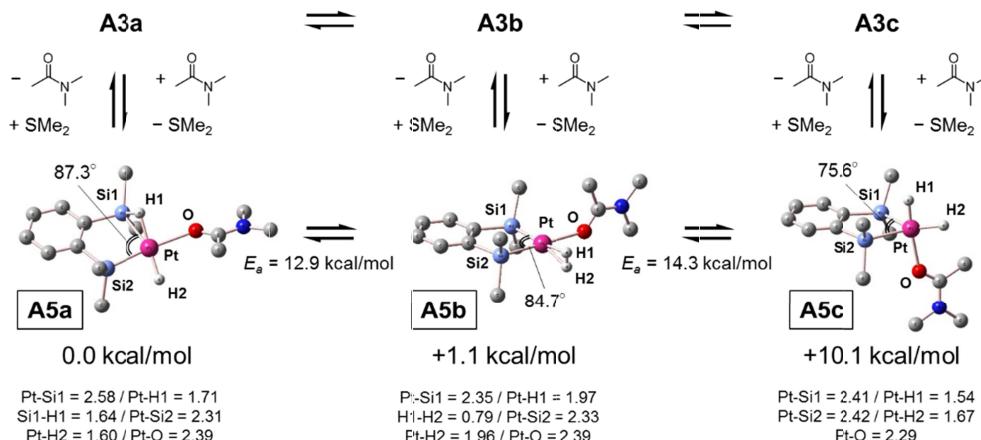


Figure 4. Optimized geometries of intermediates **A5a**, **A5b**, and **A5c**. Important bond lengths are shown in Å.

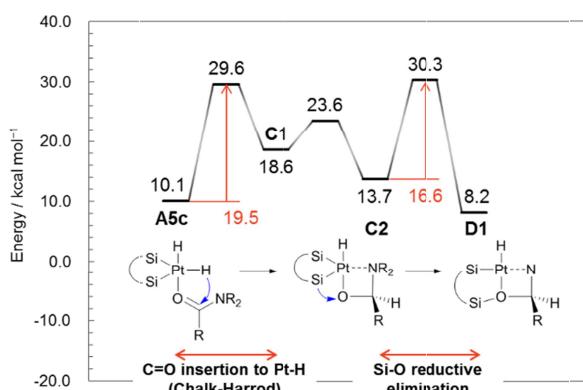


Figure 5. Energy profile for the Chalk-Harrod pathway to afford a silylhemiaminal intermediate.

In a previous section, we investigated the double oxidative addition of BDSB to $\text{Pt}(0)\text{L}_2(\text{R})$ as the initial step of the catalytic hydrosilylation, forming the intermediate **A**. In this section, the remaining reaction pathways of the Pt-catalyzed amide reduction, from the intermediate **A** to amine and siloxane products with which the initial species **R** is regenerated are discussed. Two reaction pathways, involving either the intermediate **A** to **C** (the Chalk-Harrod mechanism) or **A** to **M** (the modified Chalk-Harrod mechanism), will give a silylhemiaminal intermediate, from which products are eliminated to regenerate **R** (Scheme 5). We first provide details regarding the Chalk-Harrod pathway through **C** that represents the most plausible mechanism. Next, we discuss two alternative pathways: the modified Chalk-Harrod pathway (the reaction from **M**) and the ionic outer sphere pathway, both of which can be safely ruled out.

We considered the four- and five-coordinate intermediates **A3a**, **A3b**, and **A3c** as candidates for the active species in the hydrosilane reduction of amides, corresponding to the intermediate **A** in Scheme 5. In the actual catalytic reaction, the SMe_2 ligands in complexes **A3a**, **A3b**, and **A3c** are replaced by the amide to give the precursor complexes **A5a** [$\text{HPT}^{\text{II}}\text{Si}(\eta^2\text{-Si-H})(\text{amide})$], **A5b** [$\text{Pt}^{\text{II}}\text{Si}_2(\eta^2\text{-H}_2)(\text{amide})$], and **A5c** [$\text{H}_2\text{Pt}^{\text{IV}}\text{Si}_2(\text{amide})$], respectively (Figure 4), and the coordinated amide induces further organometallic reactions in the catalytic cycle. We considered N,N -dimethylacetamide ($\text{R}_1 = \text{R}_2 = \text{R}_3 = \text{Me}$ in Scheme 3) as a model reactant for the N,N -dimethyl-3-phenylpropionamide ($\text{R}_1 = \text{CH}_2\text{CH}_2\text{Ph}$, $\text{R}_2 = \text{R}_3 = \text{Me}$ in Scheme 3) that was used in the experiments.^{10,28a} The geometrical features of **A5a**, **A5b**, and **A5c** were found to be almost the same as those of **A3a**, **A3b**, and **A3c**, respectively. The binding energy of the SMe_2 ligand in **A3a** was computed to be 5.7 kcal/mol, while that of the amide in **A5a** was 1.1 kcal/mol. Although **A5a** is therefore slightly less stable than

A3a by 4.6 kcal/mol, the binding energies of the SMe_2 ligand and the amide are both small. As a result, the SMe_2 ligand in **A3a** can be easily replaced by an amide.

In the following discussion, for the sake of convenience, **A5a** is taken to be the energy reference (with an energy of zero). Consequently, **A5b** and **A5c** were estimated to be 1.1 and 10.1 kcal/mol less stable than **A5a**, respectively. The activation barriers from **A5a** to **A5b** and from **A5b** to **A5c** were computed to be 12.9 and 13.2 kcal/mol, respectively. These results showed that the energetics of these amide complexes (**A5a** to **A5c**) are almost the same as those of the sulfide complexes (**A3a** to **A3c**), and therefore **A5a**, **A5b**, and **A5c** are also interchangeable at ambient temperature.

Chalk-Harrod mechanism.

C=O bond insertion to the Pt-H bond of A to afford a silylhemiaminal intermediate. Here, we first investigated the Chalk-Harrod pathway for the Pt-catalyzed amide reduction, i.e. insertion of the C=O bond into the Pt-H bond of either **A5a** or **A5c**. Starting from the Pt(II) precursor **A5a**, C=O bond insertion into the Pt-H bond does not occur because the potential energy monotonically increases concurrent with the C-H bond formation (see Figure S2). Despite our attempts to optimize the geometry starting from a structure in which the C-H length was in the range of explicit C-H bonding (e.g. 1.08 Å), the structure spontaneously returned to that of **A5a**. In contrast to the platinum-catalyzed hydrosilylation of ethylene, this can be understood by considering the difference in the coordination structures of ethylene and carbonyl compounds with the Pt center. It is well known that ethylene molecules coordinate to the Pt center through a π^* orbital, whereas an amide coordinates to the Pt center via the lone pair of the carbonyl oxygen. Because of this significant difference in the nature of the bonding, large geometric changes are required before the hydride attack can occur during amide reduction, such that C=O bond insertion is more difficult than C=C bond insertion.

In contrast, starting from the Pt(IV) precursor **A5c**, insertion of the C=O bond into the equatorial Pt-H bond has an activation energy of 19.5 kcal/mol and proceeds to afford the $\text{HPT}^{\text{IV}}\text{Si}_2(\text{OCH}(\text{Me})(\text{NMe}_2))$ complex **C1** (Figure 5). This step was found to be one of the rate-determining steps for the overall reaction, in which the total activation energy was estimated to be 29.6 kcal/mol on the basis of **A5a**. It should be noted that employing any of the other functionals also resulted in the conclusion that this reaction was the rate-determining step.[†] As discussed above, the equatorial hydride is highly activated due to the strong σ -donating interactions from the two silyl groups, and so the hydride attack at the carbonyl carbon atom can occur even though a pronounced geometrical change is required. We concluded that this is the key factor that allows the hydrosilylation of the C=O bond in

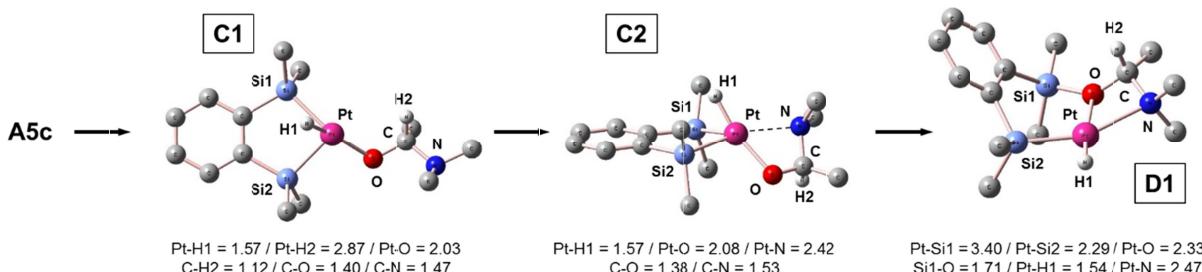


Figure 6. Optimized geometries of intermediates **C1**, **C2**, and **D1**, found in the Chalk-Harrod pathway. Important bond lengths are shown in Å.

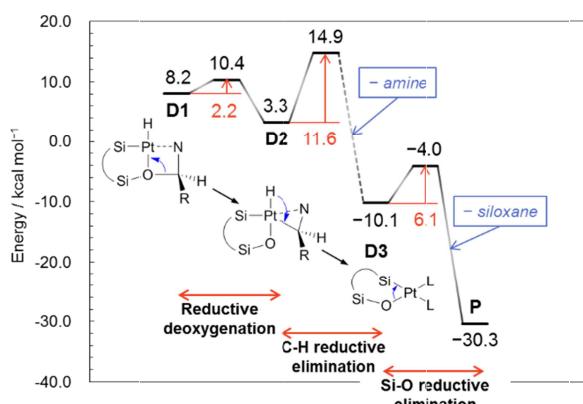


Figure 7. Energy profile for the reductive deoxygenation from a silylhemiaminal intermediate to the final product.

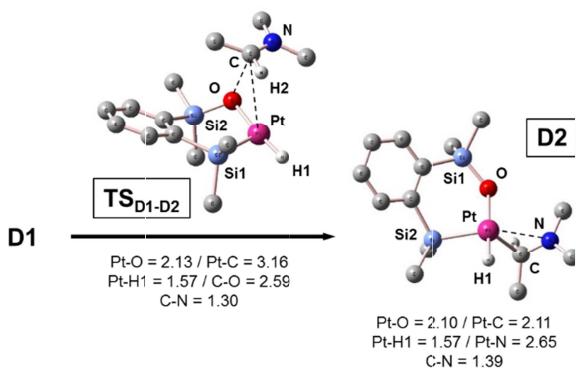


Figure 8. Optimized geometries of $\text{TS}_{\text{D}1-\text{D}2}$ and $\text{D}2$ found in the reductive deoxygenation process from $\text{D}1$. Important bond lengths are shown in Å.

this system. The reaction is then continued because rotations around the C-O and C-N bonds are able to form the stable *N*-coordinated “ $\text{HPt}^{\text{IV}}\text{Si}_2\{\text{OCH}(\text{Me})(\text{NMe}_2)\}$ ” complex intermediate **C2** (Figure 6). The energy barrier of this set of rotations was computed to be only 4.0 kcal/mol starting from **C1**, with a very small imaginary frequency value of 31i cm^{-1} , and thus the rotations occur very smoothly. The Pt-N length of **C2** was determined to be 2.42 Å, indicating that the amine moiety weakly coordinates to the Pt center so as to stabilize itself.

Subsequently, reductive elimination of the silicon-oxygen bond occurs to form the stable “ $\text{HPt}^{\text{II}}\text{Si}$ ” intermediate **D1**, in which a silylaminal moiety is bound to the platinum center by an oxygen and a nitrogen atoms (Figure 6). The Pt-O and Pt-N lengths of this moiety were determined to be 2.33 and 2.47 Å, respectively, indicating that they weakly coordinate to the Pt center. This intermediate takes on a square planar geometry that reflects the d^8 configuration of Pt(II). Intermediate **D1** was estimated to be more stable than **C2** by 5.5 kcal/mol and the energy barrier from **C2** was calculated to be 16.6 kcal/mol with an imaginary frequency of 132i cm^{-1} . Consequently, this step is another candidate for the rate-determining step, with a total activation energy of 30.3

kcal/mol from **A5a**. In the case of this reaction step, the activation energy was estimated to be somewhat smaller when applying the other functionals,[†] thus the B3LYP-calculated activation energy is expected to be the highest limit of the overall reaction. In the transition state, we found that the disilaplatinacycle had to significantly distort in order to form the Si-O bond. This is believed to be at least one of the reasons why the Si-O reductive elimination has a relatively large activation energy despite the high level of affinity between silicon and oxygen atoms.

Reductive deoxygenation to afford products and regeneration of R. As described in the introduction, a general scheme for the hydride reduction of amides is explained by a two-step process composed of addition of M-H to a C=O group of the amide $\text{R}_1\text{CONR}_2\text{R}_3$ to form a metallated hemiaminal $\text{MOCH}(\text{R}_1)\text{NR}_2\text{R}_3$ (step 1) and reductive deoxygenation of the metallated hemiaminal (step 2). Although the intermediate **D1** could be a precursor of a silylated hemiaminal by reductive elimination reaction, the reaction from **A5a** to the silylated hemiaminal was calculated to be endothermic (23.5 kcal/mol). Instead, a reasonable reaction pathway, which directly affords the amide and the siloxane, was discovered. This agreed well with the experimental fact that the silylated hemiaminal was not obtained in the platinum-catalyzed reduction of amides.¹⁰ The reaction continues to the C-O bond cleavage to form the “ $\text{HPt}^{\text{IV}}\text{Si}(\text{OSi})\{\text{CH}(\text{Me})\text{NMe}_2\}$ ” complex **D2**, found to be slightly more stable than **D1** by 4.9 kcal/mol (Figure 7). It is of considerable interest that an iminium cation is formed in the transition state and is weakly bound to the Pt-O bond (Figure 8) because this scenario is very similar to the hydride reduction of carbonyl groups by agents such as $\text{Li}[\text{AlH}_4]$, in which an iminium cation is expected to be an important intermediate. The calculated C-N bond length of 1.30 Å in this complex was somewhat shorter than the 1.37 Å length in the amide, indicating the presence of a C-N double bond in the iminium cation. It was also interesting to find that the computed activation free energy of this step was very small (2.2 kcal/mol). Indeed, the potential energy barrier determined from **D1** in gas phase calculations was 11.5 kcal/mol, with a very small imaginary frequency of 89i cm^{-1} . This indicates that the C-O bond cleavage is accomplished by overcoming a gently sloping energy barrier as the result of thermal fluctuations rather than by oxidative addition to the Pt center. In addition, the transition state is greatly stabilized by the solvation effect due to the large dipole moment of the iminium cation complex. The Pt(II)-iminium complex **D2'** [“ $\text{Pt}^{\text{II}}(\text{OSi})\{\text{CH}(\text{Me})\text{NMe}_2\}'$ ”] was also identified, as a result of the reductive elimination of the Si-H bond (Figure S3). The energy of **D2'** was computed to be 13.6 kcal/mol higher than that of **D2** and the energy barrier from **D2** was estimated to be 19.5 kcal/mol. Therefore, even if **D2'** is formed directly from **D1**, it should readily isomerize to form **D2**.

Finally, the reductive elimination of the C-H bond occurs to afford an amine product, with concomitant solvation to generate the platinum siloxide complex **D3** (Figure 7), with an associated energy barrier of 11.6 kcal/mol. Further reductive elimination of the Si-O bond takes place with an energy barrier of 6.1 kcal/mol to afford a siloxane product, and the Pt(0) catalyst is regenerated. Consequently, the overall catalytic reaction is exothermic and the reaction free energy was estimated to be -30.3 kcal/mol. We also investigated the reaction pathway in which the oxidative addition of another BDSB occurs with the concomitant reductive elimination of the Si-O bond to directly regenerate **A5a** (Figure S4). Initially, the oxidative addition of one Si-H bond of another BDSB to **Ts_{D2-D3'}** together with concomitant amine dissociation proceed, producing the 6-coordinate Pt(IV) complex **D3'**. The remaining Si-H group coordinated to the Pt center with η^1 -H hapticity via an agnostic interaction to generate an octahedral structure. The activation energy to regenerate **A5a** was computed to be 3.8 kcal/mol, which was slightly lower than that of the non-BDSB supported pathway. However, since the siloxane formation occurs readily in either the presence or absence of an additional BDSB molecule, the association of another Si-H group to the Pt center of **D2** is not essential for this step.

Modified Chalk-Harrod Mechanism

In the rhodium-catalyzed hydrosilylation of alkenes, the oxidative addition of a Si-H bond to the Rh(I) center initiates the catalytic cycle. Subsequent C=C bond insertion into the Rh-Si bond of the resulting H-Rh(III)-Si species is preferred over insertion into the Rh-H bond. This is known as the modified Chalk-Harrod mechanism (Scheme 2, right). Because silicon atoms generally exhibit a high affinity for oxygen, it seems reasonable that the modified Chalk-Harrod mechanism would be more probable than the Chalk-Harrod mechanism for the hydrosilylation of C=O bonds, as proposed by Ojima and Kogure.^{11a} Hence, the modified Chalk-Harrod pathway could be applied in the case of the Pt catalyst when considering the strong Si-O affinity (Scheme 3, left). This prompted us to investigate the C=O bond insertion into the Pt-Si bond, starting from the H-Pt-Si compounds **A5a**, **A5b**, and **A5c**.

Figure 9 summarizes the calculated potential energy changes along with the modified Chalk-Harrod cycles. Starting from **A5a**, the C=O bond insertion requires a large activation energy of 44.1 kcal/mol to form the four-coordinate Pt(IV) complex [$H_2Pt^{IV}Si\{C(Me)(NMe_2)OSi\}$] **M1a** (Figure 10), which was computed to be 31.0 kcal/mol higher than **A5a**. The reaction is followed by C-H reductive elimination with a very small activation energy of 5.1 kcal/mol to form " $Hpt''Si$ " species coordinated by a nitrogen atom of the silylaminol moiety **D1'**, which is a conformer of the compound **D1** that appears in the Chalk-Harrod pathway (Figure 10). This mechanism is, therefore, not preferable because of the large activation energy. Starting from **A5b**, the C=O bond inserted intermediate [$Pt''Si\{C(Me)(NMe_2)OSi\}(\eta^2-H_2)$] **M1b** (Figure S5) was found to be 25.9 kcal/mol less stable than **A5a** but 5.1 kcal/mol more stable than **M1a**. However, this is also ruled out as the result of the large activation barrier of 42.0 kcal/mol

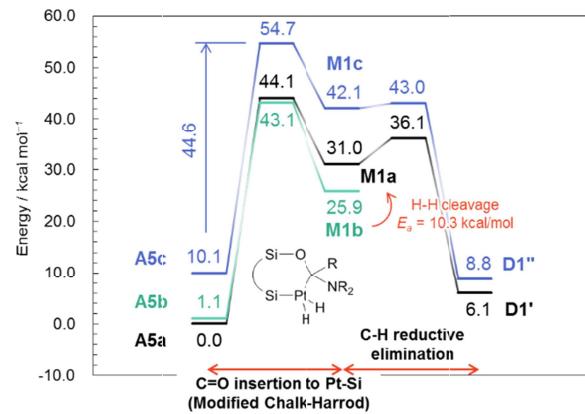


Figure 9. Energy profile for the modified Chalk-Harrod pathway to afford a silylaminol intermediate.

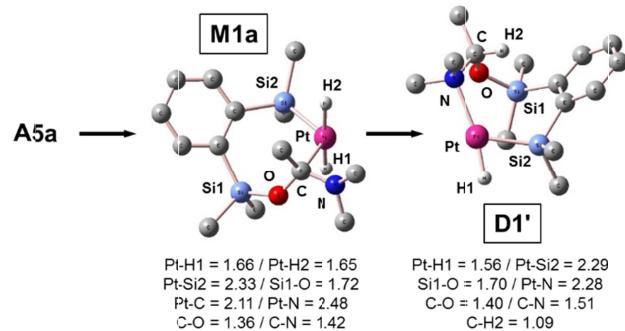


Figure 10. Optimized geometries of **M1a** and **D1'** found in the modified Chalk-Harrod pathway from **A5a**. Important bond lengths are shown in Å.

from **A5b**. Starting from **A5c**, the C=O bond inserted intermediate [$H_2Pt^{IV}Si\{C(Me)(NMe_2)OSi\}$] **M1c** (Figure S5) was found to be very unstable, being 42.1 kcal/mol higher than **A5a** with an estimated energy barrier from **A5c** of 44.6 kcal/mol. Thus, the modified Chalk-Harrod pathway from **A5c** is apparently impossible.

From these results, it is concluded that a large activation energy is required for C=O bond insertion into the Pt-Si bond in the Pt-catalyzed amide reduction. Even though the subsequent C-H reductive elimination can easily occur, the modified Chalk-Harrod mechanism is safely ruled out. In the transition state between **A5a** and **M1a**, the carbon bonded to the platinum atom is located at the trans position relative to the silyl group. This makes **Ts_{A5a-M1a}** more unstable due to the strong trans-influence of the silyl group. In contrast, during the Chalk-Harrod pathway from **A5c**, the aminomethoxy group that appears in the intermediate and has a weaker trans-influence than the alkyl group is located at the trans position of the hydride, which has a weaker trans-influence than that of the silyl group (see Table S2 and discussions[†]). Furthermore, although the oxidation state of the Pt center is expected to be Pt(IV), which is likely to generate an octahedral structure, **M1a** and **M1c** were computed to be four-coordinate complexes. Thus, **M1a** and **M1c** should be very unstable and, consequently, C-H reductive elimination occurs rapidly to recover the Pt(II)

character. These results indicate that neither the transition states nor the C=O bond-inserted intermediates are stable in

increased when the Si-O distance was decreased. In the cationic outer sphere mechanisms proposed for Ir⁺ and Ru⁺

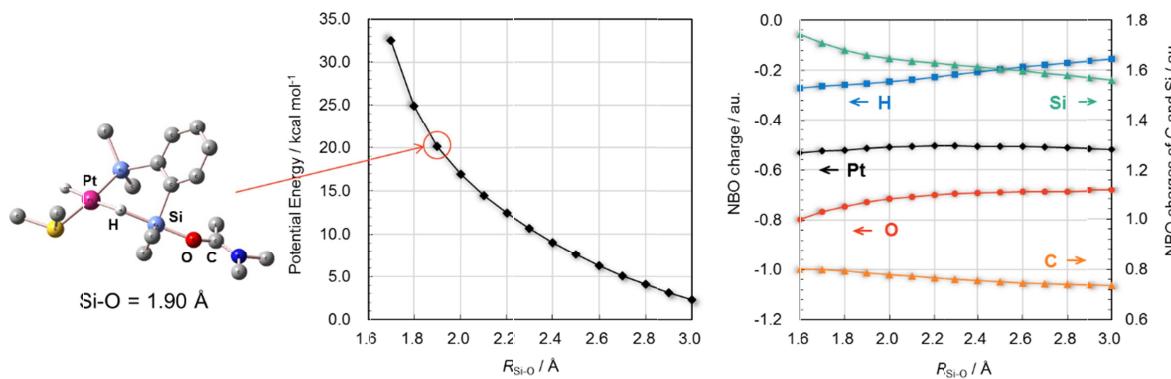


Figure 11. Changes in the potential energy (left) and the NBO charges of Pt, H, Si, and O atoms (right) along with the Si-O bond formation via the ionic outer sphere mechanism. The geometry in the left panel shows the partially optimized structure in which the Si-O bond length ($R_{\text{Si}-\text{O}}$) was fixed at 1.90 Å.

the modified Chalk-Harrod pathway.

Outer-Sphere Mechanism

Recently, the reduction of carbonyl compounds with hydrosilanes catalyzed by cationic iridium or ruthenium complexes has received much attention. Although these reactions involve hydrosilylation of a C=O bond, mechanisms that differ from the Chalk-Harrod and modified Chalk-Harrod pathways have been proposed.¹⁶ Experimental and theoretical studies have shown that the important intermediate is a cationic metal species coordinated to an η^1 - or η^2 -Si-H group, and that a lone pair on the carbonyl oxygen directly attacks the silicon atom of the Si-H group to generate activated $\text{R}_2\text{C}=\text{O}^+\text{SiR}_3$ and $\text{M}^-\text{-H}$ species ($\text{M} = \text{Ir}^+$ or Ru^+), as shown in Scheme 2, right (outer sphere mechanism).¹⁶ This reaction is followed by a hydride attack at the carbonyl carbon atom to form the corresponding silyl ether product. The reaction does not involve any oxidative additions and/or reductive eliminations. In this case, the use of a cationic metal center is the key to making the Si center of the η^1 - or η^2 -Si-H moiety sufficiently electrophilic such that it easily undergoes Si-O bond formation. Although the Pt center is not cationic, **A5a** contains an η^2 -Si-H group bound to the metal. It would therefore be worthwhile to investigate the role of the outer sphere pathway with regard to Pt-catalyzed amide reduction.

Calculations for the direct attack of amides on the coordinated η^2 -Si-H group of **A5a** did not provide evidence for any stationary intermediate because the potential energy associated with the Si-O bond formation monotonically increased (Figure 11, left). At a Si-O bond length of 1.9 Å, inversion of the silyl group stereochemistry takes place, and the potential energy is further increased by additional decreases in the Si-O distance. We also investigated the changes in the NBO charges of the Pt center, the Si and H atoms in the η^2 -Si-H group, and the C and O atoms of the carbonyl group (Figure 11, right). Interestingly, the charge of the Pt center did not change while moving along the reaction coordinate, although the hydride nature of the H atom was

complexes, the attack of an amide at the η^2 -Si-H group results in cationic $[\text{Ir}-\text{H}]^+$ or $[\text{Ru}-\text{H}]^+$ species, in which the hydride nature is compensated for by the positive charge of the metal center. Hence, the lack of any change in the charge at the Pt center implies that hydride formation could not be supported by a neutral Pt center. However, when the charge on the Si center was moderately increased (to approximately 0.18e), the charge on the carbonyl oxygen was slightly decreased (-0.11e) while that on the carbonyl carbon was marginally increased (0.07e) as the Si-O bond length was shortened. Nonetheless, these changes were very small and insufficient to induce reaction with the platinum hydride. Consequently, an anionic Pt-H bond is never formed in the disilaplatina(II) complex, because the Pt center possesses significant electron density due to the pronounced σ -donation from the two silyl groups.

With regard to the Rh-catalyzed hydrosilylation of ketones, Chan and co-workers proposed that there is an alternative to the modified Chalk-Harrod mechanism, in which the carbonyl oxygen directly attacks a silyl moiety of the oxidative adduct (an H-Rh-Si species).^{15b} Hence, we also investigated the outer sphere pathway starting from **A5a**, in which the attack of the carbonyl oxygen atom occurs at the silyl moiety of **A5a** from the opposite side of the Pt center. However, during the Si-O bond formation, the oxidative addition of the η^2 -Si-H moiety concomitant with the reductive elimination of the silyl and hydride moieties occurred, such that the conformation was changed and became equivalent to that in the ionic outer sphere pathway (Scheme S1). Consequently, the outer sphere mechanisms are also ruled out as possibilities for Pt-catalyzed amide reduction with BDSB.

Discussions of the proximity effects.

Finally, we wish to discuss the proximity effects of dual Si-H group to explain why the Chalk-Harrod pathway was adopted in the platinum-catalyzed amide reduction with BDSB. It is of considerable interest that **A3c** has a trigonal bipyramidal structure (Figure 2), which rarely occurs in either

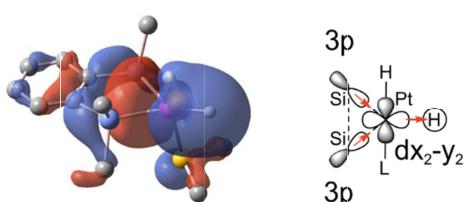
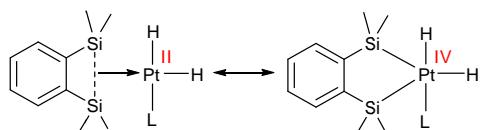


Figure 12. A 3D image of the highest occupied molecular orbital (HOMO) of **A3c** and its chemical interaction.

d^6 or d^8 transition metal complexes. The equatorial Pt-H₂ length was computed to be 1.67 Å, a value that exceeds the length of the axial Pt-H1 bond (1.56 Å). In addition, the Pt-H σ -orbital was found to be the highest occupied molecular orbital, HOMO (Figure 12, left). These indicate that the equatorial hydrogen is highly activated due to the strong trans-influence of the two silyl groups. Furthermore, the Si-Si distances of **A3a**, **A3b**, and **A3c** were computed to be 3.36, 3.16, and 2.96 Å, respectively, and the Si-Pt-Si angles of them were determined to be 85.4°, 84.1°, and 75.5°, respectively. Interestingly, the Si-Si distance and the Si-Pt-Si angle of **A3c** are somewhat shorter and more acute than those of **A3a** and **A3b**. These results provide evidence that there is an attractive interaction between the two Si atoms, as a counterpart to the σ -donation to the Pt center (Figure 12, right). This concept was previously discussed by Takagi and Sakaki with regard to a disilane bound Pt(0) N-heterocyclic carbene complex.³⁰ Consequently, a considerable amount of Pt(II) character is mixed into the ground state of **A3c**, although it is formally considered a Pt(IV) complex.



This conclusion is also supported by the results of natural bond orbitals (NBOs) analysis.[†]

Conclusion

The proposed reaction mechanism for the Pt-catalyzed reduction of amides to amines with hydrosilanes having dual Si-H groups is summarized as follows (see also Scheme 6): A key to accomplish the reduction of amide via the present mechanism is a formation of a five-coordinate Pt(IV) species, **A3c** or **A5c**, as a result of double oxidative addition of BDSB. Due to strong trans-influence from two closely located silyl groups, **A3c** or **A5c** has a highly activated Pt-H bond into which the C=O bond insertion moderately occurs with the total activation energy of 29.6 kcal/mol, even though it requires a significant geometrical change. Consequently, the classical Chalk-Harrod pathway was adopted. The reaction is followed by the Si-O bond formation via reductive elimination to form the silyloxy Pt(II) intermediate with the total activation energy of 30.3 kcal/mol. These two process are estimated to be the rate-determining step of the platinum-catalyzed reduction of amide. The modified Chalk-Harrod pathway in which the C=O bond is inserted into the Pt-Si bond, and the ionic outer-sphere pathway in which the carbonyl oxygen of an amide directly attacks the η^2 -Si-H moiety, were found to be highly unlikely because they gave very large activation energies.

It should be noted that the calculations in this study explain three experimental results. Firstly, platinum-catalysed reduction of amides has never been achieved with usual hydrosilanes, for which hydrosilanes having two closely located Si-H bonds like BDSB. The “ H_2PtSi_2 (amide)” intermediate **A5c** formed by double oxidative addition of BDSB to R has a highly reactive equatorial Pt-H bond toward insertion of a C=O bond of the amide. Although the mechanistic aspects of the rhodium, iridium, or ruthenium-catalyzed hydrosilylation of carbonyl compounds indicate that the platinum-catalyzed hydrosilylation of carbonyl groups rarely occurs because platinum-based catalysts preferentially work via the Chalk-Harrod mechanism rather than the modified Chalk-Harrod cycle or outer sphere mechanism, the present study clearly demonstrates that double oxidative addition of Si-H groups to a platinum center generates a Pt(IV)-H species, which is enough reactive to promote the

hydrosilylation of a C=O bond through the Chalk-Harrod mechanism. Secondly, experimental results showed that amines were selectively formed in the platinum catalysed reactions, and silylated hemiaminals (and aldehydes formed by hydrolysis) were not observed. This is consistent with the calculation that reductive deoxygenation from the **D1** intermediate to the product was a reasonable pathway rather than the reductive elimination of the silylated hemiaminals from **D1**. Thirdly, calculations support reversible reaction pathways among the intermediate **A**, intermediate **S**, and isolated complexes, **1**, **2**, and **3**, which explain the mechanistic studies on the experimental basis reported previously.

Several examples of the proximity effect of the two Si-H groups enhancing the rates of hydrosilylation reactions of carbonyl compounds have been observed with regard to the use of rhodium, ruthenium, iridium, and iron catalysts. Involvement of the double oxidative addition of two Si-H groups to the metal center to generate H₂MSi₂ species was postulated, and was supported by the isolation of disilametallacycles as complexes that are closely related to the catalytically active species. The results presented in this paper clearly support this hypothesis theoretically, providing several new insights as described above. Because a silyl group exhibits a large trans-influence (see Table S2), the formation of two proximal silyl groups as a result of double oxidative addition must be a characteristic feature of catalytic hydrosilylation using bifunctional hydrosilanes that show unusual reactivity. We are currently performing a systematic study of these dual Si-H effects in other metal-catalyzed reactions.

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