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Computational Study on the Reaction Mechanism of Hydrosilylation of Carbonyls Catalyzed by High-Valent Rhenium(V)−Di-oxo Complexes

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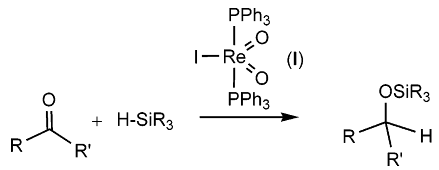

Density functional theory (DFT) calculations have been performed to elucidate the reaction mechanism of hydrosilylation of carbonyl compounds catalyzed by high-valent rhenium(V)−di-oxo complexes $ReO_2I(PR_3)_2$ (R = Me, Ph). The calculations suggest that the most favorable mechanism involves the rate-determining dissociative [2 + 2] addition of the Si−H bond across a Re═O bond to form a Re(V) hydrido siloxy intermediate; this is followed by carbonyl coordination, reduction of the carbonyl, rearrangement, and final intramolecular nucleophilic attack from the alkoxy group to the silyl center (dissociative retro-[2 + 2] addition). It was also found that the additional oxo ligand in the $ReO_2I(PR_3)_2$ complexes promotes the [2 + 2] addition across the rhenium−oxo bond both kinetically and thermodynamically, as compared to the neutral rhenium(V)−mono-oxo complex $ReOCl_3(PMe_3)_2$. The effect of different silanes on the [2 + 2] addition barriers is also studied.

Introduction

Hydrosilylation catalyzed by transition-metal complexes offers the most straightforward and atom-economic route to carbon−silicon and oxygen−silicon bond formations, which is important for organic synthesis and dendrimer and polymer chemistry.[1,2] Recently, Toste et al.[3,4] reported an unconventional hydrosilylation of aldehydes and ketones catalyzed by the high-valent rhenium(V)−di-oxo complex $[ReO_2I(PPh_3)_2]$[5] (Scheme 1). Toste proposed a novel mechanistic pathway for the rhenium(V)-catalyzed hydrosilylation reaction (Scheme 2).[3] The proposed mechanism is sharply distinct from those accepted mechanisms proposed for the hydrosilylation reactions catalyzed by low-valent late transition-metal complexes[1a,b] and by the Lewis acid $B(C_6F_5)_3$.[6,7] It consists of three major steps: (1) [2 + 2] addition of the Si−H bond across a Re═O bond to generate

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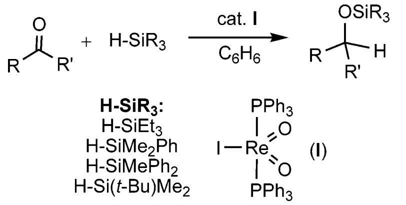
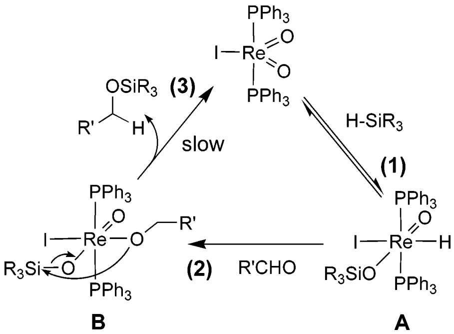
SCHEME 1



SCHEME 2

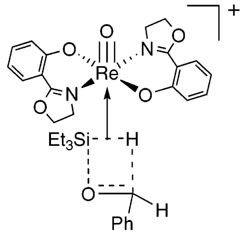


a rhenium(V) hydrido siloxy intermediate (**A**). (2) Reduction of the carbonyl from the high-valent rhenium(V) hydrido intermediate **A** (carbonyl insertion). (3) Retro-[2 + 2] addition, an intramolecular nucleophilic alkoxy attack on the silicon center, to afford a silyl ether product and to regenerate the active catalyst. The proposed Si−H bond activation process is based on two precedent reports on Ti═S and Ta═N complexes.[8]

In an attempt to test the proposed mechanism, Toste's group carried out a reaction of the catalyst with excess triethylsilane (TES-H). They observed a new rhenium complex having ^{1}H NMR chemical shifts of δ 6.60, 0.78, and −0.20 ppm. The signal of δ 6.60 ppm disappeared when TES-D was used. Therefore, they assigned the new complex as the rhenium(V) hydrido intermediate (**A**) derived from the [2 + 2] addition of the Si−H bond across the Re═O bond (Scheme 2).[3] Moreover, the intermediate **A** disappeared, and a new intermediate was observed when introducing 4-nitrobenzaldehyde under the catalytic conditions.[3] The new intermediate was assigned to be the rhenium alkoxy complex (**B**). In a recent kinetic study, the Toste group showed an inverse first-order dependence on phosphine for the hydrosilylation reaction. Furthermore, they found that hydrosilylation does not occur with the (dppe)Re(O)Cl_3 catalyst.[4]

In this connection, both Royo's and Abu-Omar's groups found that the high-valent molybdenum(VI)−di-oxo (MoO_2Cl_2) and a few rhenium(V) and (VII) oxo complexes were also capable of catalyzing the hydrosilylation of carbonyls.[9,10] Traditionally, rhenium−oxo and molybdenum−oxo complexes are usually documented for oxidation reactions, such as olefin epoxidation and oxygen transfer reactions.[11] In a stark contrast, the recent reports of reduction of carbonyl compounds catalyzed by high-valent oxometal complexes pioneered by Toste's work represent a total reverse reactivity of these complexes as oxidation catalysts.[3,4,9,10,12]

SCHEME 3



Abu-Omar's experiments provided other insight about the reaction mechanism. They utilized the cationic rhenium(V)−mono-oxo complex, [Re(O)(hoz)$_2$][TFPB] (hoz = 2-(2′-hydroxyphenyl)-2-oxazolin and TFPB = tetrakis(pentafluorophenyl) borate), as a catalyst for the hydrosilylation of carbonyls.[10] They found that the prepared coordinately saturated Re(O)(hoz)$_2$H complex did not react with benzaldehyde.[10,13] Furthermore, they also performed ^{18}O isotope labeling experiments for dehydrogenative oxidation of organosilanes with D_2O.[14] The source of oxygen in the silicon-containing product was almost all from water. They also observed that the silane (Et_3SiH) slowly reacted with the cationic catalyst to give the rhenium(III) species [Re(hoz)$_2$(CH_3CN)$_n$]$^+$. These observations lead them to cast doubt on the mechanistic proposal involving a [2 + 2] addition across the rhenium−oxo bond of the cationic rhenium(V)−mono-oxo complex. Instead, they proposed a metathesis-like pathway (Scheme 3) based on a KIE value of Et_3SiH/Et_3SiD (1.3).[10,15,16] While the unusual reduction of carbonyls catalyzed by the high-valent rhenium(V)−di-oxo complex is fascinating, several questions remain to be answered about the reaction mechanism. Is it possible to have another kind of Si−H bond activation, such as oxidative addition or the metathesis-like pathway proposed by Abu-Omar's group?[10] How does the addition of the Si−H bond across the Re═O bond occur? Is the [2 + 2] addition operative or is a [3 + 2] addition followed by a very facile tautomeric rearrangement?[17] How does the

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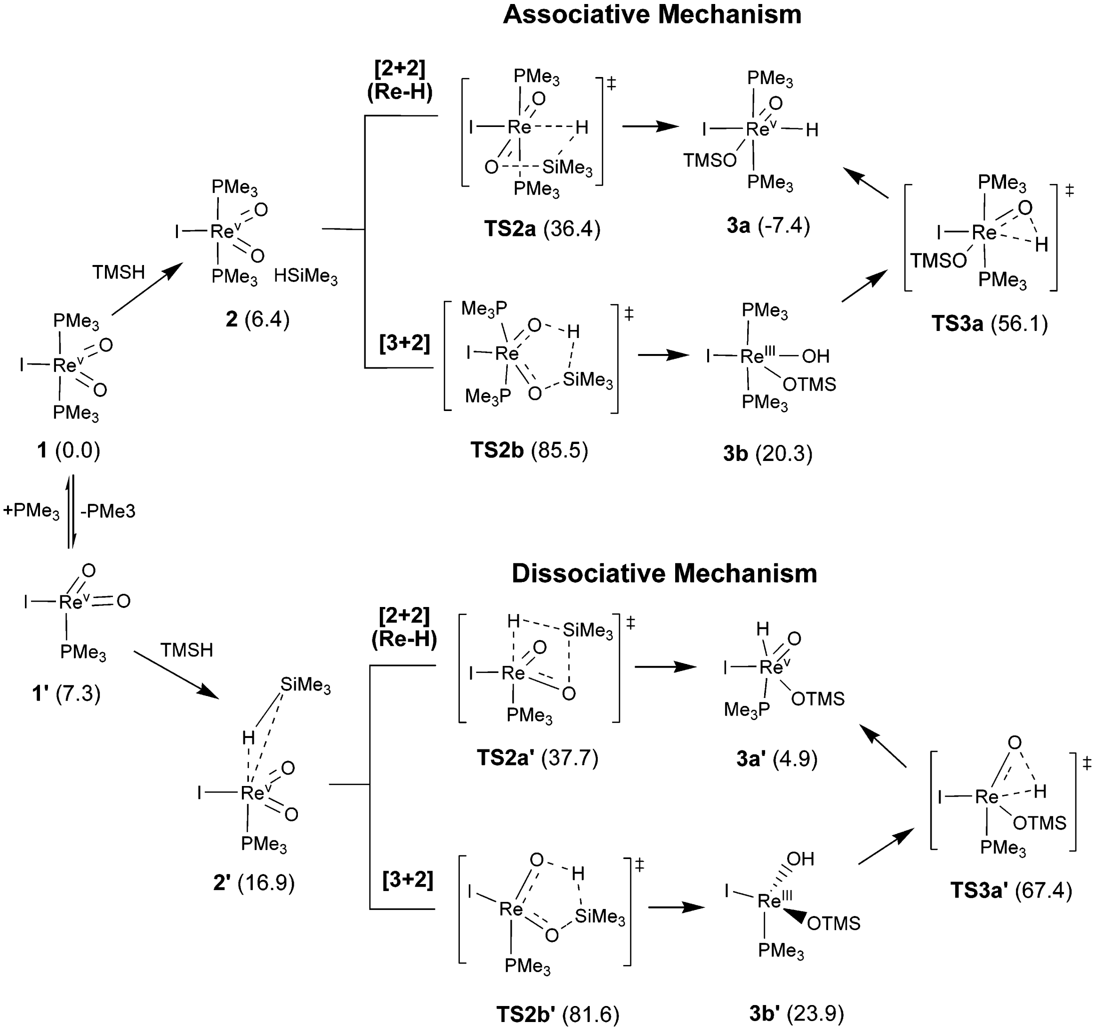

FIGURE 1. Energetics of the Si−H bond activation by the rhenium−di-oxo complex **1**. The relative free energies in parentheses are given in kcal/mol. In calculating the relative energies, we included the energies calculated for free TMS-H, aldehyde, and PMe_3 whenever necessary to make the energies comparable for all the species.

reduction of the carbonyl from the high-valent rhenium(V) hydrido complex proceed? What are the effects of the oxo ligands on the silane addition? Here, we report our DFT calculations[18,19] to elucidate the reaction mechanism of the salient hydrosilylation catalyzed by the rhenium(V)−di-oxo complex[3] and to address these questions.

Computational Methods

All calculations were carried out with the Gaussian 03 program.[20] All geometries of reactants, transition structures, and intermediates were fully optimized by the B3LYP method.[21] Basis set 6-31G* was used for H, C, and O atoms. Hay-Wadt's effective core potentials (ECP) and basis sets were adopted for the rest of the atoms.[22] One set of *f*-polarization functions was also augmented for rhenium, and one set of *d*-polarization functions was added for silicon, phosphine, chlorine, and iodine.[23,24] Harmonic vibration frequency calculations at the same level were then performed. All energies presented in the text are relative free energies with respect to the catalysts unless stated otherwise. The model catalyst $[ReO_2I(PMe_3)_2]$ (**1**) and the trimethylsilane (TMS-H) substrate were used to study all the catalytic steps (the relevant species are denoted by

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Arabic numbers). The realistic catalyst [$ReO_2I(PPh_3)_2$] (**I**) was also adopted to study several crucial steps (the relevant species are denoted by Roman numbers). The calculated structure of [$ReO_2I(PPh_3)_2$] (**I**) by the B3LYP method (Re═O: 1.73 Å; Re−P: 2.54 Å; Re−I: 2.74 Å; and O−Re−O: 137.7°) is very close to the X-ray crystal structure (Re═O: 1.74 Å; Re−P: 2.49 Å; Re−I: 2.66 Å; and O−Re−O: 138.7°).[5]

One reviewer is concerned about the effect of the polarization functions of hydrogen on the calculated relative energies of the Si−H bond activation. We test the effect by calculating the relative electronic energies of **TS2a** and **TS2a′**, the two most important transition structures in our study (see text for more details), using the DZP basis set for all hydrogens. Without the polarization functions, the relative electronic energies of **TS2a** and **TS2a′** with respect to the catalyst are 21.4 and 37.1 kcal/mol, respectively. With the polarization functions, the relative electronic energies of **TS2a** and **TS2a′** are 20.8 and 36.5 kcal/mol, respectively. Clearly, the effect of the polarization functions is small.

To test the solvent effect, we performed single-point energy calculations for several selected structures by employing the polarizable continuum model (PCM), with RADII═UAKS, available in the Gaussian 03 package. In the PCM calculations, the 6-311++G** basis set was used for C, H, and O atoms. The PCM solvation free energies in benzene solutions were estimated by summing the $\Delta G_{\mathrm{electrostatic}}$ and $\Delta G_{\mathrm{nonelectrostatic}}$ terms. The additional calculations show that the solvent effect is small in benzene solutions. The relative free energies of **TS2a**, **TS2a′**, **3a′**, **TS4a′**, **5b′**, **TS5a′**, **TS9d**, **TSIIa**, and **TSIIa′** in the gas phase and solution (in parentheses) are 36.4 (35.9), 37.7 (35.6), 4.9 (3.0), 18.4 (17.9), −7.8 (−7.1), 12.4 (11.7), 41.9 (41.3), 42.7 (42.2), and 32.0 (27.2) kcal/mol, respectively.

Results and Discussion

The outline of this paper is as follows. We first focus on the mechanistic pathway proposed by Toste's group (part I) on the basis of the three major catalytic steps (Scheme 2) (i.e., (1) the addition of the Si−H bond across one of the two rhenium−oxo bonds; (2) the reduction of the carbonyl; and (3) retro-[2 + 2] addition. Other possible Si−H bond activation processes, including oxidative addition and metathesis-like addition proposed by Abu-Omar's group (Scheme 3), will be discussed in part II.

(I) Mechanism Proposed by Toste. Addition of the Si−H Bond Across the Rhenium−Oxo Bonds. Catalysts [$ReO_2I(PMe_3)_2$] (**1**) and [$ReO_2I(PPh_3)_2$] (**I**) are formally 16e complexes and can undergo addition of the Si−H bond of TMSH via an associative mechanism. Alternatively, catalysts **1** and **I** can be regarded as 18e complexes if the bond order of each Re═O bond is considered to be two and a half.[5,11c,25,26] A dissociative mechanism for the addition of the Si−H bond, in which the catalysts first dissociate one of the phosphine ligands, also needs to be considered. As to the Si−H bond activation by the rhenium−di-oxo complex, it is difficult to distinguish between the [2 + 2] and the [3 + 2] addition pathways in experiment if the [3 + 2] addition is followed by a very fast tautomeric rearrangement step.[17] Several possible addition modes have been considered in our study: (i) [2 + 2] and [3 + 2] addition manifolds, (ii) the route to furnish Re−H and O−Si bonds or the route to obtain Re−Si and O−H bonds for the [2 + 2] addition, and (iii) an associative mechanism and a dissociative mechanism (the species involved are denoted by adding the prime (′) symbol). The calculated structures and the relative free energies for all the addition pathways are collected in Scheme S1 and Figures S1−S3 in the Supporting Information. The key computational results are shown in Figures 1 and 2 and are summarized as follows.

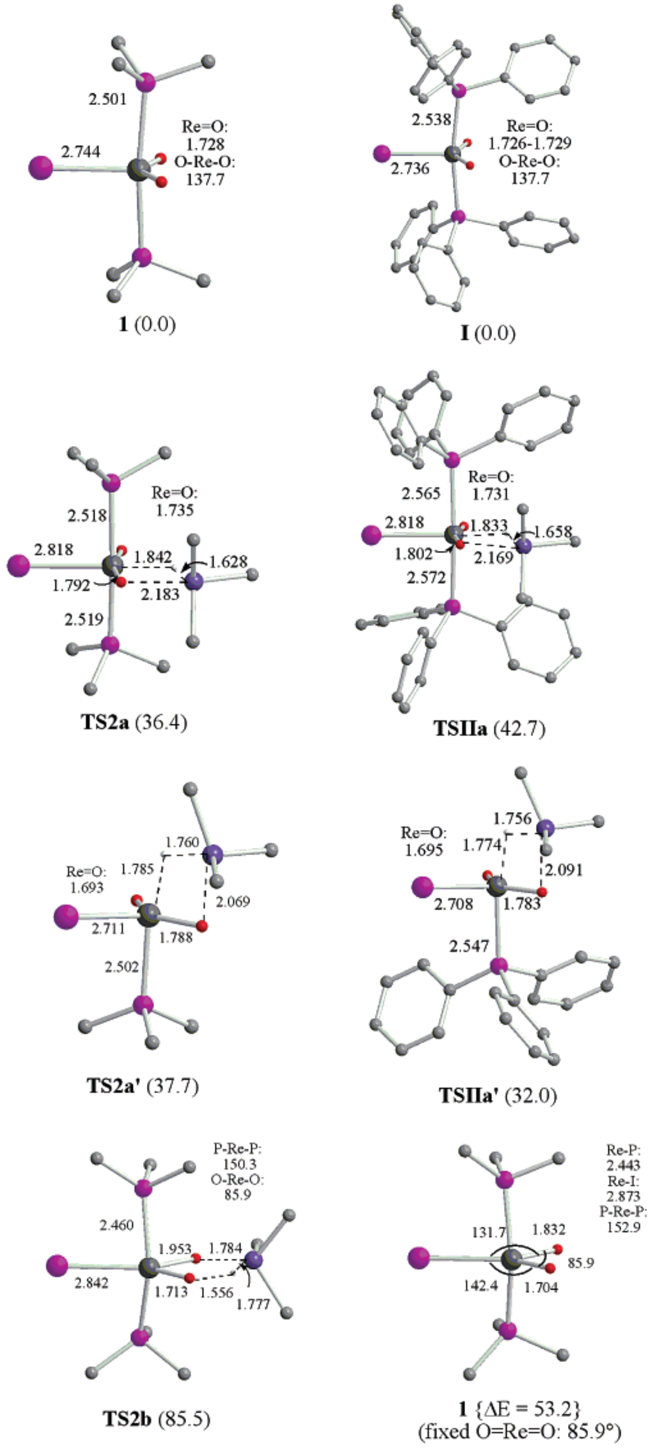

FIGURE 2. Calculated structures of the rhenium(V)−di-oxo catalysts $ReO_2I(PMe_3)_2$, **1**, and $ReO_2I(PPh_3)_2$, **I**, and the transition structures for the most favorable [2 + 2] addition and associative [3 + 2] addition of the Si−H bond across the Re═O bonds together with the relative free energies (kcal/mol in parentheses). The hydrogen atoms of the R groups in the phosphine ligands are omitted for clarity.

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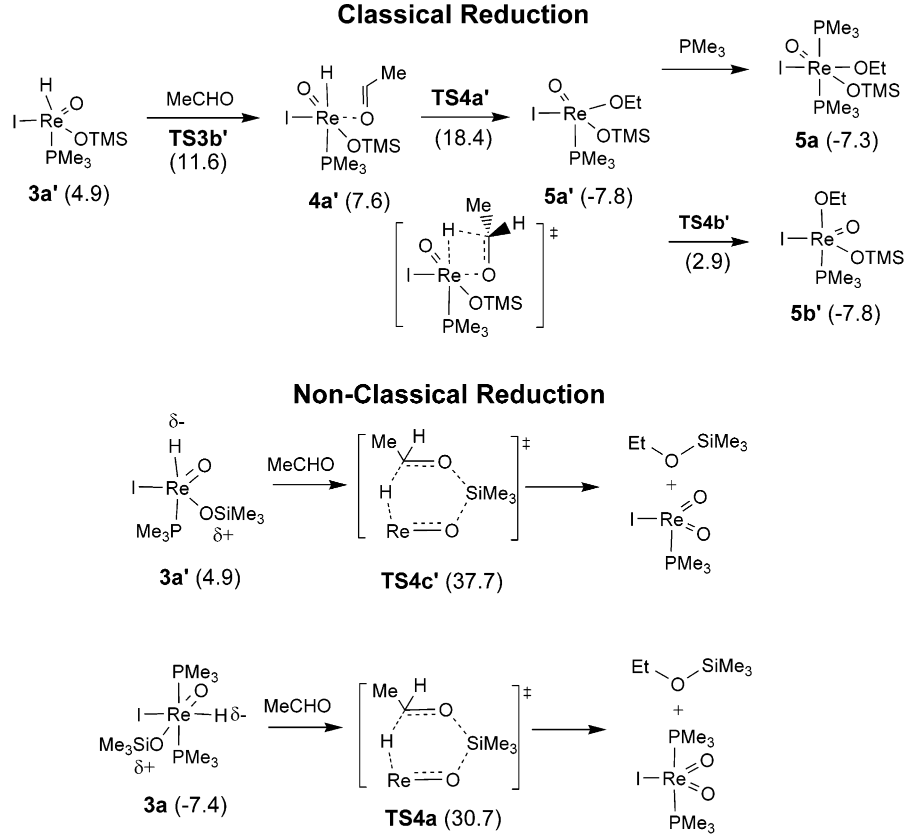

FIGURE 3. Energetics of the carbonyl reduction processes from the rhenium(V) hydrido intermediates. The relative free energies in parentheses are given in kcal/mol. The relative free energies were obtained as in Figure 1.

Figure 1 shows that both the associative and the dissociative [2 + 2] addition pathways are computed to be kinetically more favorable than the reductive [3 + 2] addition pathways.[27] Figure 1 also shows that the tautomeric rearrangement processes from **3b** to **3a** and from **3b′** to **3a′** are estimated to have high barriers (**TS3a** and **TS3a′**, $\Delta G^\ddagger = 56.1$ and 67.4 kcal/mol). These results indicate that the [3 + 2] addition pathways can be ruled out, likely due to the low stability of the rhenium(III) intermediates and the difficulty to reduce the O═Re═O angle suitable for [3 + 2] addition because many d^2 di-oxo complexes prefer to have a very large O═Re═O angle to alleviate the repulsive interaction between the metal d electrons and oxo p_π electrons.[25,26]

The proposed [2 + 2] addition pathways to form a Re−H bond and a very strong O−Si bond via **TS2a** and **TS2a′** are the most favorable routes[28] and give intermediates **3a** and **3a′**, apparently due to an electronic matching of the $Si^{\delta+}-H^{\delta-}$ and $Re^{\delta+}=O^{\delta-}$ bonds[18d] and the thermodynamic driving force to form a strong O−Si bond ($\Delta G_{rxn} = -7.4$ kcal/mol for **3a** and +4.9 kcal/mol for **3a′**).

Employing the less sterically demanding phosphine ligand PMe_3, the associative [2 + 2] addition via **TS2a** ($\Delta G^\ddagger = 36.4$ kcal/mol) is evaluated to be slightly more favorable than the dissociative [2 + 2] addition via **TS2a′** ($\Delta G^\ddagger = 37.7$ kcal/mol). However, the associative [2 + 2] addition is expected to become unfavorable in the realistic catalyst because there is a severe steric repulsion between the silyl group and the two bulky PPh_3 phosphine ligands. Steric effects on the dissociative [2 + 2] addition pathway should be negligible since the silyl group is far away from the PPh_3 ligand. The calculated barrier for the dissociative [2 + 2] addition pathway via **TSIIa′** is reduced to about 32.0 kcal/mol using the less basic but more bulky PPh_3 ligand (Figure 2). In contrast, the calculated barrier for the associative [2 + 2] addition pathway via **TSIIa** increases to 42.7 kcal/mol. Consequently, these additional DFT calculations using the realistic catalyst suggest that the dissociative [2 + 2] addition via **TSIIa′** should be responsible for the Si−H bond activation,[4] giving a rhenium(V) hydrido siloxy intermediate **IIIa′**.

In the intermediates **3a** and **3a′**, the remaining metal−oxo bond becomes shorter (Re═O: 1.663−1.685 Å), indicative of some metal−oxo triple-bond character. Similar metal−oxo bond shortening has been observed in the cycloaddition between an olefin and an oxo-containing metal carbene.[29] A very short rhenium−oxo bond is also found in the rhenium(V) hydrido intermediate **IIIa′** having a realistic PPh_3 ligand (Re═O: 1.661 Å). The origin of the metal−oxo bond shortening in the rhenium(V) hydrido intermediates will be discussed later.

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(27) A significant angular distortion was found in **TS2b** and **TS2b′** (e.g., P−Re−P = 150.3° in **TS2b**).

(28) We also considered an isomeric transition structure of **TS2a′** by adding the Si−H bond of the silane substrate to the vacant site trans to the iodide ligand and in between the two oxo ligands. The isomeric dissociative [2 + 2] addition transition structure **TS2d′** (see Scheme S1 and Figure S3 in the Supporting Information) is higher in energy than **TS2a′** by 2.3 kcal/mol, due to the greater structural reorganization of the metal fragment ($ReO_2I(PMe)_3$) that is necessary for the silane addition in **TS2d′**. **TS2d′** should be further disfavored when a realistic and bulky PPh_3 ligand is considered because of the steric repulsion between the phosphine ligand and the silyl group. We also considered another isomeric transition structure of **TS2a′** by interexchanging the iodide and PMe_3 ligands. The calculations led to **TS2d′**.

(29) Rappé, A. K.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1982**, *104*, 448.

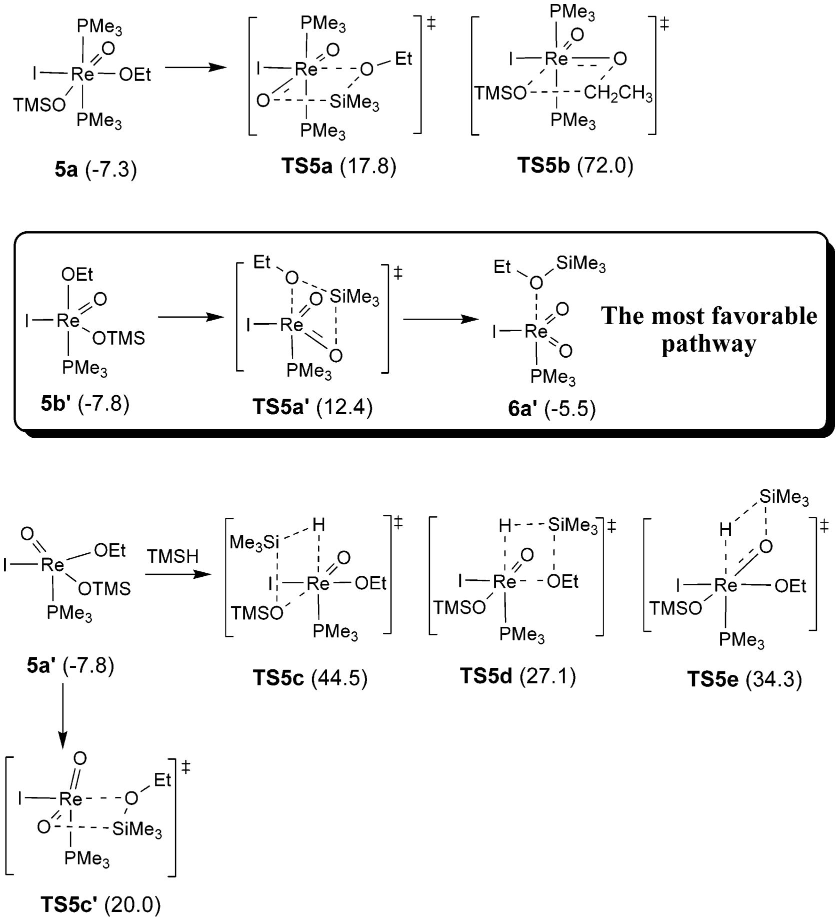

FIGURE 4. Energetics of the processes to generate the silyl ether product. The relative free energies in parentheses are given in kcal/mol. The relative free energies were obtained as in Figure 1.

Reduction. Since the calculations using the realistic catalyst show that the dissociative [2 + 2] addition is kinetically preferred by about 10 kcal/mol over the associative [2 + 2] addition, we mainly discuss reduction of the carbonyl starting from the intermediate **3a′**. After one acetaldehyde coordinates to the five-coordinated intermediate **3a′**, reduction of the carbonyl via **TS4a′** occurs to give the rhenium(V) alkoxy intermediate **5a′** (Figure 3). The energy of **TS4a′** relative to complex **3a′** is computed to be about 13.5 kcal/mol. In the realistic model, the rhenium(V) hydrido complex **IIIa′** undergoes reduction of the carbonyl via **TSIVa′** with an estimated barrier of 18.9 kcal/mol. The phosphine ligand in the intermediate **4a′** is found to weaken the Re(V)−H bond slightly (e.g., Re−H: 1.673 Å in **4a′** and 1.660 Å in **4b′**) and in turn could facilitate the carbonyl reduction via **TS4a′**.[13]

In addition to the classical reduction pathway having a four-membered-ring transition structure such as **TS4a′**, we also wonder whether it is possible to have a nonclassical one-step reduction through a six-membered-ring transition structure (i.e., **TS4c′** and **TS4a**) to generate the silyl ether product directly from the rhenium(V) hydrido intermediates **3a** and **3a′** (Figure 3). Such a nonclassical reduction is a concerted process, in which both the hydride migration and the silyl transfer occur simultaneously, analogues to those found in the bifunctional metal−ligand catalysis hydrogenation reported by Noyori's group.[30] Regrettably, the nonclassical six-membered-ring reduction processes are calculated to have higher barriers than the classical four-membered-ring pathway via **TS4a′** by more than 12.3 kcal/mol, presumably due to the low Lewis acidity of the silicon center in the silyl group.

Retro-[2 + 2] Addition. Several possible processes to generate the silyl ether (TMSOEt) product and regenerate the active catalysts are examined following the carbonyl reduction. The key results are collected in Figures 4 and 5. The pathways to afford the silyl ether product via an intramolecular nucleophilic alkoxy attack to the electrophile silicon center (retro-[2 + 2] addition) are computed to have lower barriers than the pathways via an intramolecular nucleophilic siloxy attack to the carbon center. The kinetic preference for the alkoxy attack to the silicon center can be attributed to a greater polarity of the $O^{\delta-}-Si^{\delta+}$ bond and easier access to a hypervalent silicon center in the trigonal-bipyramidal retro-addition transition structure. Interestingly, we find that the dissociative retro-[2 + 2] addition from the intermediate **5b′**, an isomer of **5a′**, via **TS5a′** is computed to be the most favorable pathway, due to both electronic and steric effects. Electronically, the bonding interaction of a metal center with an axial ligand in a trigonal-bipyramidal complex is normally weaker than the bonding interaction with an equatorial ligand.[31] In **5b′**, the metal−alkoxy bond in the axial position can be further weakened by the trans phosphine ligand.

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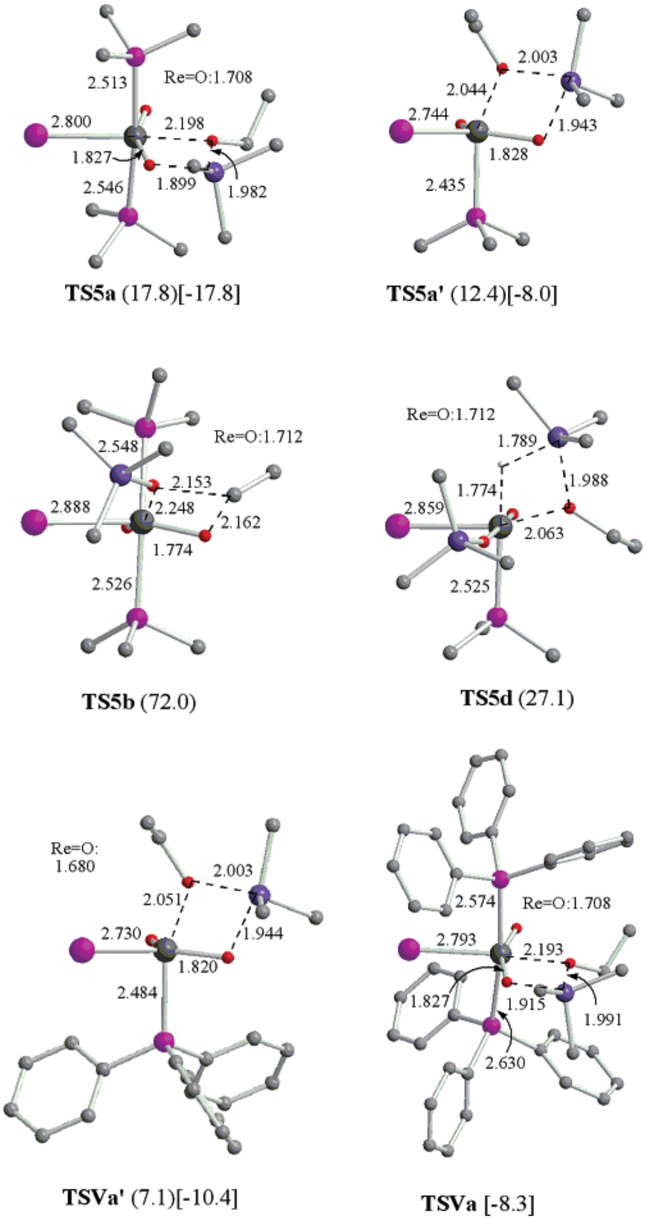
[30] (a) Noyori, R.; Hashiguchi, S. *Acc. Chem. Res.* **1997**, *30*, 97. (b) Yamakawa, M.; Ito, H.; Noyori, R. *J. Am. Chem. Soc.* **2000**, *122*, 1466. (c) Noyori, R.; Yamakawa, M.; Hashiguchi, S. *J. Org. Chem.* **2001**, *66*, 7931.

[31] (a) Rossi, A.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365. (b) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985; pp 310−338.



TS5a (17.8)[-17.8] **TS5a'** (12.4)[-8.0]

TS5b (72.0) **TS5d** (27.1)

TSVa' (7.1)[-10.4] **TSVa** [-8.3]

FIGURE 5. Calculated key transition structures to generate the silyl ether (EtOTMS) product together with the relative free energy (in parentheses) and electronic energies (in brackets) in kcal/mol. All the hydrogen atoms except the hydride ligand are omitted for clarity.

Consequently, the axial alkoxy group is a better leaving group to attack the electrophilic silicon center in **5b′**. Moreover, both the silyl and the ethyl groups in **TS5a′** can avoid steric repulsion with the phosphine ligand. As expected, the dissociative retro-[2 + 2] addition transition structure **TSVa′** is further lower in energy than the associative retro-[2 + 2] addition transition structure **TSVa** by 2.1 kcal/mol in the electronic energy when the realistic catalyst is employed in the calculations. **5a′** is comparable to **5b′** in stability. However, the retro-[2 + 2] addition transition structure (**TS5c′** in Figure 4) directly from **5a′** is 7.6 kcal/mol higher in energy than **TS5a′**. The retro-[2 + 2] addition via **TS5c′** should be further disfavored by the steric repulsion among the alkoxy, siloxy, and phosphine ligands when a realistic bulky phosphine ligand is considered.

From Figure 4, we can also see that the dissociative retro-[2 + 2] addition transition structure **TS5a′** is found to be lower in energy than those transition states related to the intermolecular silane addition to the rhenium−alkoxy and rhenium−oxo bonds (via σ-bond metathesis) by more than 14.6 kcal/mol (see **TS5c**, **TS5d**, and **TS5e** in Figure 4).[32,33] All these results indicate that the dissociative retro-[2 + 2] addition is the most favorable pathway to give the silyl ether product.

On the basis of the DFT calculations, the mechanistic pathway for the hydrosilylation reaction catalyzed by the rhenium(V)−di-oxo complexes can be summarized in Figure 6. The most favorable mechanistic pathway involves the dissociative [2 + 2] addition to give the rhenium(V) hydrido siloxy intermediate, followed by carbonyl coordination, carbonyl reduction, and rearrangement. Finally, the dissociative intramolecular nucleophilic alkoxy attack to the silicon center completes the catalytic cycle and generates the silyl ether product.

From the most favorable reaction pathway shown in Figure 6, we can see that the oxygen atom in the silyl ether product originates from the carbonyl substrate (in bold), not from the oxo ligands of the catalyst. The possibility of the oxygen exchange between acetaldehyde and rhenium−oxo catalyst was studied, and the relevant exchange processes were found to require barriers of about 35.4 kcal/mol for the associative pathway (**TS-7b**) and 29.5 kcal/mol for the dissociative pathway **TS-7b′** as shown in Scheme 4, comparable to the barriers for the most favorable silane addition pathways discussed [**TS2a** ($\Delta G^{\ddagger}$ = 36.4 kcal/mol), **TS2a′** ($\Delta G^{\ddagger}$ = 37.7 kcal/mol), and **TSIIa′** ($\Delta G^{\ddagger}$ = 32.0 kcal/mol)]. Therefore, oxygen scrambling is possibly observed in the ^{18}O isotope labeling experiments. Further experiments are needed to test this computational result.

Effects of Different Silanes and Oxo Ligands on the [2 + 2] Addition. The extraordinary hydrosilylation of carbonyls catalyzed by the high-valent rhenium(V)−di-oxo complex requires heating (60−75 °C) to give a good yield in short time.[3] To examine how different silanes affect the reaction, we employed H−SiCl$_3$ and highly strained silacyclobutane (CH$_2$)$_3$-SiMeH[34] as model substrates to examine the effects of different silanes on the dissociative [2 + 2] addition of the Si−H bond (Table 1). We found that the calculated barriers for the dissociative [2 + 2] addition are reduced from 37.7 kcal/mol for TMS-H to 33.8 kcal/mol for H−SiCl$_3$ and to 30.1 kcal/mol for silacyclobutane. Compared with the addition rate of the primary silane PhSiH$_3$, the addition rate of (CH$_2$)$_3$SiH$_2$ across a Ta═N imido bond at 35 °C was found to increase 220-fold.[8c] An increase in the Lewis acidity of the silicon center by the electron-withdrawing chlorides in the H−SiCl$_3$ substrate and by the ring strain in the silacyclobutane substrate contributes to the lower barriers for the addition of the H−Si bond. For both H−SiCl$_3$ and silacyclobutane, the silicon centers easily expand their valence structures to have a trigonal-bipyramidal geometry in the transition structure.[8c,35,36] The transition structure for the

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(32) It is interesting to find that the calculated barrier of the Si−H bond activation by the rhenium−alkoxy bond via σ-bond metathesis (**TS5d**) is about 34.9 kcal/mol, which is similar to the barriers via **TS2a** (ΔG = 36.4 kcal/mol) and **TS2a′** (ΔG = 37.7 kcal/mol). This result suggests that hydrosilylation catalyzed by the metal−alkoxy complexes is also possible.

(33) Recent reports on the C−H bond activation by manganese(III) hydroxide, ruthenium(II) hydroxide complexes, and iridium(III) methoxyl complex: (a) Goldsmith, C. R.; Cole, A. P.; Stack, T. D. P. *J. Am. Chem. Soc.* **2005**, *127*, 9904. (b) Feng, Y.; Lail, M.; Barakat, K. A.; Cundari, T. R.; Gunnoe, B.; Petersen, J. L. *J. Am. Chem. Soc.* **2005**, *127*, 14174. (c) Tenn, W. J., III; Young, K. J. H.; Bhalla, G.; Oxgaard, J.; Goddard, W. A., III; Periana, R. A. *J. Am. Chem. Soc.* **2005**, *127*, 14172.

(34) Miura, K.; Hosomi, A. In *Main Group Metals in Organic Synthesis*; Yamamoto, H., Oshima, K., Eds.; Wiley-VCH Verlag GmbH and Co.: Weinheim, 2004; pp 561−592 and references therein.

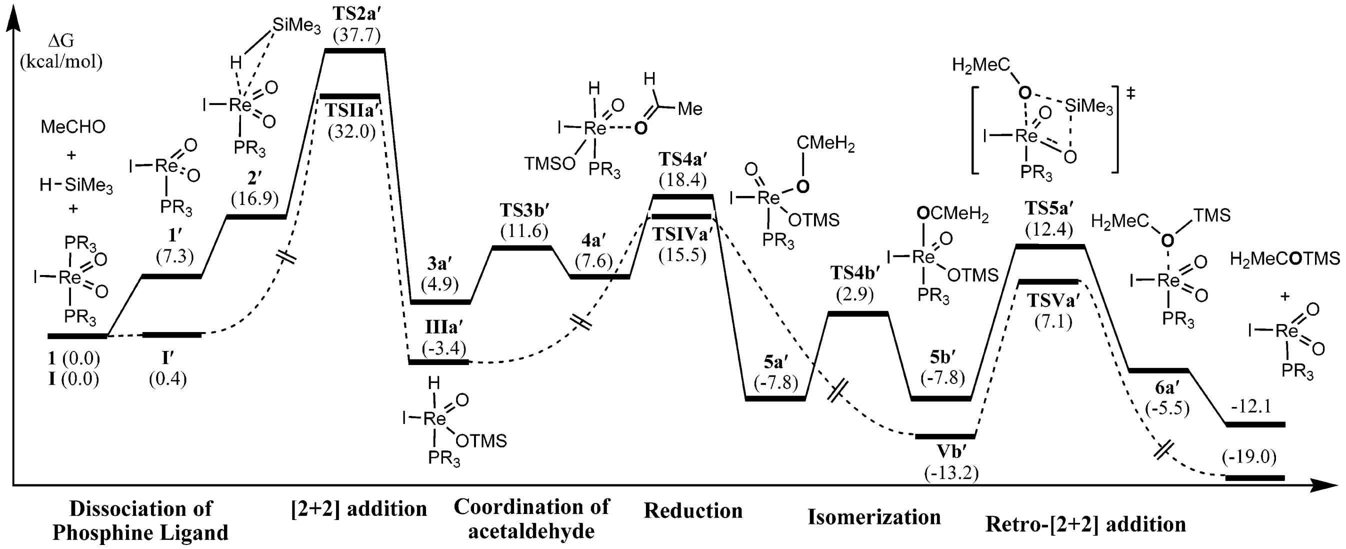
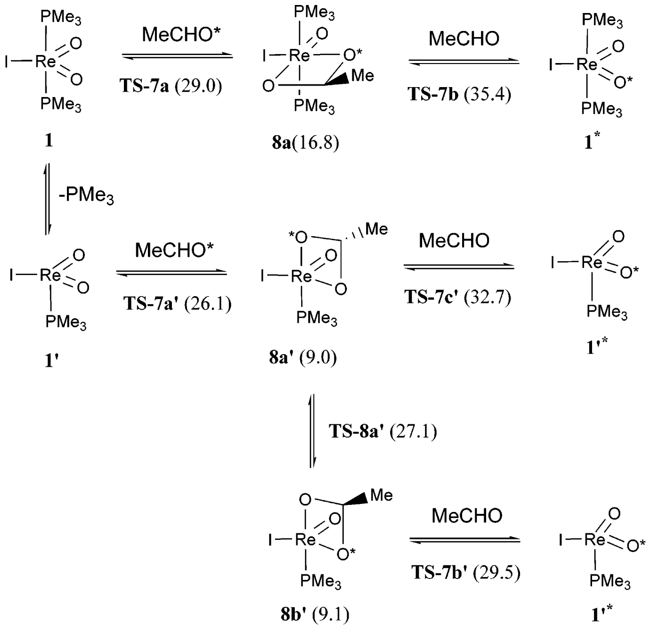


FIGURE 6. Potential energy surface for hydrosilylation of acetaldehyde via the dissociative pathway catalyzed by $ReO_2I(PMe_3)_2$ (**1**, solid lines) and $ReO_2I(PPh_3)_2$ (**I**, dashed lines). The relative free energies were obtained as in Figure 1.

SCHEME 4. Calculated Favorable Oxygen Exchange Processes between Acetaldehyde and Rhenium−Di-oxo Catalyst 1 Together with Relative Free Energies (kcal/mol)[a]



[a] The relative free energies were obtained as in Figure 1.

TABLE 1. Calculated Relative Free Energies (kcal/mol) of the Dissociative [2 + 2] Si-H Addition Transition Structures (TS) and Addition Products (P) for Various Silanes Catalyzed by Complex 1

silanes	TS	P
TMS-H	37.7	4.9
Cl_3Si-H	33.8	0.3
$(CH_2)_3SiMeH$	30.1	2.9
$(CH_2)_4SiMeH$	34.7	
$(CHCH_2)_2SiMeH$	34.4	

[2 + 2] addition of one of the three Si−Cl bonds to the rhenium−oxo bond is computed to be even lower in energy than that for the [2 + 2] addition of the Si−H bond by about 10 kcal/mol for the $H-SiCl_3$ substrate.[37] This result suggests that $HSiCl_3$ is not a good substrate. The addition barriers for the silacyclopentane $(CH_2)_4SiMeH$ and silacyclopentene $(CHCH_2)_2SiMeH$ model substrates were also calculated. We also see a modest decrease in the barriers for their dissociative [2 + 2] addition of the Si−H bonds (Table 1).

As mentioned in the Introduction, the rhenium(V)−mono-oxo complex $(dppe)ReOCl_3$ cannot catalyze the hydrosilylation reaction. The reaction condition of the hydrosilylation reaction catalyzed by the rhenium(V)−mono-oxo complex $ReOCl_3(PPh_3)_2$ used by Royo's group[9c] is more rigorous than that of the reaction catalyzed by the rhenium(V)−di-oxo complex **I**.[3] We used the coordinately saturated rhenium(V)−mono-oxo complex $ReOCl_3(PMe_3)_2$ to calculate the dissociative [2 + 2] addition of the $H-SiMe_3$ bond across the rhenium−oxo bond. The addition barrier is calculated to be about 51.6 kcal/mol, which is much higher than the barriers calculated for the rhenium−di-oxo catalysts. Scheme 5 shows the structures of the rhenium−di-oxo and mono-oxo catalysts and the corresponding addition products together with important Re−O and Si−O bond distances. On the basis of the calculated bond distances, the dominant Lewis structures (in parentheses) are derived considering the possible rhenium−oxo triple-bond and Si−O double-bond character. Comparing the calculated structure of $ReOCl_3(PMe_3)_2$ with those of $ReO_2I(PMe_3)_2$ (**1**) and $ReO_2I(PPh_3)_2$ (**I**), we found that the rhenium−oxo bond (1.66 Å) in the mono-oxo complex is much shorter than those (1.73 Å) complexes in the di-oxo complexes.[11c] Clearly, in the di-oxo complexes, the two oxo ligands compete for bonding with the metal center, weakening the two rhenium−oxo bonds. The [2 + 2] addition products derived from the mono- and di-oxo complexes are of different stabilities. The [2 + 2] addition products derived from the mono- and di-oxo catalysts are formally 14e complexes (see those structures outside the

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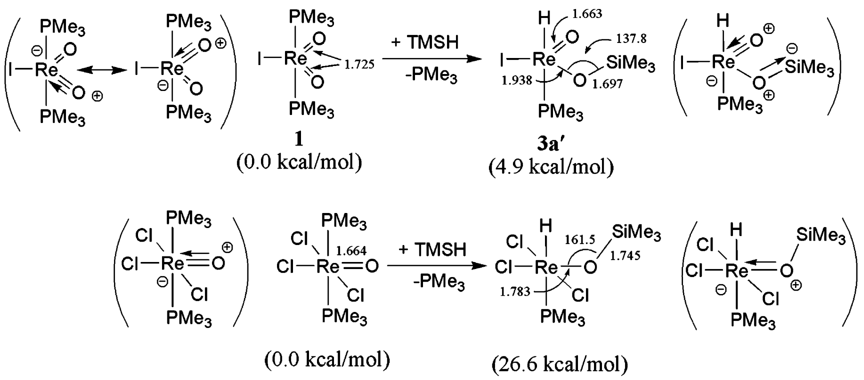
[35] The use of silacyclobutane as a substrate is also calculated to reduce the activation barrier of the retro-[2 + 2] addition (9.5 kcal/mol).

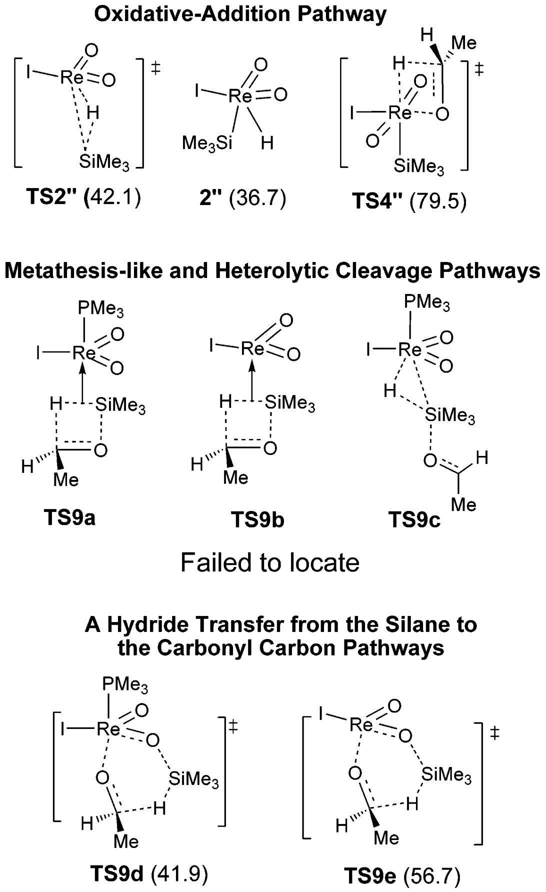
[36] Nelson, S. G.; Kim, B. K.; Peelen, T. J. *J. Am. Chem. Soc.* **2000**, *122*, 9318 and references therein.

[37] Paulo, A.; Domingos, Â.; Garcia, R.; Santos, I. *Inorg. Chem.* **2000**, *39*, 5669.

SCHEME 5



SCHEME 6. Other Si−H Bond Activation Processes (kcal/mol)



parentheses in Scheme 5). The addition product (intermediate **3a′**) derived from the di-oxo catalyst, due to the presence of the additional oxo ligand, gains stabilization through forming a rhenium−oxo triple bond (Re≡O: 1.66 Å) and a strong silicon−oxygen bond possessing silicon−oxygen double-bond character (Si−O: 1.70 Å and Si−O−Re: 138°; see the Lewis structure in parentheses for **3a′**).[38] For the addition product derived from the mono-oxo catalyst, the absence of an oxo ligand, the silicon−oxygen bond is significantly weakened (Si−O: 1.75 Å) because the siloxy oxygen forms a partial π-bond with the electron-poor rhenium center (Re−O: 1.78 Å). Consequently, weaker rhenium−oxo bonds of the rhenium(V)−di-oxo catalysts and a greater stability of the corresponding addition products render the [2 + 2] addition across the rhenium−oxo bond easier. It is envisioned that the hydrosilylation reaction catalyzed by the rhenium(V)−mono-oxo catalyst containing a bidentate phosphine ligand (dppe) is even more difficult. Dissociation of one arm of the bidentate phosphine ligand from the (dppe)-$ReOCl_3$ complex has to occur first to provide a vacant site for the silane addition. Then, the dppe ligand has to be completely dissociated from the rhenium metal center for the carbonyl insertion.

(II) Other Si−H Bond Activation Processes. We also scrutinized other possibilities of the Si−H bond activation mediated by the neutral rhenium(V)-di-oxo complex **1** (Scheme 6). First, oxidative addition of the Si−H bond of $HSiMe_3$ to the Re(V) metal center is investigated. The calculations show that the oxidative-addition intermediate **2″**[39] ($\Delta G = 36.7$ kcal/mol) and the transition structure **TS2″** ($\Delta G^{\ddagger} = 42.1$ kcal/mol) are very unstable with respect to the catalyst **1**.[40] Upon the oxidative addition of the Si−H bond to the rhenium(V) metal center, the metal center can no longer hold the two phosphine ligands. The calculations show the dissociation of the phosphine ligands to give the intermediate **2″**. When adding one PMe_3 ligand to the intermediate **2″**, the calculations give a rhenium(V)−silane complex **2′** in which the H−Si bond is not oxidatively added. Furthermore, the carbonyl reduction transition structure **TS4″** (Scheme 6) is calculated to be higher in energy than the corresponding carbonyl reduction transition structures **TS4a′** (Figure 3) and **TSIVa′** by about 52.0−61.1 kcal/mol.[40] Therefore, our computational results suggest that oxidative addition of the H−$SiMe_3$ bond to the rhenium(V)−di-oxo catalyst **1** to afford the high-valent Re(VII) hydrido silyl intermediate and the carbonyl reduction from the rhenium(VII) intermediate are energetically unfavorable.

We also examined the possibility of having the reaction via the metathesis-like transition structures (**TS9a** and **TS9b** in Scheme 6), similar to the one proposed by Abu-Omar and co-workers. In addition, a transition structure (**TS9c**) analogous to silane alcoholysis catalyzed by electrophilic transition metals is considered.[39a,41] However, we failed to locate these transition structures. Instead, two four-membered-ring carbonyl reduction transition structures, in which the metal fragments ($ReIO_2(PMe_3)$)

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[38] The Si−O bond distance and the Si−O−Re bond angle calculated for **3a′** are similar to those calculated for $EtOSiMe_3$ (Si−O: 1.68 Å and Si−O−C: 125°).

[39] The intermediate **2″** has a close hydrido-silyl contact (H--Si: 2.20 Å, Figure S9). (a) Kubas, G. J. *Metal Dihydrogen and σ-Bond Complexes*; Kluwer Academic/Plenum Publishers: New York, 2001. (b) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175. (c) Nikonov, G. I. *J. Organomet. Chem.* **2001**, *635*, 24. (d) Lin, Z. *Chem. Soc. Rev.* **2002**, *31*, 239.

[40] The relative free energies of **2″**, **TS2″**, and **TS4″** with respect to the catalyst **I** are 24.8, 30.1, and 67.5 kcal/mol, respectively.

and $ReIO_2$) have no interaction with silane (TMSH) and acetaldehyde, were located. These four-membered-ring uncatalyzed carbonyl reduction transition structures are extremely high in energy ($\Delta G^{\ddagger} = 69.0-96.1$ kcal/mol). In these transition structures, the silicon center is forced to adopt a six-coordination geometry, when there are no electronegative substituents present at the silicon center prior to the nucleophilic attack by the aldehyde oxygen, in the proposed metathesis-like transition structures. Thus, we failed to locate the proposed metathesis-like transition structures.

We also investigated the feasibility of another mechanistic pathway:[42] a hydride transfer from the silane substrate to the carbon center of a coordinated carbonyl via a six-membered-ring transition structure (**TS9d** or **TS9e** in Scheme 6) proceeds to give a rhenium(V) alkoxy intermediate followed by a silyl migration to give the product, without the intervention of the rhenium(V) hydrido intermediates (e.g., **3a′** in Figure 1). However, **TS9d** and **TS9e** are found to be higher in energy than the two most favorable [2 + 2] addition transition structures **TS2a** and **TS2a′** by more than 4.2 kcal/mol. The results are understandable because the acidity of the silicon center and the basicity of the hydride in the TMSH substrate are poor.

Conclusion

The mechanism of the $ReO_2I(PR_3)_2$-catalyzed (R = Me, Ph) hydrosilylation of carbonyl compounds has been investigated by DFT calculations. The computational results support a mechanistic pathway involving a dissociative [2 + 2] addition of the Si−H bond across one of the two rhenium(V)−oxo bonds giving a Re(V) hydrido intermediate, followed by coordination of carbonyl, reduction of carbonyl, rearrangement, and finally dissociative intramolecular nucleophilic attack of the alkoxy group on the silicon center. Our calculations also indicate that the rhenium(V)−di-oxo catalysts $ReO_2I(PR_3)_2$ have advantages over the $ReOCl_3(PMe_3)_2$ and (dppe)$ReOCl_3$ catalysts in the [2 + 2] addition of the Si−H bond across the metal−oxo bond in that the two oxo ligands of the rhenium−di-oxo catalysts compete for bonding with the metal center, giving rise to weaker rhenium−oxo bonds for the Si−H addition. In addition, the remaining one oxo ligand plays a stabilizing role in the Re(V) hydrido intermediate. Reduction of the carbonyl from the rhenium(V) hydrido intermediate is aided by the strong trans-influence phosphine ligand due to its ability to weaken the metal−hydrido bond and facilitate reduction of the carbonyl.

Our calculations do not support a concerted metathesis-like pathway for the neutral $ReO_2I(PR_3)_2$-catalyzed hydrosilylation of carbonyls, which involves a direct addition of a coordinated Si−H bond across a carbonyl double-bond unit. The metathesis-like pathway proposed by Abu-Omar and co-workers is based on their experiments with the cationic $[ReO(hoz)_2]^+$ complex. How the cationic $[ReO(hoz)_2]^+$ complex catalyzes the hydrosilylation reactions requires further experimental and theoretical studies. We will continue our theoretical calculations based on the cationic complex and hope to see if there is new mechanistic insight that can be derived from the $[ReO(hoz)_2]^+$-catalyzed reactions.

Acknowledgment. We thank the Research Grants Council of Hong Kong, the National Natural Science Foundation of China for financial support of the research, and the reviewers for their invaluable suggestions and comments.

Supporting Information Available: All calculated structures collected in Figures S1−S9 accompanied by the corresponding Cartesian coordinates and complete citation of ref 20 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(41) Fe and Ir cases: (a) Luo, X.; Crabtree, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 2527. (b) Scharrer, E.; Chang, S.; Brookhart, M. *Organometallics* **1995**, *14*, 5686. (c) Chang, S.; Scharrer, E.; Brookhart, M. *J. Mol. Catal.* **1998**, *130*, 107. (d) Bühl, M.; Mauschick, F. T. *Organometallics* **2003**, *22*, 1422.

(42) One of the referees suggested this mechanistic pathway.