Practical Procedures for Hydrosilylation of Ketones and Silane-induced Ring-opening Polymerization of Cyclic Ethers by Prior Activation of the Cluster Catalyst by Hydrosilanes : Improved Synthetic Procedures and Mechanistic Implication on the Catalytically Active Species

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Practical Procedures for Hydrosilylation of Ketones and Silane-induced Ring-opening Polymerization of Cyclic Ethers by Prior Activation of the Cluster Catalyst by Hydrosilanes: Improved Synthetic Procedures and Mechanistic Implication on the Catalytically Active Species

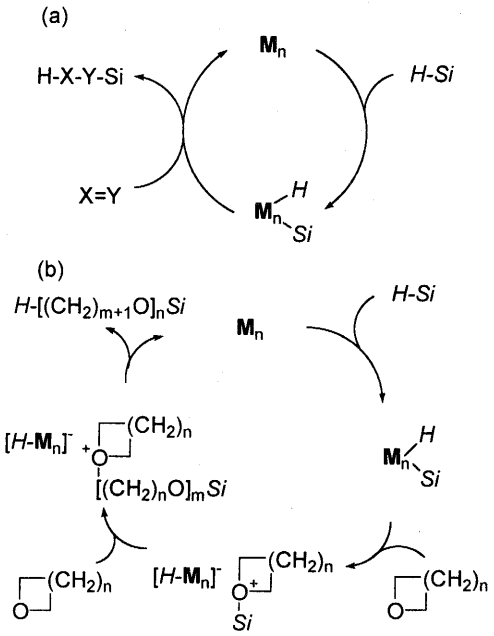
Kouki Matsubara, Takafumi Iura,[a] Tomoyuki Maki,[a] Jun-ichi Terasawa,[a] and Hideo Nagashima

Pre-activation of ($\mu_2,\eta^2:\eta^3:\eta^5$-acenaphthylene)$Ru_3(CO)_7$ (**1**) by hydrosilanes in a small amount of dioxane provides novel convenient and useful procedures for hydrosilylation of carbonyl compounds and silane-induced ring-opening polymerization of cyclic ethers and a cyclic siloxane. The initial step of the catalytic cycle was investigated by NMR detection of products formed by the oxidative addition of hydrosilanes to **1**. A possibility for the involvement of cluster species in the catalytic cycle is discussed.

Introduction

Hydrosilylation of unsaturated molecules is generally catalyzed by a variety of transition metal complexes, being useful for synthesis of various organosilicon compounds.[1)] As the initial step of the catalytic reaction, the oxidative addition of a H-Si bond to a metallic species ML_n (M = metal, L = ligand) leads to insertion of unsaturated molecules X=Y between the H-Si bond, which is followed by a reductive elimination of H-X-Y-SiR_3 to complete the catalytic cycle as shown in Scheme 1.[1)] Many mononuclear transition metal complexes such as $RhCl(PPh_3)_3$[2a)] and olefin complexes of platinum[2b)] are known to be active towards the catalytic hydrosilylation, and elucidation of the mechanism has been actively investigated both experimentally and theoretically.[3)] The hydrosilylation catalyzed by transition metal clusters such as $Co_2(CO)_8$,[4)] $Rh_4(CO)_{12}$,[5)] and $Ru_3(CO)_{12}$,[6)] recently investigated showed high reactivity and/or selectivity towards the hydrosilylation; however, the active species in these cluster-catalyzed reactions is not clear at present.

We have recently reported that a triruthenium cluster bearing acenaphthylene in a face-capping mode, ($\mu_2,\eta^2:\eta^3:\eta^5$-acenaphthylene)$Ru_3(CO)_7$ (**1**),[7)] exhibits high reactivity towards hydrosilylation of ketones and aldehydes.[8)] Of particular interest in the catalysis of this cluster is that **1** catalyzes reduction of acetals and cyclic ethers, which is hardly accomplished by conventional hydrosilylation catalysts. Furthermore, in the reaction of organosilanes with excess amounts of strained cyclic ethers, silane-induced ring-opening polymerization takes place to form polyalkylene oxides bearing alkyl and siloxy groups at their termini. The results are summarized in Scheme 2.[8-10)] Although we usually carried out these catalytic reactions in a sealed tube, the reactions in a sealed tube are not convenient for a



Scheme 1. (a) A general catalytic cycle for hydrosilylation of unsaturated molecules (X=Y); M = transition metals. (b) A proposed catalytic cycle for silane-induced ring opening polymerization of cyclic ethers

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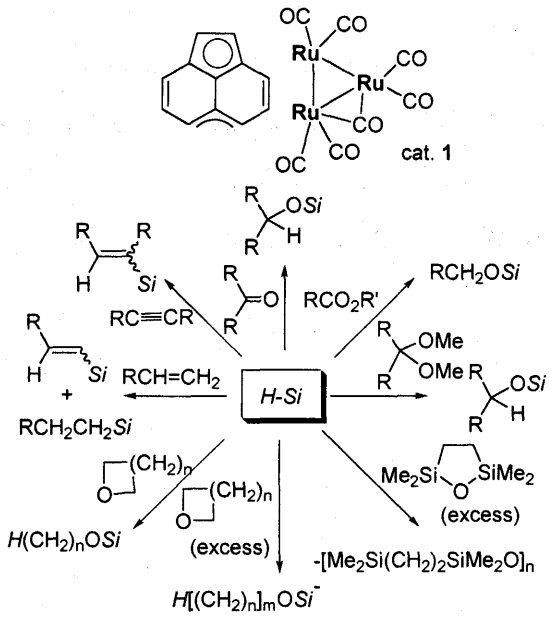
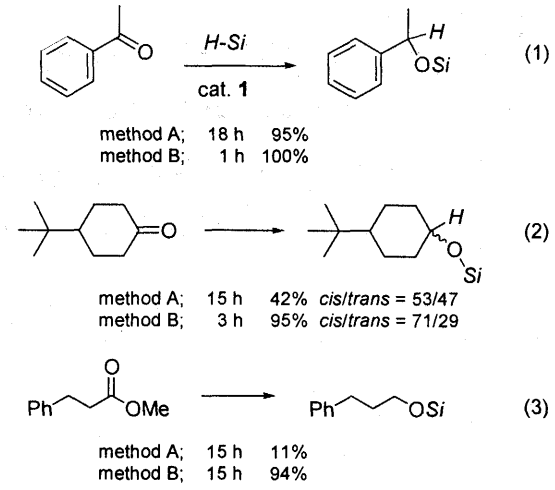


Scheme 2. Catalytic hydrosilylation of unsaturated molecules, hydrosilane reduction of acetals and cyclic ethers, and silane-induced ring opening polymerization of cyclic ethers and a cyclic siloxane by **1**.

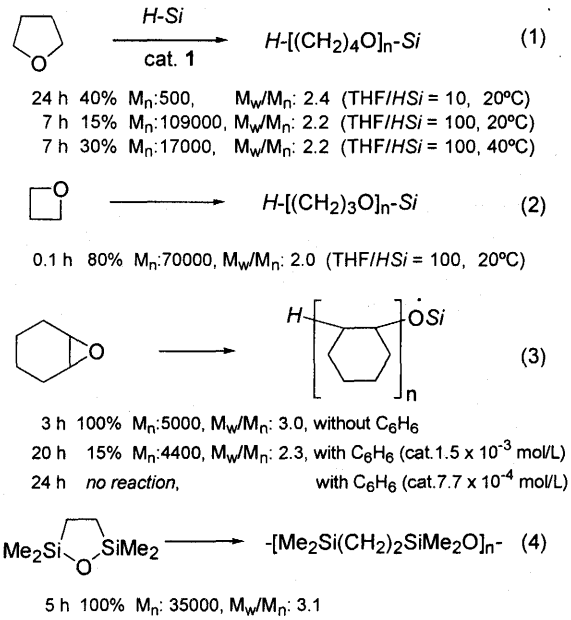
synthesis of large amounts of the products. Therefore, improvement of the reaction procedure, in which the reactions proceed under an inert gas atmosphere in a flask, is desirable. In this paper, we wish to report that activation of the catalyst by hydrosilanes prior to the addition of ketones or cyclic ethers in dioxane provides convenient procedures for these reactions, necessitating only short reaction times. Furthermore, NMR studies to detect catalytic species provide results suggesting the involvement of multinuclear species in the catalytic cycle.

Results and Discussion

1. Improved procedures for hydrosilylation by prior activation of the catalyst. As reported earlier, hydrosilylation of ketones with organosilanes was carried out in benzene in a sealed tube.[8] Although the reaction can also be performed under a nitrogen atmosphere, only the reactions with a particular organosilane, $HMe_2Si(CH_2)_2SiMe_2H$,[11] were quick enough to produce the corresponding silyl ethers within a few hours. The reactions with monofunctional organosilanes such as $PhMe_2SiH$ and Et_3SiH required longer reaction times. In the silane-induced ring-opening polymerization of cyclic ethers, it is necessary to carry out the reaction in a tube sealed in vacuum, and no reaction takes place under a nitrogen atmosphere. The reason why the reaction is accelerated in vacuum may be attributed to the fact that dissociation of a CO ligand from **1** to generate a vacant site for the oxidative addition of hydrosilanes could be facilitated by keeping the reaction medium in vacuum (10^{-1} Pa). In other words, it is important to generate



Scheme 3. Hydrosilylation of carbonyl compounds. Method A (conventional method); cat. **1** (1 mol %), in C_6H_6 at 20°C. Method B (improved method); cat. **1** (1 mol %), in C_6H_6 at 20°C; prior activation of **1** with $HSiMe_2Ph$ in dioxane was carried out for 0.5 h.



Scheme 4. Silane-induced polymeization of cyclic ethers and a siloxane. Standard conditions: cat. **1** (0.01 ~ 0.1 mol %), at 20°C, THF/*HSi* ratio: 10/1; prior activation of **1** with $HSiMe_2Ph$ in dioxane was carried out for 0.5 h.

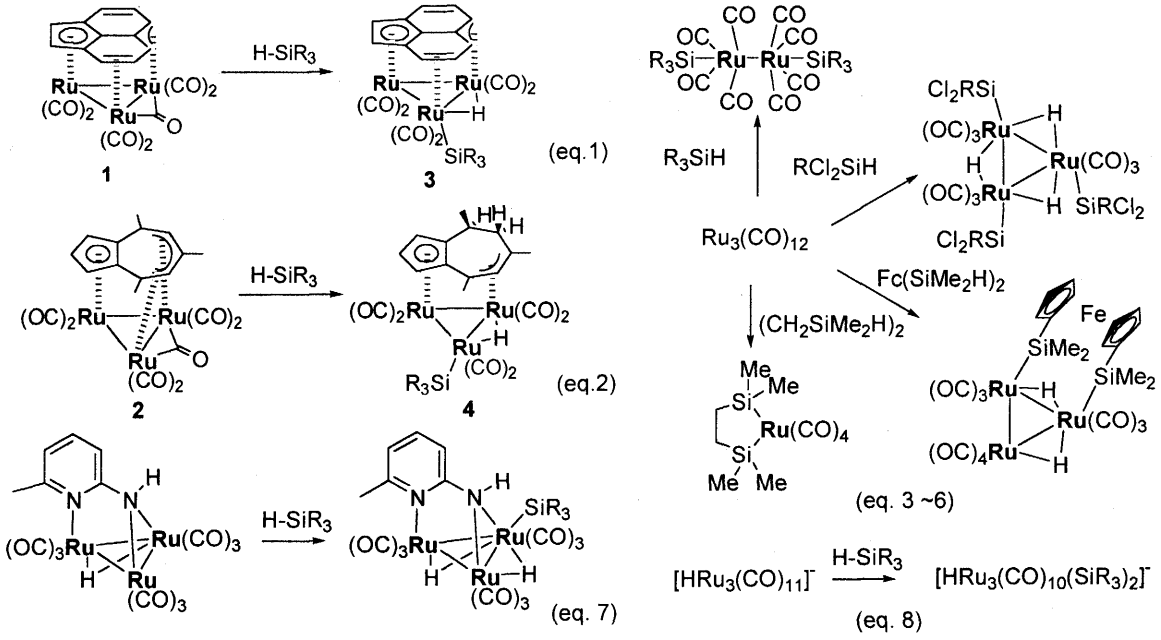
active species, which undergo facile oxidative addition of hydrosilanes to **1**.

We discovered that prior activation of the catalyst by organosilanes facilitated the reaction; this provided a method for the rapid hydrosilylation of carbonyl compounds with monofunctional organosilanes within a few hours (Scheme 3) and for silane-induced polymerization of cyclic ethers under a nitrogen atmosphere (Scheme 4). A typical example for the hydrosilylation of ketones is as follows: the catalyst **1** was dissolved in dioxane, and treated with $PhMe_2SiH$ for 0.5 h. Then, acetophenone and benzene was introduced. The reaction

was over within an hour to afford $(PhMe_2SiO)CH(CH_3)$-Ph in good yield (Scheme 3, eq. 1). In the conventional method, a mixture of acetophenone, $PhMe_2SiH$, and **1** reacted in a solution of benzene. Reaction time of over 18 h was required to consume all of the starting material. It is important in considering the utility of **1** as a hydrosilylation catalyst that $Ru_3(CO)_{12}$, which is inactive under the conditions of the "conven-tional method", does not catalyze the hydrosilylation of acetophenone even with the preactivation method in dioxane. Hydrosilylation of 4-*t*-butylcyclohexanone with a catalytic amount of **1** pretreated with $PhMe_2SiH$ also occurred more quickly than with the conventional procedure to form the corresponding silyl ether (*cis/trans* ratio = 71/29) in good yield (Scheme 3, eq 2). Interestingly, the hydrosilylation of an ester with $PhMe_2SiH$, which can be accomplished only with great difficulty with transition metal catalysts, proceeds with this pre-activated catalyst more easily than with the conventional method (method A).[9] A representative example is given in Scheme 3, eq 3.

In a similar fashion, **1** pretreated with $PhMe_2SiH$ in dioxane induces the polymerization of THF under a nitrogen atmosphere. As shown in Scheme 4, eq. 1, conversion of THF reached 40% after 24 h at room temperature to give the polyTHF with M_n = 500, M_w / M_n = 2.4 when reacting a 10 : 1 mixture of THF and $PhMe_2SiH$ in the presence of a catalytic amount of **1**. In changing the THF/$HSiR_3$ ratio from 10 / 1 to 100 / 1, polyTHF with higher molecular weight (M_n = 109000, M_w / M_n = 2.2) was formed. Similar reaction at 40°C yielded a polymer with a lower molecular weight (M_n = 17000, M_w / M_n = 2). Similarly, the new method offered a convenient way to polymerize oxetane and cyclohexene oxide; addition of these monomers to preactivated **1** in dioxane resulted in the ring-opening polymerization of these monomers at room temperature (Scheme 4, eq. 2 and 3). The polymerization of cyclohexene oxide took place to form polycyclohexene oxide even in a dilute solution of benzene (cat.: 1.5×10^{-3} mol/L), though the conversion of the monomer was low. The preactivated **1** is also useful to polymerize a cyclic siloxane as shown in Scheme 4, eq. 4.[10] Thus, all of the results suggest that the new procedure using **1** preactivated with hydrosilanes is useful for hydrosilylation of carbonyl compounds and the silane-induced ring-opening polymerization of cyclic ethers and cyclic siloxanes.

*2. NMR observations of the oxidative adduct of **1** in benzene and dioxane.* As described above, the initial step of the catalytic hydrosilylation is believed to be the oxidative addition of a H-Si bond in hydrosilanes to metallic species.[3] In the hydrosilylation reactions catalyzed by cluster compounds, it is of great importance to know whether the reaction involves an oxidative adduct having an intact multinuclear framework as the catalytically active species or a mono- or dinuclear adduct as a result of cluster fragmentation. We have already found that oxidative addition of $PhMe_2SiH$ to **1** or to a triruthenium cluster bearing 4,6,8-trimethylazulene in the facial capping mode, (μ_3-4,6,8-trimethylazulene)$Ru_3(CO)_7$ (**2**),[12] proceeds in keeping the triruthenium cluster framework to form the corresponding (π-ligand)$Ru_3(H)(SiMe_2Ph)$-$(CO)_6$, **3**[8] and **4**,[13] respectively, as shown in Scheme 5, eq. 1 and 2. Interestingly, it was proven experimentally that **3** was inactive towards the catalytic hydrosilylation of ketones,[8] whereas **4** catalyzed the reaction more quickly than **2**.[13] In both of the cases, unstable species having Ru-H moieties were detected by ^1H NMR at higher than –13 ppm, at which protons assignable to bridging



Scheme 5.

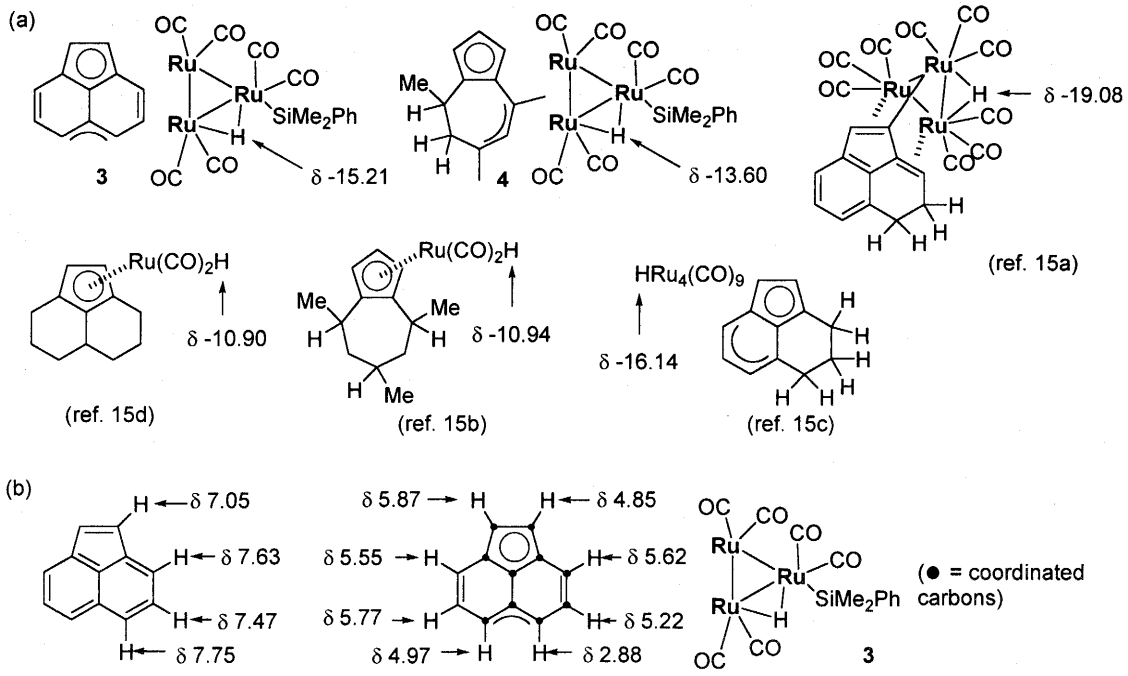


Fig. 1 (a) Typical ^{1}H resonances of Ru-H of monohydride ruthenium carbonyl clusters. (b) Comparison of the NMR spectrum of uncoordinated acenaphthylene with that of **3**.

hydrides are often seen (vide infra). Thus, regardless of whether the isolated complexes **3** and **4** are active or inactive towards the catalytic hydrosilylation, the active species for the hydrosilylation is likely to have a multinuclear framework.

Isolation of products having Ru-Si bonds was investigated by several groups in the reactions of several hydrosilanes with $Ru_3(CO)_{12}$ (Scheme 5, eq. 3-6).[14] It is important to note that the reaction was accompanied by cluster fragmentation, and their oxidative addition to an intact triruthenium framework was only accomplished by using special silanes as shown in eq. 5 and 6. Triruthenium silyl complexes were synthesized in the reactions of trialkylsilanes with triruthenium carbonyl clusters bearing a bridging aminopyridine ligand (Scheme 5, eq. 7) or a bridging hydride (Scheme 5, eq. 8). These results as well as our findings described above, i.e. successful preparation of **3** and **4**, suggest the importance of bridging ligand in the activation of hydrosilanes with triruthenium clusters, when cluster fragmentation is not involved.

In this context, we carried out the ^{1}H NMR detection of the catalytically active species formed by treatment of **1** with $PhMe_2SiH$ in dioxane under similar reaction conditions to those of the preactivation method described in this paper. In this NMR study, we were interested in two points that first is the chemical shift of the Ru-H species, which is a good indication of whether the observed metallic species is mononuclear or multinuclear. Corey and Braddrock-Wilking reported extensive reviews on the spectroscopic properties of many transition metal complexes containing metal-silicon bonds.[14] Monoruthenium carbonyl complexes having H-Ru-Si moieties reportedly show the NMR signals of the hydrides at -1 ~ -12 ppm, whereas the bridging hydrides of multiruthenium compounds resonate at -9 ~ -17 ppm. We have prepared a series of triruthenium carbonyl clusters bearing conjugate π-ligands as illustrated in Fig. 1. The Ru-H signals of monoruthenium hydride complexes, (η^5-3,4,5,6,7,8,12-heptahydroacenaphthylene)Ru(H)$(CO)_2$[15d] and (η^5-4,5,6,7,8-pentahydro-4,6,8-trimethylazulene)Ru(H)$(CO)_2$,[15b] appear at -10 ~ -11 ppm. In sharp contrast, resonances due to the bridging Ru-H moiety in **3**,[8] **4**,[13] (μ_3,η^1:η^2:η^2-dihydroacenaphthylene)Ru_3(H)$(CO)_9$,[15a] and (μ_3-trihydroacenaphthylene)Ru_4(H)$(CO)_9$[15c] were observed at a higher magnetic field than –13 ppm. The second point is the chemical shift of the coordinated π-ligand. As shown in Fig 1 (b) as selected examples, typical upfield shifts in the ^{1}H NMR resonance due to protons close to the metal centers were observed in all of the compounds we have prepared.

The ruthenium cluster **1** was dissolved in dioxane-d_8, and $PhMe_2SiH$ (5.0 eq. to **1**) was added to this solution. Soon after the addition, several peaks at –9 to –23 ppm assigned to Ru-H moieties appeared in ^{1}H NMR. Among them, a peak at –18.3 ppm had relatively high intensity. For a prolonged reaction time applied, intensity of the peak at –18.3 ppm was reduced, and instead, a peak at –13.9 ppm grew in size. After 12 h, this peak at –13.9 ppm became the major peak. At this stage, ^{1}H and ^{1}H-^{1}H COSY spectra were measured to

assign the peaks at 2 ~ 8 ppm due to the π-ligand. Despite some overlap of the signals, we confirmed the existence of at least four protons appearing a region of the CH protons of the acenaphthylene ligand, and at least four protons assignable to the hydrogenated CH_2 moieties on the π-ligand as seen in the analogous compound, **4**.[9]

These two observations are similar to our previous results. Firstly, a peak at −18 ppm was also seen in a transient species in the ^{1}H NMR spectrum of a mixture of **1** and $PhMe_2SiH$ (25 eq.) in C_6D_6.[8] This Ru-H signal in C_6D_6 was observed as the major peak in the ^{1}H NMR, and further analysis of the ^{1}H and ^{1}H-^{1}H COSY spectra provides clues for the assignment of the π-ligand; six protons showed typical higher field shift due to the coordination of the carbons bonding to these protons.

The second point is the spectroscopic analogy of the Ru-H species appearing its Ru-H signal at −14 ppm to that of the isolable triruthenium cluster **4**, which affords the Ru-H peak at −13.6 ppm.[13] The compound **4** was formed by the reaction of **2** with HMe_2SiPh at 40°C. The oxidative addition of HMe_2SiPh to **4** proceeded in keeping the triruthenium cluster, being accompanied by hydrogenation of one carbon-carbon double bond of the azulene ligand. The result that the triruthenium hydride cluster has a partially hydrogenated azulene ligand is similar to a possible structure of the transient species in the reaction of **1** with $PhMe_2SiH$ in dioxane-d_8, which showed the Ru-H signal at −13.9 ppm. In other words, the species showing the Ru-H signal at −13.9 ppm can be similar in having a partially hydrogenated conjugated π-ligand.

An important consequence of these ^{1}H NMR observations is that preactivation of **1** with $PhMe_2SiH$ in dioxane could lead to generation of a triruthenium species active for the hydrosilylation of carbonyl compounds or silane-induced ring-opening polymerization of cyclic ethers. The active species should be derived from the oxidative addition of $PhMe_2SiH$ to **1**. Involvement of the species in the catalytic cycle was proven experimentally by the addition of acetophenone to the solution showing the Ru-H signal at −13.9 ppm, which resulted in rapid hydrosilylation to form the corresponding silyl ether in good yields. Although further investigation including the structural determination of a small amount of other detected reaction intermediates, which may be active towards the activation of organosilanes, should be undertaken for elucidation of net catalytic intermediates, the present results are important in suggesting a possibility that the hydrosilylation or silane-induced ring-opening polymerization involves cluster species as the catalytic inter-mediates.

Conclusion

As described in this paper, preactivation of **1** with excess amounts of organosilanes opens a convenient way for the hydrosilylation of carbonyl compounds and the silane-induced ring-opening polymerization of cyclic ethers and cyclic siloxanes. This brings about a convenient access to silyl ethers or silylated polymers. Furthermore, ^{1}H NMR detection of the intermediate strongly suggests the involvement of a metal cluster as a catalytic intermediate; this contributes to the investigation on cluster catalysis. These two new findings not only contribute to emphasizing the utility of **1** as a unique catalyst for these reactions involving the activation of Si-H bonds in hydrosilanes but also provide novel supporting evidence for the involvement of cluster species in catalysis. Organometallic clusters should be important as the next generation of molecular catalysts, in which the nature of the catalyst can be altered by changing its nuclearity, metal, and auxiliary ligands. As described in this paper, **1** is a more active catalyst than $Ru_3(CO)_{12}$; this indicates the importance of the acenaphthylene ligand as a conjugate π-ligand for the triruthenium species. We consider that the high reactivity of **1** should be attributed to facile ring-slippage (hapticity change) of the conjugate π-ligand in the triruthenium moiety, which produce a coordination site for the hydrosilane. That may be facilitated in a coordinating solvent, i.e. dioxane. Further investigation to explore the catalysis of **1** and other multiruthenium clusters bearing conjugate π-electrons from both synthetic and mechanistic points of view is currently underway.

Experimental section

General. All of the manipulations were carried out in a nitrogen or argon atmosphere. THF, benzene, toluene, oxetane, cyclohexane, and benzene-d_6 were distilled from benzophenone ketyl and stored under an argon atmosphere. Dioxane was dried with CaH_2 and distilled before use. $HSiMe_2Ph$, $Me_2SiH(CH_2)_2HSiMe_2$, acetophenone, and 2,2,5,5-tetramethyldisila-1-oxacyclopentane were distilled just before use. Other reagents were used as received. ^{1}H and ^{13}C NMR spectra were taken with a JEOL Lambda 400 or 600 spectrometer. Chemical shifts were recorded in ppm from the internal standard (^{1}H, ^{13}C: solvents). Size exclusion chromatography (SEC) analysis of the polyethers was carried out using a JASCO HPLC system in THF using a standard sample of polystyrene. The ruthenium complexes **1**, **2**, **3**, and **4** were prepared according to published methods.[8,12,13]

Typical procedures for hydrosilylation of carbonyl compounds. *Method A*: A representative example of the conventional method of hydrosilylation of ketones[8] is given in the following: acetophenone (120.2 mg, 1.00 mmol), $HSiMe_2Ph$ (150.0 mg, 1.10 mmol), and **1** (6.6 mg, 0.01 mmol, 1 mol %) were added to a 20 mL two necked round-bottom flask and were dissolved in benzene (1.9 mL). The mixture was stirred at room temperature (20°C) for 18 h. The solvent was removed *in vacuo*.

Bulb-to-bulb distillation of the residue gave (PhMeCHO)$SiMe_2Ph$ (243 mg, 95%). *Method B*: An example of the improved method is given in the following: $HSiMe_2Ph$ (150.0 mg, 1.10 mmol) and **1** (6.6 mg, 0.01 mmol, 1 mol %) were added to a 20 mL two necked round-bottom flask and they were dissolved in a small amount of dioxane (0.085 mL). The mixture was stirred at room temperature for 0.5 h. Then, benzene (1.8 mL) and acetophenone (120.2 mg, 1.00 mmol) were added. After the mixture was stirred for 1 h, the solvent was removed *in vacuo*. Bulb-to-bulb distillation of the residue afforded (PhMeCHO)$SiMe_2Ph$ (255 mg, 100%).

Typical procedure for silane-induced ring-opening polymerization of cyclic ethers or a cyclic siloxane. In a typical example, $HSiMe_2Ph$ (105 mg, 0.770 mmol) and **1** (0.50 mg, 7.7×10^{-4} mmol, 0.1 mol %) were added to a 20 mL two necked round-bottom flask filled with dinitrogen and they were dissolved in a small amount of dioxane (0.066 mL). The mixture was stirred at room temperature for 0.5 h. Then, THF (55.5 mg, 0.770 mmol) was added, and the mixture was stirred for 24 h. The conversion of THF (40%) was determined on the basis of ^1H NMR analysis of the crude reaction mixture using an internal standard (dioxane). Removal of the dioxane and $HSiMe_2Ph$ gave polyTHF (90 mg, 33%, M_n = 500, M_w/M_n = 2.4).

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