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Supported Catalysts

Synthesis, Characterization, and Catalytic Activity of a Well-Defined Rhodium Siloxide Complex Immobilized on Silica**

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Molecular compounds incorporating a TM−O−Si group (TM = transition metal) are of great interest, particularly as models of metal complexes immobilized on silica and silicate surfaces.[1–3] Since 1982, more than 100 new TM siloxide complexes have been synthesized and characterized by X-ray and spectroscopic methods to determine their molecular structure.[1a]

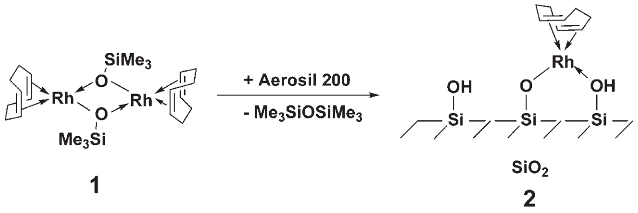
The properties of siloxide as ancillary ligand in the system TM−O−SiR$_3$ can be exploited in molecular catalysis, particularly in such reactions as polymerization[4] olefin metathesis,[5] epoxidation of alkenes[6] and dehydrogenative coupling of silanes.[7] In addition, in the last few years the synthesis and characterization of well-defined surface siloxy complexes [(≡SiO)Re(*t*Bu)(=CH*t*Bu)CH$_2$*t*Bu)][8] and [(≡SiO)Mo(=NAr)(=CH*t*Bu)(CH$_2$*t*Bu)][9] as highly active heterogeneous olefin metathesis catalysts have been published.

In contrast to the abundance of data published on the early TM siloxides, information on late TM siloxide complexes is scarce.[1a] During the last decade we have developed a synthetic method to obtain and characterize a variety of molecular rhodium and iridium siloxide complexes that are efficient catalysts for hydrosilylation,[10] silylative coupling,[11] and other reactions of silicon compounds.[12] Tilley et al. recently reported the synthesis of well-defined tri-*tert*-butoxysiloxy iron(III) complex,[13] as well as analogous molecular siloxide complexes of Co[14a] and Cu,[14b] which act as precursors for their grafting onto silica and use as catalysts for oxidation of alkanes, alkenes, and arenes by hydrogen peroxide.[13]

The groups of Basset and Santini[15] and Schwartz[16] reported a strategy for forming surface rhodium complexes by reaction of organometallic precursors (e.g., [Rh(η^3-C$_3$H$_5$)$_3$][16a,c] and [Rh(CO)(Me)(PMe$_3$)$_2$][16b]) with silica. Immobilized complexes have been characterized by IR, UV, and ^{31}P MAS-NMR spectroscopy.

We report herein the synthesis and characterization of the well-defined rhodium siloxide complex obtained directly by reaction of molecular rhodium siloxide precursor [{Rh(μ-OSiMe$_3$)(cod)}$_2$] (**1**, cod = 1,5-cyclooctadiene)[17] with aerosil silica.

When a mixture of SiO$_2$ (aerosil 200 dried at 350 °C, 1.27 mmol SiOH per gram, determined by the hydrothermal method[18]) and **1** was stirred in pentane (benzene) for 24 h at room temperature, surface organometallic complex **2** (**2a**) was formed (see Scheme 1 and the Supporting Information).



Scheme 1. Synthesis of surface siloxide rhodium complex.

The orange solid thus prepared contained 0.217 mmol Rh per gram of solid **2** (0.410 mmol Rh per gram of solid **2a**), which is in agreement with consumption of the surface silanol groups (35 % **2** and 66 % **2a**). Moreover, compound **2a** contained on average 8.9 C per grafted Rh (as obtained from elemental analysis), consistent with the theoretically proposed structure, for which 8 C/Rh was predicted.

Rhodium siloxide complexes, in particular **1**, appeared to be much more effective then the respective chloro complex (as well as the commercially available Pt Karstedt catalyst) in hydrosilylation of a variety of olefins such as 1-hexene,[19] vinyl silanes,[20] and allyl alkyl ethers[21] (for a recent review, see reference [10]). Therefore, the well-defined silica-supported heterogeneous catalysts **2** and **2a** were tested in selected hydrosilylation reactions of 1-alkenes and vinylsiloxanes by heptamethylhydrotrisiloxane as a model of (poly)hydrosiloxanes.

The results (Table 1) show the high effectiveness of these catalysts, which moreover were subjected to recycling tests. After completion of each test cycle, the post-reaction mixture was decanted and the catalyst left on the bottom of the reaction vessel was used in subsequent reactions. In the majority of reactions, the catalytic activity of the silica-

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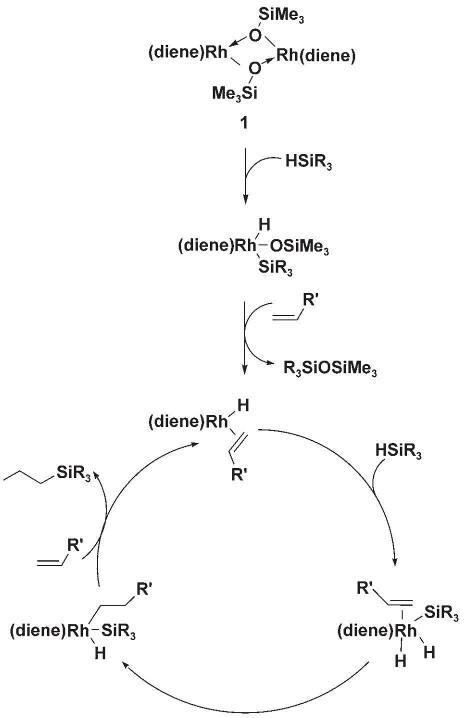
Table 1: Hydrosilylation of 1-alkenes and vinyl siloxane by heptamethylhydrotrisiloxane.[a]

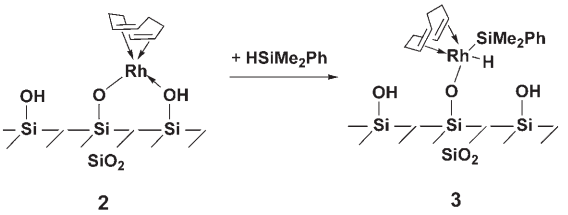
$$(Me_3SiO)_2MeSi{-}H + H_2C{=}CHR \longrightarrow (Me_3SiO)_2MeSi{-}CH_2CH_2R$$

R	Cat.	Cycles	Yield[b] [%] (TOF[c] [min^{-1}])
$(CH_2)_4CH_3$	**2**	1	97 (162)
		5	98
		10	95
		15	87
$(CH_2)_{13}CH_3$	**2a**	1	97 (162)
		5	98
		10	95
		15	88
$CH_2C_6H_3$-3,4-OMe	**2a**	1	90 (150)
		5	97
		10	60
$SiMe(OSiMe_3)_2$	**2**	1	88 (160)
		5	90
		10	86
		15	83
		20	91

[a] $[SiH]/[H_2C{=}CHR]/[Cat.] = 1:1:10^{-4}$, $T = 100$ °C, $t = 1$ h. [b] Yields were determined by GC analysis. [c] Initial turnover frequency (TOF) measured after 1 h of reaction and expressed as moles of heptamethylhydrotrisiloxane per mole of Rh per minute.



Scheme 2. Mechanism of hydrosilylation catalyzed by soluble binuclear rhodium siloxide complex.



Scheme 3. Oxidative addition of silicon hydride to surface rhodium siloxide complex.

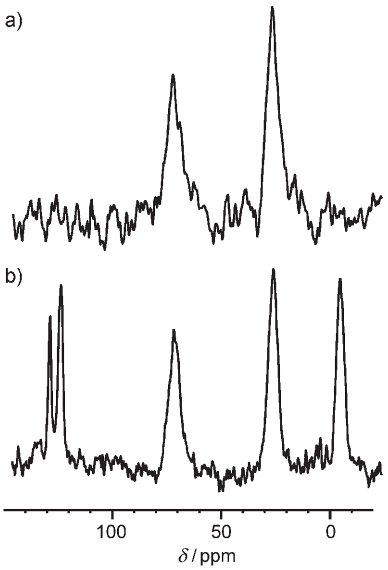


Figure 1. 75.46 MHz ^{13}C NMR solid-state CP/MAS spectra of **2** (a) and **3** (b) at a spinning rate of 10 kHz.

supported rhodium complexes remained practically unchanged even after more than ten cycles. In particular, catalyst **2** was shown to maintain a similar catalytic activity in the hydrosilylation of vinylsiloxanes even after 20 cycles. As shown by inductively coupled plasma (ICP) analysis, the content of rhodium in the sample of catalyst **2** after 20 cycles in this reaction was 156 mmol per gram of silica, that is, 72 % of the initial amount of this element in catalyst **2**.

It is well known from earlier studies that in the presence of a silicon hydride the Rh–O–$SiMe_3$ complex undergoes oxidative addition and subsequent elimination of disiloxane to generate a low-coordinate complex (16e hydride complex with already coordinated alkene molecule) with initiation of a direct hydrosilylation process according to Scheme 2.

If such initiation of an Rh–H complex containing no siloxide ligand also took place in the heterogeneous system, leaching of rhodium diene complex should be observed. Therefore, in view of the unusually successful recycling of heterogeneous rhodium catalyst **2** in selected hydrosilylation reactions, it is necessary to consider a different mechanistic pathway for the heterogeneous catalyst, which remains stable and active for reuse.

A number of experimental techniques can be used for structural studies on heterogeneous catalysts. High-resolution solid-state NMR spectroscopy has become an indispensable method for characterization of products and pathways of organometallic syntheses and catalysis.[9] We used this method to confirm the reaction pathway shown in Scheme 3 and fully characterize product **3**.

Figure 1 shows ^{13}C CP/MAS spectra of **2** and **3** recorded at a spinning rate of 10 kHz at ambient temperature. Two well-defined ^{13}C NMR signals at $\delta = 29$ and 75 ppm correspond respectively to methylene and olefinic carbon atoms of **2**

(Figure 1a). The spectrum of **3** (Figure 1b) contains five resolved peaks, which can be assigned as follows: $\delta = 0$ ($(CH_3)_2Si$), 30 (CH_2 of cod), 76 (CH of cod), 128, and 135 ppm (Ph). The ^{29}Si CP/MAS spectra of both samples confirmed formation of product **3** [$\delta = 99.68$ (Q^2), 106.88 (Q^3), 110.38 (Q^4)]. The NMR spectra of the above compounds were compared with the data for parent complex **1**. (The ^{29}Si CP/MAS and ^{13}C CP/MAS spectra of **1** are provided as Supporting Information.) From analysis of the spectra it is clear that compared to samples of **2** and **3**, resolution for the parent system is much better. The four resonances at $\delta = 77.1$, 74.6, 72.6, and 70.2 ppm can be assigned to crystallographically and magnetically non-equivalent vinyl carbon atoms of the cod ligand. In contrast, three of the crystallographically nonequivalent methylene groups are magnetically equivalent. In consequence, we observed only two lines at $\delta = 30.8$ and 29.5 ppm with 3:1 integration. The methyl groups bonded to Si resonate at $\delta = 9.3$ ppm. The ^{29}Si chemical shift is $\delta = 9.3$ ppm.

Further evidence for formation of **3** and assignment of the chemical shifts of cod and trisubstituted silane were obtained by heteronuclear $^{13}C,^{1}H$ FSLG HETCOR 2D correlation. Figure 2 shows the 2D spectrum recorded at a spinning rate of 10 kHz and a contact time of 2 ms. The cross-peaks are clear-cut, and each proton signal can be assigned to a specific carbon atom. It is noteworthy that the chemical shifts of the methylene and vinyl protons of cod coordinated to rhodium are very similar. The spread of proton signals for the methylene carbon atoms is much larger than that of the vinyl protons.

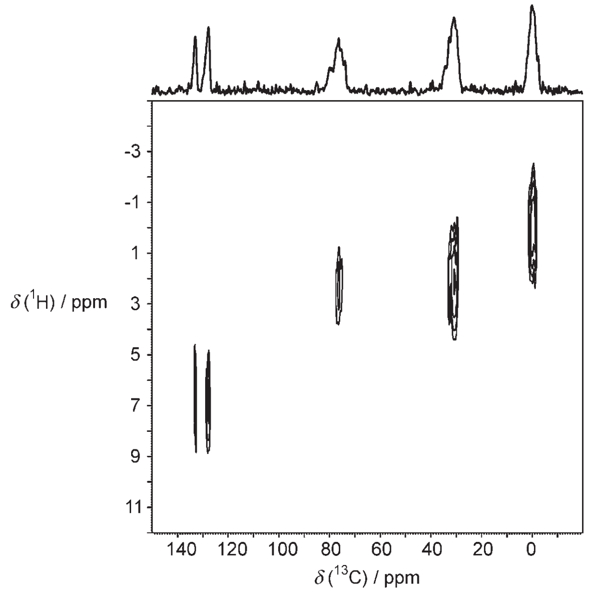
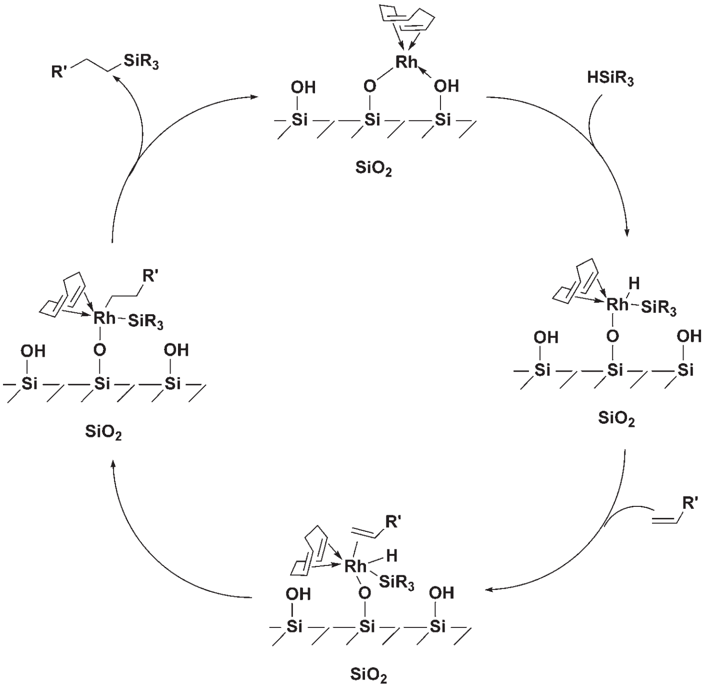


Figure 2. $^{1}H,^{13}C$ FSLG HETCOR MAS spectrum of **3** recorded at a spinning rate of 10 kHz and a contact time of 2 ms.

The groups of Emsley[22] and Schrock[23] recently reported that for molecules on surfaces, the magic-angle spinning alone at moderate frequencies (10 kHz) is usually sufficient to obtain fairly well-resolved proton spectra. This is because the grafted compounds, although covalently linked to the surface, still have several degrees of motional freedom that partially average out the dipolar interactions. Moreover, single-site catalysts are usually dispersed on the surface, typically separated by more than 10 Å, which significantly reduces the proton density at a given site. In our project, proton SS NMR spectroscopy was employed for characterization of sample **3**. A full description of the ^{1}H CRAMPS FSLG spectra is provided as Supporting Information.

The results of solid-state NMR spectroscopy have shown the presence of $(\equiv SiO)Rh(H)SiMe_2Ph$ surface organometallic complexes, formation of which is strong evidence for the absence of the siloxane elimination observed in the homogeneous system catalyzed by **1**. Therefore, the catalytic cycle of heterogeneously catalyzed hydrosilylation is different from that of the homogeneous case and occurs by the well-known Chalk–Harrod mechanism initiated by stable immobilized $[(\equiv SiO)Rh^{I}(cod)]$ complex **2** according to Scheme 4.



Scheme 4. Mechanism of hydrosilylation catalyzed by surface rhodium siloxide complex.

In conclusion, we have shown that the rhodium siloxide surface complex **2** (**2a**), prepared from molecular precursor **1** as a well-defined rhodium siloxide complex immobilized on silica and characterized by solid-state NMR spectroscopy and elemental analysis, is a highly effective catalyst for hydrosilylation of 1-alkenes and vinylsiloxanes. We believe that silanol groups in **2** are responsible for the high stability of the heterogeneous catalyst, which can be recycled at least 10–20 times without a decrease in the yield and selectivity.

Experimental Section

All experiments were performed under dry and oxygen-free argon by using standard Schlenk techniques for organometallic synthesis.

See the Supporting Information for full experimental procedures, ^{1}H, ^{13}C, and ^{29}Si NMR spectra, GC–MS, and elemental analyses of products.

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