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ARTICLE TYPE

The First Ruthenium-Silsesquioxyl Complexes – Synthesis, Structure and Mechanistic Implications in Silylative Coupling

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The first ruthenium-silsesquioxyl complexes have been synthesised and characterized via spectroscopic and X-ray methods. Mechanistic studies were performed and the complexes obtained were proved to be intermediates in the catalytic cycle of silylative coupling of olefins with vinylsilsesquioxane. Moreover, a mechanism of silylative coupling of styrene with vinylsilsesquioxanes was proposed.

Introduction

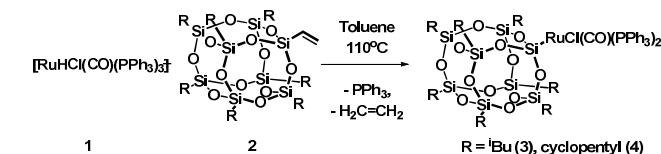
Polyhedral oligosilsesquioxanes (POSS) of the general formula $(\text{RSiO}_{3/2})_n$ and particularly those ($n=8$) containing inorganic cubic core of Si-O-Si bonds make a class of versatile building blocks for the production of inorganic-organic materials thanks to the three-dimensional highly symmetrical nature of the POSS core [1]. The properties of the core permit a wide range of technological applications of silsesquioxanes that can be used as nanofillers for the preparation of nanostructured composites, catalysts [2-4], dendrimers [5], as precursors for optoelectronic materials [6-9], dry resists in microelectronics [10] and precursors for SiO deposition [11].

Mono- and octa-functionalized silsesquioxanes and spherosilicates have been synthesized by TM catalyzed reactions such as hydrosilylation by Si-H [12] substituted POSS and silylative coupling [13-16] by vinylsubstituted POSS with olefins, which occurs via intermediates containing TM-silicon bond. Mechanism of the silylative coupling of olefins with vinylsubstituted silicon compounds has been a subject of our earlier study [17, for review see 18,19]. So far only two reports have been published on isolation and crystal structure of the complexes containing a TM-silicon bond (exactly cobalt-silicon bond) [20, 21].

This paper reports the synthesis of the first silsesquioxyl
35 complexes of ruthenium containing Ru-Si bonds and describes
the crystal structure of one of them. Moreover, the catalytic
activity of this complex in the silylative coupling of
vinylheptaalkylsilsesquioxane with styrenes is analysed.

Results and discussion

When a toluene solution of ruthenium hydride complex [RuHCl(CO)(PPh₃)₃] **1** was heated in the presence of 1 equiv of vinylheptaisobutylsilsesquioxane at 110°C the color of the solution gradually turned yellow-brown within 48 h. The ¹H NMR spectrum of the post-reaction mixture revealed disappearance of signals at δ = -6.60 (dt) ppm characteristic of Ru-H bond and formation of a new singlet at δ = 5.25 ppm which can be assigned to ethylene. Moreover, the appearance of a new singlet at δ = 37.49 ppm was observed in the ³¹P NMR spectrum. On the basis of these observations, a general scheme for the synthesis of ruthenium silsesquioxyl complexes was proposed (Scheme 1)



60 **Scheme 1** Synthesis of ruthenium silsesquioxyl complexes

Further experiments led to the development of efficient synthetic procedures for the synthesis of silsesquioxyl complexes **3** and **4** (see supporting information). The compounds were isolated in high yields (89% and 86% respectively) as pale yellow powders. The obtained products were fully characterized by ^1H , ^{13}C , ^{29}Si , ^{31}P NMR spectroscopy and high resolution mass spectrometry (see supporting information). Moreover the structure of complex (**3**) was confirmed via X-ray analysis (**Fig. 1**). Single crystals were obtained by slow evaporation of pentane solution. Ru is 5-coordinated in square-pyramidal fashion. Four atoms: P1, P2, Cl1 and C1 are almost coplanar (maximum deviation from the least-squares plane is 0.053(3)Å) while the fifth one, Si1, is 2.485Å out of this plane. Ru atom is also slightly displaced, by 0.0219Å, from the basal plane towards the apical Si1. Because of static disorder, in approximately one per six molecules the CO

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and Cl ligands are interchanged (cf. Experimental part) without significant influence on the complex geometry. The Si_8O_{12} moiety is quite regular, with the deviations from the ideal symmetry caused mainly by the presence of Ru-coordination. The Si-O distances involving the coordinated silicon atom are systematically longer than the other Si-O bonds; the mean values are 1.636(4) Å for Si1 and 1.620(5) Å for all other ones. In fact, Si1-O distances are the three longest Si-O distances in the molecule. Also, the majority (8 of 12) of Si-O-Si angles are within quite a narrow range, with the mean value of 145.4(16)°, while the other four (O4, O8, O9, O10) are significantly larger 154°-161°.

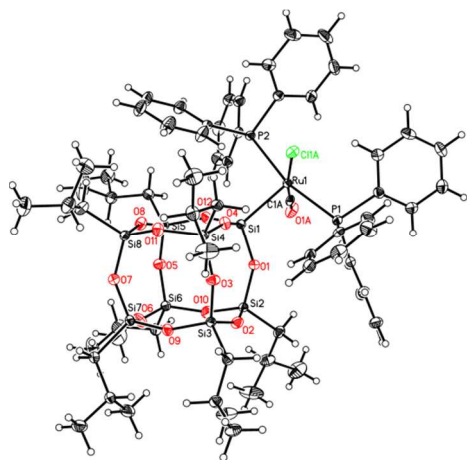
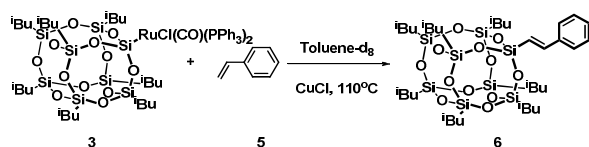


Fig. 1 A perspective view of complex **3**, the ellipsoids are drawn at the 33% probability level. Hydrogen atoms are drawn as the spheres of arbitrary radii. Some relevant geometrical parameters (Å, °): Ru1-Cl1 1.793(4) [1.690(16), Ru1-Cl12.4229(9) [2.491(5), Ru1-Si1 2.2992(6), Ru1-P1 2.3944(5), Ru1-P22.3572(5), Cl1-O1 1.166(5) [1.19(2)], <Si-O> 1.624(11), Cl1-Ru1-Cl1 170.55(10) [171.1(5), P1-Ru1-P2 165.16(2).

Stoichiometric reactions of ruthenium silsesquioxyl complex with styrene

As we previously demonstrated for the silylative coupling mechanism of vinylsilicon compounds and olefins, complexes **3** and **4** can be treated as intermediate ones in the catalytic cycle. In order to better understand the mechanism of the silylative coupling of styrenes with vinylsilsesquioxanes an equimolar reaction between ruthenium silsesquioxyl complex **3** and styrene was performed (**Scheme 2**):



Scheme 2 Stoichiometric reactions of styrene with ruthenium silsesquioxyl complex

The tests were monitored by ^1H NMR spectroscopy. Addition of 1 equiv. of styrene and 5 equiv. of CuCl to the solution of complex **3** followed by heating the reacting mixture at 110°C resulted in formation of the cross-coupling product **6**. Although spectroscopic examination does not confirm the formation of a complex **9** containing Ru-H bond, we observed signals at $\delta = 6.47$ ppm (d, 1H, $J=19.2$ Hz, $=\text{CHSi}$) and $\delta = 7.56$ ppm (d, 1H, $J=19.2$ Hz, $=\text{CHPh}$) characteristic of product **6**. The intermediate

complex containing Ru-H bond was also not observed in the reaction of Ru-Si complexes with olefins, which was previously reported by our group [18, 19]. Moreover, GC-MS analysis confirmed the formation of the desired coupling product **6**. Formation of compound **6** is the evidence for insertion of styrene into the Ru-Si(POSS) bond in complex **3** followed by β -H elimination and evolution of *E*-phenyl(silyl)ethene.

In the above stoichiometric reaction, the desired product was formed only when the reaction was conducted in the presence of CuCl. Moreover, complex **3** exhibited almost no reactivity when the reaction was performed without Cu(I) salt. To better understand the role of CuCl in the reaction mixture we performed a series of stoichiometric reactions monitored by ^1H and ^{31}P NMR spectroscopy. When a toluene solution of ruthenium silsesquioxyl complex $[\text{Ru}(\text{POSS})\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ **3** was heated in the presence of 5 equiv. of CuCl at 110°C for 24 h we observed disappearance of the signals at $\delta = 37.49$ ppm characteristic of complex **3** and formation of a new singlet at $\delta = 25.95$ ppm in the ^{31}P NMR spectrum (**Fig. 2**):

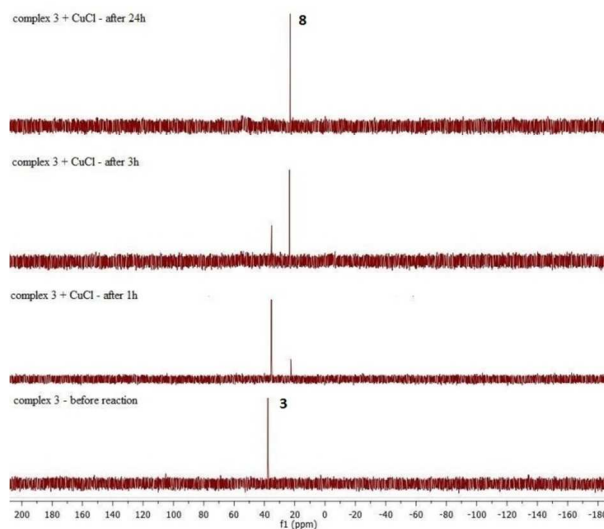
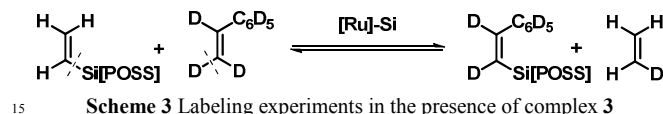


Fig. 2 ^{31}P NMR spectra of stoichiometric reaction of **3** with CuCl

The formation of this new complex **8** was accompanied by precipitation of insoluble grey-brown $[\text{CuPPh}_3]$ complex, whose appearance proves the dissociation of phosphine in the proposed reaction system. ^1H NMR spectrum of the post-reaction mixture revealed changes in the aliphatic region. We observed disappearance of two multiplets at 1.85–2.06 and 2.06–2.31 and formation of a new multiplet at 2.15–2.38 ppm. All attempts to isolate this new complex **8** from the post-reaction mixture failed. However, the obtained results indicate that as a consequence of addition of CuCl to the reaction system, phosphine undergoes dissociation, as proved by $[\text{CuClPPh}_3]$ complex precipitation, and a new four-coordinated intermediate complex **8** is formed. The addition of CuCl is needed because of a large steric hindrance in the intermediate complex having the Ru-Si(POSS) bond. The presence of the steric hindrance in the intermediate complex is supported by the fact that in the analogous silyl complex $[\text{RuSiMe}_3\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ the insertion of styrene is effective without the addition of CuCl [17].

Isotopic labelling experiments

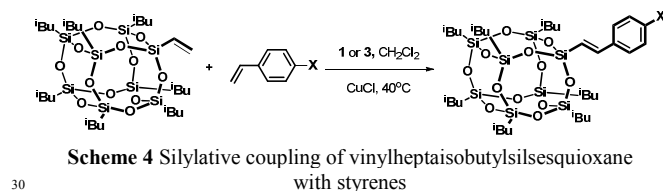
In order to confirm that the coupling process in the presence of **3** proceeds *via* insertion–elimination mechanism which is characteristic of silylative coupling reaction [17–19], we performed a series of labeling studies. In these experiments monitored by ^1H NMR spectroscopy, a solution of equimolar amounts of styrene- d_8 and complex **3** was heated. The insertion–elimination mechanism should afford the formation of silylstyrene- d_7 and ethylene- d_1 (**Scheme 3**), at least at the initial stage of the reaction. ^1H NMR spectroscopic analysis of the products formed in the equimolar reaction carried out in the presence of **3** revealed the formation of *E*-1-phenyl-2-(silyl)ethene- d_7 and ethylene- d_1 .



The results obtained in the experiments with deuterium labelled styrene clearly demonstrate that functionalisation of vinylsilsesquioxanes with styrenes proceeds according to the silylative coupling mechanism involving the activation of $=\text{C}-\text{H}$ and $\text{Si}-\text{C}=\text{C}$ bonds.

Catalytic examinations and mechanistic implications

The ruthenium silsesquioxyl complex **3** was examined in the silylative coupling of selected styrenes with vinylheptaisobutylsilsesquioxane and its catalytic activity was compared to that of its parent complex $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ **1** and the previously studied more reactive complex $[\text{RuHCl}(\text{CO})(\text{PCy}_3)_2]$ **7** [15].



Selected data for **1** and **3** are presented in **Table 1** Entry 1. As indicated in this table, the silsesquioxyl catalyst **3** exhibits higher catalytic activity than catalyst **1**. For example after five hours in the reaction of vinylsilsesquioxane with styrene catalysed by **3**, the conversion of the silsesquioxane reached 33%, while the reaction catalysed by **1** revealed almost no conversion (6%). The activity of catalysts **1** and **3** was examined in a wide temperature range. Our experiments demonstrated that increasing temperature of the reacting mixture from 40°C to 110°C did not give higher yield of the coupling product. We compared the catalytic activity of complexes **1** and **3** with that of complex **7** bearing PCy_3 ligands. In all cases, complex **7** was the most active in silylative coupling of vinylheptaisobutylsilsesquioxane with styrenes, however because of its high reactivity we were unable to isolate ruthenium-silsesquioxyl complex bearing PCy_3 ligands.

Table 1. Silylative coupling of vinylheptaisobutylsilsesquioxane with styrenes in the presence of **1**, **3** and **7** with co-catalyst (CuCl)

X =	catalyst	Yield of silylstyrene [%]
H	3	33
	1	6
	7	100 ^b
OMe	3	35
	1	7
	7	100 ^b
Cl	3	32
	1	6
	7	100 ^b
Br	3	34
	1	5
	7	100 ^b

^aReaction condition: CH_2Cl_2 , reflux, argon, 5h
 $[\text{Ru}]:[\text{H}_2\text{C}=\text{CHSiR}_3]:[\text{styrene}] = 10^{-2}:1:3, [\text{Ru}]:\text{CuCl} = 1:5$; ^b ref. [15].

Mechanistic implications

On the basis on stoichiometric experiments and labelling studies we proposed a mechanism for the coupling of styrenes with vinylsilsesquioxanes in the presence of $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ **1** and CuCl as co-catalyst (**Fig. 3**):

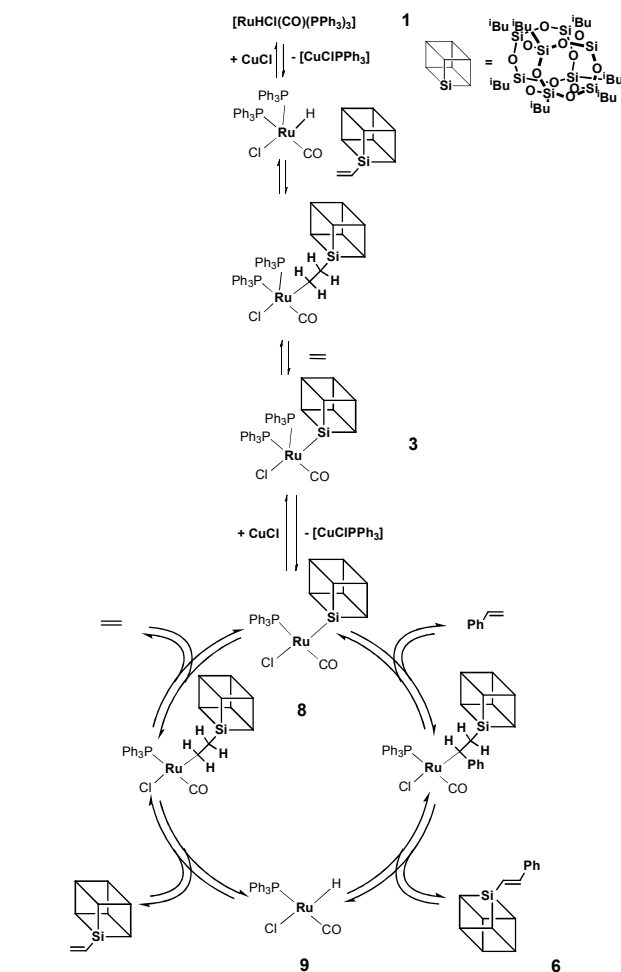


Fig. 3 Mechanism of silylative coupling of styrene with vinylsilsesquioxane

Our studies have shown that the coupling reaction proceeds according to the well-recognized insertion-elimination mechanism [17] in which, in the first step vinylsilsequioxane reacts with hydride complex **1** to give β -silylethyl complex. This compound decomposes *via* β -silsequioxyl group migration to ruthenium and evolution of ethylene to give Ru-Si[POSS] complex **3**. Addition of CuCl to complex **3** causes dissociation of phosphine to produce less sterically hindered four-coordinate complex **8** which reacts with styrene. The next step of the catalytic cycle involves the migratory insertion of styrene into a Ru-Si bond followed by β -H elimination to give *E*-phenyl(silyl)ethene **6**.

Experimental

General methods and chemicals

Unless mentioned otherwise, all operations were performed by using standard Schlenk techniques. ¹H- and ¹³C-NMR spectra were recorded on a Varian 400 operating at 402.6 and 101.2 MHz, respectively. ³¹P NMR spectra were recorded on a Mercury 300 operating at 121.5 MHz. ²⁹Si NMR spectra were recorded on a Varian Avance 600 operating at 119.203 MHz. All FT-IR spectra were recorded with an IFS 113v FT-IR and VERTEX 70 spectrophotometers (Bruker, Karlsruhe). GC analyses were carried out on a Varian CP-3800 (column: Rtx-5 30m I.D. 0.53mm) equipped with TCD. Mass spectrometry analyses were performed using Synapt G2-S mass spectrometer (Waters) equipped with the Electrospray ion source and quadrupole-Time-of-flight mass analyzer. Acetonitrile was used as a solvent. The measurement was performed in positive ion mode with the desolvation gas flow 200 L/h and capillary voltage set to 5000 V with the flow rate 20 μ L/min.

The chemicals were obtained from the following sources: vinyltrichlorosilane from ABCR, dichloromethane, acetone, n-pentane, ethanol, dichloromethane-d₂, benzene-d₆, toluene-d₈, styrene-d₈, decane, dodecane, styrene, 4-chlorostyrene, 4-bromostyrene, 4-methoxystyrene, 2-methoxyethanol, triphenylphosphine, formaldehyde, copper(I) chloride, anthracene, calcium hydride and anhydrous magnesium sulphate from Aldrich, triethylamine and silica gel 60 from Fluka, ruthenium(III) chloride hydrate from Lancaster, trisilanolisobutyl POSS from Hybrid Plastics [22], toluene and n-hexane from Chempur. [RuHCl(CO)(PPh₃)₃] was prepared according to the literature procedure [23]. Monovinylheptaisobutylsilsequioxane was prepared according to the literature procedure [15]. Monovinylheptacyclopentylsilsequioxane was prepared using the same procedure. All solvents were dried prior to use over CaH₂ and stored under argon. CH₂Cl₂ was additionally passed through a column with alumina and after that it was degassed by repeated freeze-pump-thaw cycles.

Synthesis and characterization of ruthenium-silyl complexes

Synthesis and characterization of complex **3**

A 50 mL high-pressure Schlenk vessel connected to gas and vacuum line was charged under argon with 0.2 g (2.1×10^{-4} mol) of [RuHCl(CO)(PPh₃)₃] and 20 mL of dry toluene. The mixture was warmed up in an oil bath to 110°C and stirred for 15 minutes. Subsequently, monovinylheptaisobutylsilsequioxane

(0.177 g 2.1×10^{-4} mol) was added to the reacting mixture and the suspension was refluxed for 48h to give a yellow-brown solution. After this time the solvent was evaporated under vacuum and n-hexane (5mL) was added to the remaining contents to form a yellow precipitate. Then the resulting solution was decanted from the precipitate and the solid obtained was dried under vacuum (isolated yield = 89%).

Analytical data:

¹H NMR (C₆D₆, δ , ppm): 0.35–0.53 (m, 14H, CH₂), 0.81–1.27 (m, 42H, CH₃), 1.85–2.06 (m, 3H, CH), 2.06–2.31 (m, 4H, CH), 6.99–7.30 (m, 12H, Ph), 7.72–7.93 (m, 18H, Ph); ¹³C NMR (C₆D₆, δ , ppm): 23.05, 23.25, 23.44, 23.62, 23.81, 24.72, 24.75, 24.78, 26.15, 26.20, 26.27, 26.38, 26.43, 30.45, 128.78 (t, J=5.0 Hz), 130.49, 131.83 (d, J=2.5 Hz), 132.61, 132.70, 132.85, 133.07, 133.29, 135.59 (t, J=5.8 Hz), 200.70; ²⁹Si NMR: (C₆D₆, δ , ppm): -66.05 (Ru-Si), -67.32, -69.60 (core); ³¹P NMR: (C₆D₆, δ , ppm): 37.49; IR (v, cm⁻¹): 1931 (CO); MS (FD): m/z (%): 1231.24 (31), 1263.20 (37), 1264.20 (61), 1265.20 (99), 1267.20 (100), 1268.20 (67), 1269.20 (50), 1275.23 (30), 1287.25 (42), 1288.24 (63), 1289.25 (97), 1290.24 (80), 1292.24 (55), 1299.09 (35), 1300.09 (30), 1465.13 (33), 1466.13 (40), 1467.13 (45), 1469.13 (42), 1470.13 (30), 1525.29 (38), 1526.29 (60), 1527.29 (95), 1529.29 (100), 1530.29 (77), 1531.29 (60), 1532.29 (33), 1543.29 (31), 1551.32 (39), 1552.32 (47), 1553.32 (62), 1554.32 (51), 1555.32 (47), 1556.32 (34), 1565.34 (38), 1566.33 (61), 1567.32 (92), 1568.33 (81), 1570.34 (57), 1571.33 (37), 1715.03 (33), 1717.03 (38), 1719.03 (34), 1803.38 (34), 1804.38 (54), 1805.37 (91), 1806.38 (93), 1807.38 (100), 1808.37 (82), 1809.38 (62), 1810.37 (37); HRMS (FD) for C₆₅H₉₃ClO₁₃P₂RuSi₈Na: calc. 1527.2875; found: 1527.2871

Synthesis and characterization of complex **4**

Complex **4** was prepared using the same procedure and the following reagents: [RuHCl(CO)(PPh₃)₃] (0.2 g, 2.1×10^{-4} mol) and monovinylheptacyclopentylsilsequioxane (0.1948 g, 2.1×10^{-4} mol). Finally, a yellow precipitate was obtained (isolated yield = 86%).

Analytical data:

¹H NMR (C₆D₆, δ , ppm): 0.64–2.2 (m, 72H, C₅H₉-), 6.68–7.95 (m, 30H, Ph); ¹³C NMR (C₆D₆, δ , ppm): 23.10, 23.19, 27.21, 27.45, 27.56, 27.59, 27.80, 27.83, 27.86, 28.07, 28.31, 128.47 (t, J=4.5 Hz), 130.07, 131.59 (d, J=2.5 Hz), 132.34, 132.44, 135.44 (t, J=5.8 Hz), 199.82; ²⁹Si NMR: (C₆D₆, δ , ppm): -48.47 (Ru-Si), -66.14, -68.75 (core); ³¹P NMR: (C₆D₆, δ , ppm): 38.47; IR (v, cm⁻¹): 1932 (CO); MS (FD): m/z (%): 1550.32 (24), 1551.33 (65), 1553.33 (100), 1554.33 (85), 1555.33 (82), 1556.33 (60), 1557.33 (37); HRMS (FD) for C₇₂H₉₃O₁₃P₂RuSi₈: calc. 1553.3289; found: 1553.3273

Procedure for equimolar reactions of ruthenium-silyl complex **3** with styrene

The stoichiometric reactions were performed in J-Young valve NMR tubes and controlled by ¹H NMR spectroscopy. In a typical procedure ruthenium complex **3** 0.015 g (9.96×10^{-6} mol) and anthracene 0.0001g (internal standard) were dissolved in 0.65 mL of toluene-d₈. Then the ¹H NMR spectrum was recorded and 1.2 μ L (9.96×10^{-6} mol) styrene was added under argon by microliter syringe. Then the reaction mixture was warmed up in an oil bath to 110°C and 0.0049 g (4.98×10^{-5} mol) CuCl was added. The

mixture was heated for 24 h and after this time the ^1H NMR spectrum of the reaction mixture was taken. The corresponding reactions with styrene- d_8 were performed using the same procedure.

5 Procedure for stoichiometric reactions of ruthenium-silyl complex **3** with CuCl

The stoichiometric reactions were performed in J-Young valve NMR tubes and controlled by ^1H and ^{31}P NMR spectroscopy. In a typical procedure, ruthenium complex **3** 0.01 g (6.64×10^{-6} mol) and anthracene 0.0001 g (internal standard) were dissolved in 0.65 mL of toluene- d_8 . Then the ^1H and ^{31}P NMR spectra were recorded and 0.0032 g (3.32×10^{-5} mol) CuCl was added under argon. Then the reaction mixture was heated at 110°C and after 1 h, 3 h and 24 h, the ^1H and ^{31}P NMR spectra of the reaction mixture were taken.

General procedure for the catalytic examinations

The oven dried 5 mL glass reactor equipped with a condenser and a magnetic stirring bar was charged under argon with 2 mL of CH_2Cl_2 , monovinylsilsequioxane (0.1 g, 1.19×10^{-4} mol), styrene (41 μL , 3.56×10^{-4} mol) and 20 μL of internal standard (decane or dodecane). The reaction mixture was placed in an oil bath and preheated to 40°C . Then ruthenium complex **1** or **3** (0.0011 g (complex **1**) or 0.0017 (complex **2**), 1.19×10^{-6} mol) was added under argon. After 5 min of the reaction copper(I) chloride (0.0006 g, 5.93×10^{-6} mol) was added. The reaction mixture was heated at 40°C under a gentle flow of argon. Reaction yields were calculated on the basis of the ^1H NMR spectra of the reaction mixture. The corresponding reactions with 4-methoxystyrene, 4-bromostyrene and 4-chlorostyrene were performed using the same procedure.

X-ray analysis (complex **3**)

X-ray diffraction data were collected at 100(1) K by the ω -scan technique, on an Agilent Technologies four-circle Xcalibur diffractometer equipped with Eos detector [24] with an MoK_α radiation source ($\lambda = 0.71073 \text{ \AA}$). The temperature was controlled with an Oxford Instruments Cryosystem device. The data were corrected for Lorentz-polarization effects as well as for absorption (multiscan) [24]. Accurate unit-cell parameters were determined by a least-squares fit of and 12093 reflections of highest intensity, chosen from the whole experiment. The calculations were mainly performed within the WinGX program system [25]. The structures were solved with SIR92 [26] and refined with the full-matrix least-squares procedure on F^2 by SHELXL97 [27]. Scattering factors incorporated in SHELXL97 were used. The function $\Sigma w(|F_o|^2 - |F_c|^2)^2$ was minimized, with $w^{-1} = [\sigma^2(F_o)^2 + (0.0313 \cdot P)^2 + 2.2712 \cdot P]$, where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$. All non-hydrogen atoms were refined anisotropically, hydrogen atoms from methyl groups were placed geometrically, in idealized positions, and refined as riding group with their U_{iso} 's set at 1.2 (1.5 for methyl groups) times U_{eq} of appropriate carrier atom. Disorder was detected during structure refinement: Cl and CO ligands are partially exchanged (site occupation factors 0.83/0.17), and in one iPr group the methyl groups are disordered over two positions (s.o.f.'s 0.70/0.30). Crystallographic data (excluding structure factors) for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, No.

CCDC-919730. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: +44(1223)336-033, e-mail: deposit@ccdc.cam.ac.uk, or www: www.ccdc.cam.ac.uk.

Crystal data: $\text{C}_{65}\text{H}_{93}\text{ClO}_{13}\text{P}_2\text{RuSi}_8$, $M_r = 1505.57$, triclinic, $P-1$, $a = 13.4910(3) \text{ \AA}$, $b = 14.8072(3) \text{ \AA}$, $c = 19.0764(4) \text{ \AA}$, $\alpha = 89.338(2)^\circ$, $\beta = 81.060(2)^\circ$, $\gamma = 77.729(2)^\circ$, $V = 3677.57(13) \text{ \AA}^3$, $F(000) = 1580$, $d_x = 1.36 \text{ g cm}^{-3}$, $\mu(\text{MoK}_\alpha) = 0.48 \text{ cm}^{-1}$, 33625 reflections measured, 14864 unique ($R_{\text{int}} = 0.024$), 12507 with $I > 2\sigma(I)$. Final $R(\text{obs}) = 0.031$, $R(\text{all}) = 0.042$, $wR2(\text{obs}) = 0.071$, $wR2(\text{all}) = 0.075$, $S = 1.04$, max/min $\Delta\rho$ in the final ΔF map: $0.49/-0.62 \text{ e} \cdot \text{\AA}^{-3}$.

Conclusions

New silsesquioxyl ruthenium complexes (**3** and **4**) have been synthesized and their structures were confirmed by spectroscopic and X-ray methods. These complexes are proved to be intermediates in the silylative coupling of vinylsilsesquioxane with styrene. The reaction between vinylsilsesquioxanes and styrenes in the presence of ruthenium hydride complex **1** was confirmed to proceed *via* the insertion-elimination mechanism. Moreover, the obtained complex **3** exhibits higher catalytic activity than that of its parent hydride complex **1**.

Acknowledgements

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The first ruthenium-silsesquioxyl complexes have been synthesised and characterized via spectroscopic and X-ray methods. Mechanistic studies were performed and the complexes obtained were proved to be intermediates in the catalytic cycle of silylative coupling of olefins with vinylsilsesquioxane.

