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Silsesquioxyl rhodium(I) complexes - synthesis, structure and catalytic activity[†]

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The first bi- and mononuclear rhodium(I) complexes $[{Rh(\mu-OSi_8O_{12}(i-Bu)_7)(cod)}_2]$ (5), $[Rh(cod)(PCy_3)(OSi_8O_{12}(i-Bu)_7)]$ (6) with a hindered hepta(*iso*-butyl)silsesquioxyl ligand bonded to the rhodium(I) center through Rh–O–Si bonds have been synthesized and their structures have been solved by spectroscopic methods and X-ray analysis. Their exemplary catalytic properties in silylative coupling of vinylsilanes with styrene are also presented.

Introduction

According to a general idea presented by Wolczanski, TM alkoxides and siloxides are alternatives to cyclopentadienyl complexes¹ (TM = transition metal). Moreover, siloxy groups with hindered substituents at silicon, e.g. OSi(O-t-Bu)₃, OSi(t-Bu)₃ or OSiCy₃, can act as ancillary ligands in formation of low-coordinate reactive metal centers at a low oxidation state, which particularly applies to molecular catalysis.1 Since 1982 more than 120 new TMsiloxide complexes including terminal and/or also bridging siloxy ligands have been synthesized and characterized by spectroscopic and X-ray methods to determine their molecular structure² (for a review see^{2a,b} and references therein). Molecular compounds containing a TM-O-Si moiety are also regarded as models for metal complexes immobilized on silica and silicate surfaces,1-4 particularly in the case of silsesquioxyl5-7 ligands bonded to a metal centre, which are structurally more relevant to silica than simple triorganosubstituted siloxyl groups. While complexes of early transition elements containing siloxyl⁸ and silsesquioxyl⁶ ligands are well-known and characterized, the data on the late TM-complexes with such ligands in molecular form are scarce. Since 1995 we have also been involved in TM-siloxide chemistry, particularly of the late TM-complexes. We had earlier reported synthetic methods and crystal structures of various binuclear and mononuclear cobalt(I),9 rhodium(I),10 iridium(I)11 and ruthenium(II)12 siloxide complexes and applied them in catalytic transformations of organosilicon compounds, i.e. silylative coupling of olefins with vinylsilanes,^{11,13} curing of polysiloxanes via hydrosilylation¹⁴ as well as hydroformylation¹⁵ and silylcarbonylation¹⁶ of vinylsilanes. In this communication we present an efficient method for preparation of bi- and mononuclear silsesquioxyl rhodium(I) complexes as molecular models of TM-complexes immobilized on silica or silicate surfaces and discuss their potential application to catalysis.

Results and discussion

Starting organosilicon materials, *i.e.* chlorohepta(*iso*butyl)silsesquioxane (Si₈O₁₂(Cl)(*i*-Bu)₇) (1) as well as the appropriate hydroxyl derivative (Si₈O₁₂(OH)(*i*-Bu)₇) (2) were synthesized according to modified well-known methods¹⁷ (see Experimental section). Treatment of lithium salt (LiO)Si₈O₁₂(*i*-Bu)₇ (3), obtained after the reaction of HO-silsesquioxane (2) with *n*-BuLi (see Experimental section), with binuclear complexes [{Rh(μ -Cl)(cod)}₂] (4) in benzene solution gave silsesquioxyl binuclear rhodium(1) complexes [{Rh(μ -OSi₈O₁₂(*i*-Bu)₇)(cod)}₂] (5), according to Scheme 1.



Scheme 1 Synthesis of complex 5.

The product was fully characterized by ¹H, ¹³C NMR and ²⁹Si NMR spectroscopy. The ¹H NMR spectrum of [{Rh(μ -OSi₈O₁₂(*i*-Bu)₇)(cod)}₂] shows two chemically non-equivalent cod-olefinic resonance lines which appear as broad singlets (presumably owing to the unresolved coupling and not chemical exchange) at δ = 2.57 and 4.52 ppm. The cod-aliphatic signals are hidden between broad multiples in range 0.84–2.40 ppm assigned to protons of *i*-Bu groups bonded to silsesquioxyl core. The ¹³C NMR spectrum of **5** is also consistent with a dimeric folded structure and the cod-olefinic resonance lines are not equivalent and appear at δ = 74.14 ppm (¹J_{Rh-C} = 12.49 Hz); 78.48 ppm (¹J_{Rh-C} = 12.24 Hz). Magnetic inequivalence of carbon atoms in the cod ligands bonded to Rh centres is apparent that the complex has the A-frame

Adam Mickiewicz University, Faculty of Chemistry, ul. Grunwaldzka 6, 60-780, Poznań, Poland. E-mail: marcinb@amu.edu.pl; Tel: +48618291366 † CCDC reference numbers 776149 and 776150. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt01631d

bis-square planar geometry and the two pairs of top olefinic carbons are close to each other, but the bottom pairs of olefinic carbons are adjacent to the silsesquioxyl ligands. The cod-aliphatic signals are located between the lines assigned to *i*-Bu groups. The Rh–O–Si(Q⁴) resonance appears on ²⁹Si NMR spectrum as a singlet at $\delta = -101.07$ ppm. X-Ray analysis of single crystals, obtained at -30 °C by slow evaporation of toluene, confirmed the binuclear structure of the complex obtained, as shown in Fig. 1.



Fig. 1 The perspective view of complex 5, with hydrogen atoms omitted for clarity. For disordered fragments only those of larger occupancy are shown. Selected distances (X1A, X1B are the midpoints of double bonds in cod fragment): Rh1–O1 2.091(4) Å, Rh1–O1^{*i*} (*i*: 2-x, *y*, 1/2-z) 2.111(4) Å, Rh1–X1A 1.962(5) Å, Rh1–X1B 1.973(5) Å, <Si–O> 1.615(9) Å, X1A–Rh1–X1B 88.5(3)°, X1A–Rh1–O1–173.9(2)°, X1A–Rh1–O1^{*i*} 95.4(2)°, X1B–Rh1–O1 96.8(2)°, X1B–Rh1–O1^{*i*} 173.9(2)°, O1–Rh1–O1^{*i*} 79.14(15)°, Rh1–O1–Rh1^{*i*} 88.69(13)°, Si1–O1–Rh1 127.5(2)°, Si1–Rh1–O1^{*i*} 143.8(2), <Si–O–Si> 150(5)°.

Formation of $[Rh(cod)(PCy_3)(OSi_8O_{12}(i-Bu)_7)]$ (6) complex (see Fig. 2) occurs *via* a cleavage of two Rh–O–Rh bridging bonds in the binuclear complex **5** in the presence of PCy₃,^{10d,11b} according to Scheme 2 (see Experimental section).



Fig. 2 The perspective view of complex 6, with hydrogen atoms omitted for clarity. Selected geometrical parameters: (X1A, X1B are the midpoints of double bonds in cod fragment): Rh1–O1 2.041(3) Å, Rh1–P1 2.3251(14) Å, Rh1–X1A 2.090(5) Å, Rh1–X1B 1.990(5) Å; <Si–O> 1.623(8) Å; X1A–Rh1–X1B 86.7(2)°, X1A–Rh1–O1 91.1(2)°, X1A–Rh1–P1 174.11(14)°, X1B–Rh1–O1 172.6(2)°, X1B–Rh1–P1 96.67(15)°, O1–Rh1–P1 86.16(10)°, Si1–O1–Rh1 143.1(2)°, <Si–O–Si> 149(8)°.

The ¹H NMR spectrum of **6** shows two cod-olefinic resonance lines which appear as broad singlets at $\delta = 3.30$ and 5.59 ppm. The



Scheme 2 Synthesis of complex 6.

cod-aliphatic signals are hidden between broad multiples in the range 0.83–2.39 ppm assigned to protons of *i*-Bu and -Cy groups bonded to silsesquioxyl core and phosphorus atom respectively. The ¹³C NMR spectrum of **6** shows non-equivalent cod-olefinic resonance lines at $\delta = 63.35$ (${}^{1}J_{Rh-C} = 15.09$ Hz), 100.76 (${}^{1}J_{Rh-C} = 16.09$ Hz). The cod-aliphatic signals are located between the lines assigned to *i*-Bu and -Cy groups.

To the best of our knowledge, 5 and 6 are the first rhodiumsilsesquioxyl complexes synthesized, whose structures have been determined by the X-ray method.

The geometry of complex **5**, is generally similar to that of rhodium(1) and iridium(1) trimethylsiloxy analogues, *i.e.* [{M(μ -OSiMe_3)(cod)}₂] (M = Rh,^{10b} Ir,^{11a} whose structures were reported previously. Complex **5** has the exact crystallographic C_2 symmetry (the twofold axis runs between the Rh atoms).

The coordination of Rh ions is square-planar, if the midpoints of double bonds from cyclooctadiene fragments are regarded as the coordination sites. Overall the complex has an A-frame bis-square planar geometry; the roof angle is 125.9° and it is larger than in simpler analogues (120.4° in OSiMe₃, ¹⁰⁶ 109.6° in OSiPh₃^{10e}). This larger angle results also in longer Rh \cdots Rh contact, of 2.937(1) Å (2.812 Å in OSiMe₃, 2.785 Å in OSiPh₃), and might be connected with the larger substituent at the bridging oxygen atom. Similar geometry to that observed in **5** (roof angle of 129.8°, Rh \cdots Rh distance 2.983 Å) was described for the μ -OSiMe₃ complex when cod ligand was exchanged by the norborna-2,5-diene one, ^{10e} which led to the different disposition of the coordination centres at the double bonds.

In the mononuclear complex **6** the Rh ion is again coordinated in a square-planar fashion, with the midpoints of double bonds as coordination centres. Interestingly, the position, with respect to the O–Si bond, of the substituents at the Si atom closest to the Rh atom can be described as +sc, -sc, ap (Rh–O–Si–C torsion angles approximately $+60^{\circ}, -60^{\circ}, 180^{\circ}$) similarly to previously described alkyl-substituted siloxyle Rh complexes;^{10d} while this position was different in the alkoxy-substituted siloxide, ^{10d} where it is +ac, -ac, sp (Rh–O–Si–O values are close to $+120^{\circ}, -120^{\circ}, 0^{\circ}$).

In both structures the cyclooctadiene ligands are very close to the lowest-energy C_2 boat conformation; the deviations from this ideal symmetry, measured by the combination of the dihedral angles called asymmetry parameters,¹⁸ are as small as 2.8° in 5 and 3.8° in **6**.

+	SiR ₃ - H ₂	C=CH2	SiR3
Catalyst	[Rh] mol%)	Conversion of CH ₂ =CHSiR ₃ (%)	Yield of product (%)
$\mathbf{R}_3 = \mathbf{M}\mathbf{e}_2\mathbf{P}\mathbf{h}$			
$[{Rh(\mu-OSiMe_3)(cod)}_2]$	0,1	100	98
	0,01	60	54
[Rh(cod)(PCy ₃)(OSiMe ₃)]	0,1	92	84
	0,01	51	45
5	0,1	100	96
	0,01	87	79
6	0,1	100	95
	0,01	61	57
$R_3 = (OC_2H_5)_3$			
$[{Rh(\mu-OSiMe_3)(cod)}_2]^a$	1^a	100 ^a	100 ^a
5	0,1	100	95
6		97	95

Reaction conditions: $[CH_2 \longrightarrow CHSiR_3]$: [styrene] = 1:3, T = 100 °C, t = 1 h, under argon;^{*a* $} <math>[CH_2 \implies CHSiR_3]$: [styrene] = 1:10, 90 °C, 24 h, under argon.^{13*a*}

The rhodium(I) siloxide complexes 5 and 6 were examined in the silvlative coupling of styrene with PhMe₂SiCH=CH₂ and (EtO)₃SiCH=CH₂, as the testing reactions, and their catalytic activities were compared with those of siloxide rhodium(I) precursors containing -OSiMe₃ ligand. The data compiled in Table 1 show that the new complexes (5 and 6) efficiently catalyze formation of trans-\beta-silylstyrene in the presence of 0.01 mol% of rhodium, particularly in the system consisting H₂C=CHSiMe₂Ph, contrary to isostructural trimethylsiloxyl analogues, which catalyzed the silvlative coupling of the substrates mentioned when 1 mol% of rhodium and tenfold excess of styrene were used in the reaction system. Slight differences in efficiency of new rhodium silsesquioxyl complexes were observed when H₂C=CHSi(OEt)₃ was used instead of H₂C=CHSiMe₂Ph. We suppose that it is an effect of three ethoxy groups bonded to the silicone atom in the initial vinylsilane.

Generally, the complex **5** seems to be more efficient than precatalyst **6** because the cleavage of the binuclear complex *via* coordination of styrene is easier than the substitution of PCy_3 ligand by styrene in complex **6**.

We suppose that better efficiency of the complexes studied is a result of the steric hindrance and strong electron-withdrawing effect of silsesquioxyl ligand bonded to the rhodium centre, which electronic properties are similar to -CF₃ group.¹⁹ These two effects make the rhodium centre more reactive in activation of the vinylic C–H bond in styrene.

As we have reported earlier, rhodium binuclear siloxyl complex as well as mononuclear siloxide, phosphine complex catalyze efficiently silylative coupling under milder conditions, than those reported with well-defined Ru, Rh and Co complexes containing initially M–H and M–Si bonds (for review see Ref. 20).

The reaction mechanism is proposed on the basis of our previous mechanistic studies preformed for $[{Rh(\mu-OSiMe_3)(cod)}_2]^{13b}$ complex as well as for iridium(1)^{11a} structural analogue. These studies have shown that the coupling reaction proceeds according to the non-metalacarbene mechanism in which, in the first step olefin (styrene) reacts with binuclear complex **5**, giving very labile

and impossible to isolate, formally 16e species (a) with olefin molecule bonded to the rhodium centre. The formation of a similar four-coordinated complex of type (a) has been confirmed spectroscopically for the reaction of $[{Ir(\mu-OSiMe_3)(cod)}_2]$ with H₂C=CHSi(OSiMe₃)₃ and H₂C=CHSi(OEt)₃. Further transformation involving Rh 16e intermediate which is generated in situ, via oxidative addition of = C-H bond of styrene as a coordinated molecule to the rhodium atom (see Scheme 3, $(\mathbf{a}) \rightarrow (\mathbf{b})$, was confirmed for -OSiMe₃ analogue by catalytic vinylic H/D exchange^{13b} between styrene and styrene-d₈. The insertion of vinylsilane into M-H bond (b) \rightarrow (c) \rightarrow (d) is followed by evolution of ethylene (B-Si-transfer) to get five coordinated Rh-Si intermediate (e). Our previous^{13b} study revealed no traces of siloxane, PhMe₂SiOSiMe₃, which would have been the evidence for replacement of the siloxy ligand by reductive elimination from the [Rh](SiMe₂Ph)(OSiMe₃) intermediate. The latter process is observed in the hydrosilylation of alkene catalyzed by I, i.e., when [Rh]-H is formed directly by oxidative addition of trisubstituted silanes, Et₃SiH²¹ and (EtO)₃SiH.²²



Scheme 3 Mechanism of the silvlative coupling catalyzed by 5 and 6.

In view of the foregoing, it can be assumed that the complex **5**-catalyzed silylative coupling occurs along the same rules as those catalysed by complex $[{Rh(\mu-OSiMe_3)(cod)}_2]$ or $[{Ir(\mu-OSiMe_3)(cod)}_2]$. When complex **6** is used instead of **5** the substitution of phosphine ligand by styrene substrate leads to the formation of complex **(a)**. Further steps of the mechanism proceed similarly as for complex **5**.

In contrast to the previously reported silvlative coupling of olefins with M–H and M–Si complexes (when M = Ru, Rh, Co, Ir),²⁰ the proposed catalytic cycle does not involve migratory insertion of olefin into the Rh–Si bond since the final step of the product formation occurs *via* reductive elimination of the product (the dissociative mechanism) regenerating in excess of styrene complex (**a**).

Conclusions

Two silsesquioxyl bi- (5) and mononuclear (6) rhodium(I) complexes have been synthesized and their structure were solved by spectroscopic and X-ray methods. Those complexes appeared to be efficient homogeneous catalysts in the silylative coupling of vinylsilane with styrene. It is necessary to emphasise, that the mechanism of catalysis illustrated in Scheme 3 indicates that 5 and 6 are excellent molecular models for transition metal complex immobilized on silica as a heterogeneous catalyst since TM–O–Si bond is not cleaved in the catalytic cycle.

Experimental Section

Materials and Methods

All synthesis and manipulations were carried out under argon using standard Schlenk-line and vacuum techniques. The $(Si_8O_{12}(Cl)(i-Bu)_7)$ (1), $(Si_8O_{12}(OH)(i-Bu)_7)$ (2), and $(LiO)Si_8O_{12}(i-Bu)_7$ (3) ligands were synthesized according to a published method.¹⁷ The binuclear complex [{Rh(μ -Cl)(cod)}₂]²³ was synthesized according to the literature. ¹H, ¹³C and ²⁹Si NMR spectra were recorded on a Varian Gemini 300 VT spectrometer and Varian Mercury 300 VT in C₆D₆.

The chemicals were obtained from the following sources: dimethylphenylvinylsilane, tri(ethoxy)vinylsilane, styrene, *n*butyllithium, cyclooctadiene and C_6D_6 from Aldrich Chemical Co.; benzene, pentane from POCH Gliwice (Poland); tricyclohexylphosphine from ABCR; RhCl₃·3H₂O from Pressure Chemicals Company; and TriSilanoIIsobutyl POSS® from Hybrid Plastics. All solvents were dried and distilled under argon prior to use.

Crystallography

Diffraction data were collected at room temperature for **5** and at 100(1) K for **6** by the ω -scan technique, on an Xcalibur Eos diffractometer²⁴ with graphite-monochromatized Mo-K α radiation ($\lambda = 0.71073$ Å). The temperature was controlled by an Oxford Instruments Cryosystems cooling device. The data were corrected for Lorentz polarization and absorption effects.²⁵ Accurate unit-cell parameters were determined by a least-squares fit of 13335 (**5**) and 9078 (**6**) reflections of highest intensity, chosen from the whole experiment. The structure was solved with SIR92²⁵ and refined with the full-matrix least-squares procedure on F² by SHELXL97.²⁶

Scattering factors incorporated in SHELXL97 were used. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were placed in calculated positions, and refined using a 'riding model' with the isotropic displacement parameters set at 1.2 (1.5 for methyl groups) times the U_{eq} value for the appropriate non-hydrogen atom. In both cases some of the *i*-Bu groups were refined

 Table 2
 Crystal data, data collection and structure refinement

Complex	5	6
Formula	$C_{72}H_{150}O_{26}Rh_2Si_{16}$	$C_{54}H_{108}O_{13}PRhSi_8$
Formula weight	2087.18	1324.00
Crystal system	Monoclinic	Triclinic
Space group	C2/c	$P\overline{1}$
a/Å	20.084(2)	10.9023(12)
b/Å	19.082(2)	14.8954(18)
c/Å	28.570(3)	21.769(3)
α (°)	90	99.731(12)
β(°)	98.940(10)	98.469(9)
γ (°)	90	104.467(10)
$V/Å^3$	10816.2(19)	3306.6(7)
Z	4	2
$d_x/\mathrm{g}\mathrm{cm}^{-3}$	1.28	1.33
F(000)	4416	1416
μ/mm^{-1}	0.54	0.48
Θ range (⁰)	2.49 - 27.96	2.85 - 26.00
hkl range	$-26 \le h \le 25$	$-13 \le h \le 13$
	$-24 \le k \le 24$	$-17 \le k \le 18$
	$-37 \le l \le 36$	$-26 \le l \le 26$
Reflections:		
collected	50571	24946
unique (R_{int})	12106 (0.051)	12709 (0.049)
with $I > 2\sigma(I)$	7342	7712
Number of parameters	501	719
$R(F)\left[I > 2\sigma(I)\right]$	0.068	0.056
$wR(F^2)[I > 2\sigma(I)]$	0.195	0.131
R(F) [all data]	0.110	0.096
$wR(F^2)$ [all data]	0.204	0.137
Goodness of fit	1.181	0.960
max/min $\Delta \rho/e \text{ Å}^{-3}$	0.86/-1.08	2.31/-0.80

as disordered, and weak constraints were applied to the geometry of the disordered fragments. Relevant crystal data are listed in Table 2, together with refinement details.

Crystallographic data (excluding structure factors) for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, No. CCDC 776149 (5) and CCDC 776150 (6). 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.ccdc.cam.ac.uk.

Synthetic procedure

Synthesis of $[{Rh(cod)(\mu-OSi_8O_{12})(i-Bu)_7)}_2]$ (5). To a portion of [{Rh(cod)(µ-Cl)}2] (4) (0.5g; 1 mmol) placed in a Schlenk flask under argon, a solution of $(LiO)Si_8O_{12}(i-Bu)_7$ (3) (1.76 g; 2.1 mmol) in 25 mL of benzene was added. The reaction mixture was stirred for 24 h at room temperature. After this time it was heated to 50 °C for 1 h. Subsequently the benzene was evaporated and $2 \times$ 20 mL of dried and deoxygenated pentane was added. The entire mixture was filtered off by a cannula system. Thorough drying and recrystallization from toluene gave (5) as a yellow microcrystalline material (3.13 g, 1.50 mmol, 75%). ¹H NMR (C_6D_6 , δ , ppm): 0.84–2.40 (d, 84H, -CH₃, *i*-Bu; t, 28H, -CH₂-Si, *i*-Bu; m, 14H, -CH-, *i*-Bu; bs, 8H, -CH₂-, cod); 4.52, 2.57 (bs, 8H, = CH, cod). ¹³C NMR (C₆D₆, δ, ppm): 22.78, 23.01, 24.38, 24.42, 25.92, 26.41, 31.29 (28C, -CH₃; 14C, -CH₂-Si; 14C, -CH-; 8C, -CH₂-); 74.14 $({}^{1}J_{C-Rh} = 12.49 \text{ Hz}); 78.48 ({}^{1}J_{C-Rh} = 12.24 \text{ Hz}) (8C, = CH-) {}^{29}\text{Si NMR}$ (INEPT) (C_6D_6 , δ , ppm): -67.42(Q³); -67.52(Q³); -101.07(Q⁴). Elemental Anal. Calcul. for C₇₂H₁₅₀O₂₆Rh₂Si₁₆ C, 41.44; H, 7.58 Found: C 42.05; H 7.69.

Synthesis of $[Rh(cod)(PCy_3)(\mu-OSi_8O_{12})(i-Bu)_7)]$ (6). Portions of $[{Rh(cod)(\mu-OSi_8O_{12})(i-Bu)_7)}_2]$ (5) (0.5g; 0.24 mmol) and PCy₃ (0.134 g, 0.48 mmol) were placed in a Schlenk flask in an argon atmosphere. Then 10 ml of dried and deoxygenated benzene were added. The reaction was carried out for 12 h at room temperature. After this time the benzene was removed yielding a yellow solid of (**6**) (0.616 g, 0.475 mmol, 98%).¹H NMR (C₆D₆, δ, ppm): 0.83– 2.39 (d, 42H, -CH₃, *i*-Bu; t, 14H, -CH₂-Si, *i*-Bu; m, 7H, -CH-, *i*-Bu; bs, 4H, $-CH_2$, cod); 3.30 (bs, 2H, = CH, cod), 5.59 (bs, 2H, = CH, cod).¹³C NMR (C₆D₆, δ, ppm): 23.27, 23.83, 24.49, 24.57, 26.01, 26.29, 26.93, 28.10, 28.20, 28.75, 30.53, 31.41, 32.58, 33.85 (14C, $-CH_3$; 7C, $-CH_2$ -Si; 7C, $-CH_2$; 8C, $-CH_2$ -); 63.35 (${}^{1}J_{C-Rh} = 15.09$ Hz), 100.76 (${}^{1}J_{C-Rh}$ = 16.09 Hz) (4C, = CH-). ${}^{31}P$ NMR (C₆D₆, δ, ppm): 26.27 (d, J_{Rh-P} = 149.15 Hz) ²⁹Si NMR (INEPT) (C₆D₆, δ , ppm): -67.53(Q³); -68.20(Q³); -102.21(Q⁴). Elemental Anal. Calcul. for C₅₄H₁₀₈O₁₃PRhSi₈ C, 48.98; H, 7.86 Found: C 49.05; H 7.95.

Catalytic examinations in silylative coupling of styrene with trisubstituted vinylsilane

The catalytic tests of the rhodium(1) silsesquioxide complexes in silylative coupling reactions were performed in glass ampoules or Schlenk tubes filled with a mixture of reagents: (1.8 mmol) styrene and (0.6 mmol) dimethylphenylvinylsilane or tri(ethoxy)vinylsilane, appropriate amounts of catalyst (3 × 10^{-4} mmol (3 × 10^{-5} mmol) of (5) or 6 × 10^{-4} mmol (6 × 10^{-5} mmol) of (6)) and decane as an internal standard. The ampoules (or Schlenk tubes) were heated at 100 °C for one hour under an argon atmosphere. The distribution of substrates and products, conversion of substrates and the yield of products were determined by GC and GC-MS analyses.

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