Synthesis, first structures, and catalytic activity of the monomeric rhodium(I)-siloxide phosphine complexes[1]

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Abstract: Four new square-plane rhodium siloxide complexes of the general formula [Rh(cod)(PR_3')($OSiR_3$)] (where R = Me, *i*-Pr, O-*t*-Bu, R′ = Cy, Ph) were synthesized and the structures of three of them were resolved by the X-ray method. [Rh(cod)(PCy_3)($OSiMe_3$)] (**1**) appeared to be a very efficient catalyst for hydrosilylation of allyl glycidyl ether to yield, selectively, 3-glycidoxypropyltriethoxysilane, a commercially important silane coupling agent. Catalytic measurements and stoichiometric experiments of **1** with triethoxysilane suggest a mechanism where an unsaturated Rh-H species is responsible for the catalysis.

Key words: rhodium (phosphine) siloxides, hydrosilylation, catalysis.

Résumé : On a synthétisé quatre nouveaux complexes siloxyde de rhodium de géométrie plan carré et de formule générale [Rd(cod)(PR_3')($OSiR_3$)] (dans lesquels R = Me, *i*-Pr, O-*t*-Bu; R′ = Cy; Ph) et on a déterminé les structures de trois d'entre eux par diffraction des rayons X. Il semble que le [Rh(cod)(PCy_3)($OSiMe_3$)] (**1**) est un catalyseur très efficace pour l'hydrosilylation de l'oxyde d'allyle et de glycidyle conduisant à la formation sélective du 3-glycidoxypropyltriéthoxysilane, un silane commercialement important comme agent de couplage. Des mesures catalytiques et des expériences stoechiométriques du composé **1** avec le triéthoxysilane suggèrent un mécanisme dans lequel l'espèce Rh-H insaturée est responsable de la catalyse.

Mots clés : rhodium(phosphine)siloxydes, hydrosilylation, catalyse.

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Introduction

Siloxides similar to alkoxides have been employed as ancillary ligands of transition metal (TM) complexes, markedly influencing the reactivity of a metal center by electronic and steric effects of the substituents at silicon. They can be regarded as very good molecular models of metal complexes supported on silica and silicate surfaces, which are known to catalyze a variety of organic and organometallic transformations particularly by early transition metal complexes (1). Unlike the early TM-siloxides the information on the late TM-siloxides is scarce. Only exceptional siloxy derivatives of Fe (2), Co (3), Ni (4), Ru (5), Rh (6–9), Pt (10), Os (11), and Ir (10*c*) have been synthesized and characterized spectroscopically, and the structures of all of them have been a subject of recent interest. The dimeric complexes included $[Rh(CO)_2(\mu\text{-}OSiR_3)]_2$, where R = Me (8), Ph (6*b*), and $[Rh(cod)(\mu\text{-}OSiPh_3)]_2$ (6*b*), $[Rh(diene)(\mu\text{-}OSiMe_3)]_2$, where diene = cod (7*a*, 7*b*), nbd (7*c*).

Catalytic activity of $[Rh(cod)(\mu\text{-}OSiMe_3)]_2$ has been illustrated in some reactions, i.e., in the hydrosilylation of alkenes (12) and allyl alkyl ethers (13, 14) and in the silylative coupling of vinylsilanes with alkenes (15).

The aim of this work was to prepare monomeric rhodium-siloxide complexes, to determine their structures by X-ray methods, and to assess their catalytic activity in the hydrosilylation process.

Experimental section

General methods and chemicals

All syntheses and operations were carried out using standard Schlenk techniques under a carefully deoxygenated and dried argon. ^1H, ^{13}C, ^{31}P, and ^{29}Si NMR spectra were recorded on Varian Mercury and Varian Gemini 300 VT spectrometers. The reagents were obtained from the following sources: C_6H_6 from OBR PR Plock (Poland), PPh_3 from Fluka, sodium trimethylsilanolate from Aldrich, THF and

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Dedicated to celebrate Professor John Harrod's productive career and in recognition of his great contribution to organosilicon chemistry and catalysis.

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C_5H_{12} from POCh Gliwice (Poland), HOSi(O-*t*-Bu)$_3$ and *i*-Pr$_3$SiCl from ABCR Co. All solvents were distilled in an inert atmosphere prior to use. [{Rh(cod)(μ-Cl)}$_2$] (16, 17), [{Rh(cod)(μ-OSiMe$_3$)}$_2$] (**5**) (7*a*) were prepared according to the previously reported procedures.

Synthesis of the complex [Rh(cod)(PCy$_3$)(OSiMe$_3$)] (1)

Portions of 0.1 g [{Rh(cod)(μ-OSiMe$_3$)}$_2$] (0.33 mmol) and 0.2 g (0.71 mmol) PCy$_3$ were placed in a Schlenk flask under Ar. Then 6 mL of dried and deoxygenated C_6H_6 was added. The reaction was carried out for 4 h at room temperature (r.t.). After this time, C_6H_6 was evaporated and 5 mL of dried and deoxygenated C_5H_{12} was added. The precipitate was decanted three times by C_5H_{12}. The complex was dried in vacuum for about 3 h. It was obtained with a yield of 75%. ^{1}H NMR (C_6D_6) δ: 0.46 (s, 9H, -CH$_3$), 1.20–2.02 (m, 33H, -Cy), 2.35 (m, 4H, -CH$_2$-), 3.26 (m, 4H, -CH$_2$-), 5.41 (m, 4H, =CH-). ^{13}C NMR (C_6D_6) δ: 6.0 (-OSiMe$_3$, -CH$_3$), 27.21, 28.28, 28.40, 29.07, 30.80, 31.80, 31.97, 32.50, 32.71, 34.07 (-Cy, -CH$_2$-), 62.83, 63.01 (cod, -CH$_2$-), 99.15, 99.26, 99.32, 99.42 (cod, =CH-). ^{31}P NMR (C_6D_6) δ: 25.28 (d, $J_{\text{Rh-P}}$= 151 Hz). ^{29}Si NMR δ: –3.35. Anal. calcd. for RhPSiOC$_{29}$H$_{54}$: C 59.98, H 9.37; found: C 60.22, H 9.44.

Synthesis of the complex [Rh(cod)(PPh$_3$)(OSiMe$_3$)] (2)

Complex **2** was prepared in a similar way to complex **1**, except for the fact that PPh$_3$ (0.09 g, 0.34 mmol) was used instead of PCy$_3$. The yellow complex was obtained with the yield of 70%. ^{1}H NMR (C_6D_6) δ: 0.30 (s, 9H, -CH$_3$), 1.68 (m, 4H, -CH$_2$-), 2.18 (m, 4H, -CH$_2$-), 2.88 (m, 2H, -CH=), 5.62 (m, 2H, -CH=), 7.07 (m, 9H, -Ph), 7.75 (m, 6H, -Ph). ^{13}C NMR (C_6D_6) δ: 5.06 (-OSiMe$_3$, -CH$_3$), 29.02, 33.67 (cod, -CH$_2$-), 64.60, 64.78 (cod, -CH=), 103.18 (bs, cod, =CH-), 130.10, 131.57, 132.38, 135.23 (-Ph). ^{31}P NMR (C_6D_6) δ: 25.21. ^{29}Si NMR (C_6D_6) δ: 21.55. Anal. calcd. RhPSiOC$_{29}$H$_{36}$ for: C 61.92, H 6.45; found: C 62.18, H 6.37.

Synthesis of the complex [Rh(cod)(PCy$_3$)(OSi-*i*-Pr$_3$)] (3)

*Preparation of HOSi-*i*-Pr$_3$*

i-Pr$_3$SiCl (10 mL) was added to a water–ether mixture (H$_2$O (300 mL), ether (150 mL)) that was stirred with a magnetic stirrer for 24 h at r.t. Then the aqueous phase was removed and the ether solution was dried by addition of CaCl$_2$. After 24 h it was filtered off by a cannula system and the solvent was evaporated to dryness. The product was obtained with a yield of 87%.

*Preparation of NaOSi-*i*-Pr$_3$*

Thirty mL portions of anhydrous and deoxygenated THF and 1.20 g (53 mmol) of metallic Na were placed into a 50 mL double-necked round-bottomed flask equipped with a reflux condenser and an attachment for gas supply. Then 7.8 g of HOSiO-*i*-Pr$_3$ (45 mmol) was added over 30 min with constant stirring by a magnetic stirrer. After this time, the mixture was heated at a boiling point for 6 h. After the reaction, the contents of the flask were filtered off hot by a cannula to a Schlenk flask. Having cooled the contents, the solvent was evaporated and the product was dried in vacuum for about 3 h. It was obtained with a 90% yield. ^{1}H NMR (C_6D_6) δ: 1.02 (m, 3H, -CH=), 1.20 (d, 18H, -CH$_3$). Anal. calcd. for NaOSiC$_9$H$_{21}$: C 55.06, H 10.78; found: C 54.82, H 11.11.

Synthesis of the complex [Rh(Cl)(cod)(PCy$_3$)]

Portions of 0.22 g (0.8 mmol) of PCy$_3$ and 0.21 g (0.4 mmol) of [{Rh(cod)(μ-Cl)}$_2$] were placed in a Schlenk flask in an Ar atmosphere. Then 5 mL of dried and deoxygenated C_6H_6 was added and the mixture was stirred with a magnetic stirrer. After 2 h, C_6H_6 was evaporated and 5 mL of dried and deoxygenated C_5H_{12} was added. The precipitate was decanted three times by C_5H_{12}. The complex was dried in vacuum for about 3 h. It was obtained with a yield of 95%. ^{1}H NMR (C_6D_6) δ: 1.20–2.19 (m, 33H, -Cy), 2.32 (m, 4H, -CH$_2$-), 3.60 (m, 4H, -CH$_2$-), 5.72 (m, 4H, =CH-). ^{31}P NMR (C_6D_6) δ: 27.33 (d, $J_{\text{Rh-P}}$ = 350.7 Hz). Anal. calcd. for RhPClC$_{26}$H$_{45}$: C 59.26, H 8.61; found: C 59.82, H 8.84.

Synthesis of 3

Portions of 0.2 g (0.38 mmol) [Rh(cod)(PCy$_3$)(Cl)] and 0.08 g (0.42 mmol) NaOSi-*i*-Pr$_3$ were placed in a Schlenk flask in an Ar atmosphere. Then 5 mL of dried and deoxygenated C_6H_6 was added. The reaction was conducted for 24 h at r.t. After this time, C_6H_6 was evaporated and 8 mL of dried and deoxygenated C_5H_{12} was added. The entire mixture was filtered off by a cannula system. The solvent was evaporated from the obtained filtrate leaving a yellow solid. The complex was isolated with a yield of 85%. ^{1}H NMR (C_6D_6) δ: 1.22 (m, 3H, -CH=), 1.48 (d, 18H, -CH$_3$), 1.57–2.28 (m, 33H, -Cy), 2.30 (m, 4H, -CH$_2$-), 3.47 (m, 4H, -CH$_2$-), 5.28 (m, 4h, =CH-). ^{13}C NMR (C_6D_6) δ: 16.99–20.32, 26.49–34.04 (m, -OSi-*i*-Pr$_3$ + -Cy), 61.75, 61.93 (cod, -CH$_2$-), 97.92, 98.03, 98.09, 98.19 (cod, =CH-). ^{31}P NMR (C_6D_6) δ: 27.40 (d, $J_{\text{Rh-P}}$ = 149 Hz). ^{29}Si NMR (C_6D_6) δ: –21.51. Anal. calcd. for RhPSiOC$_{35}$H$_{66}$: C 63.23, H 10.01; found: C 62.91, H 10.11.

Synthesis of the complex [Rh(cod)(PCy$_3$){OSi(O-*t*-Bu)$_3$}] (4)

*Preparation of NaOSi(O-*t*-Bu)$_3$*

Fifty mL portions of anhydrous and deoxygenated THF and 0.35 g (15 mmol) of metallic Na were placed into a 100 mL double-necked round-bottomed flask equipped with a reflux condenser and an attachment for gas supply. Then 4 g of HOSi(O-*t*-Bu)$_3$ (15 mmol) was added and the mixture was heated at a boiling point for 4 h. After the reaction, the contents of the flask were filtered off hot by a cannula to a Schlenk flask. Having cooled the contents, the solvent was evaporated and the white solid was washed with diethyl ether (3 × 5 mL). The product was obtained with a 90% yield. ^{1}H NMR (C_6D_6) δ: 1.57 (s, 27H, -CH$_3$).

Preparation of 4

Complex **4** was prepared in a similar way to complex **3**, except for the fact that NaOSi(O-*t*-Bu)$_3$ (0.12 g, 0.42 mmol) was used instead of NaOSi-*i*-Pr$_3$. The yellow complex was obtained with the yield of 90%. ^{1}H NMR (C_6D_6) δ: 1.56 (s, 27H, -CH$_3$), 1.81 (m, 33H,-CH$_2$-), 2.50 (m, 4H, -CH$_2$-), 3.25 (m, 4H, -CH$_2$-), 5.05 (m, 4H, =CH-). ^{13}C NMR (C_6D_6) δ: 26.91, 27.83, 27.96, 28.78, 30.87, 31.68, 32.62, 33.58, 33.80,

Table 1. Crystal data.

Compound	**1**	**3**	**4**
Formula	$RhPSiOC_{29}H_{54}$	$RhPSiOC_{35}H_{66}$	$RhPSiO_4C_{38}H_{72}•0.5(C_5H_{12})$
Formula weight	580.69	664.85	791.00
Colour, shape	Yellow, block	Pale-yellow, plate	
T (K)	293(2)	293(2)	110(1)
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	P-1	P-1	$P2_1/c$
a (Å)	10.3468(5)	10.814(2)	9.9104(7)
b (Å)	10.6222(5)	11.696(2)	22.3863(13)
c (Å)	16.5714(7)	15.956(3)	19.2440(12)
α (°)	94.299(4)	80.06(3)	90
β (°)	93.677(3)	75.94(3)	96.002(5)
γ (°)	110.484(4)	68.51(3)	90
V (Å^3)	1693.35(13)	1813.7(6)	4246.0(5)
Z	2	2	4
d_x (Mg m^{-3})	1.139	1.217	1.237
μ (mm^{-1})	0.604	0.572	0.504
F(000)	620	716	1708
Crystal size (mm)	0.2 × 0.3 × 0.3	0.1 × 0.15 × 0.3	0.2 × 0.2 × 0.3
θ Range for data collection (°)	3.4–27	3.1–24	3.03–27
Reflections collected	14221	13858	36670
Independent reflections	7260	6343	9248
[R_{int}]	[0.028]	[0.040]	[0.085]
R ($I > 2\sigma(I)$)	0.0405	0.0468	0.0587
$wR2$ ($I > 2\sigma(I)$)	0.1040	0.0772	0.1184
R (all data)	0.0479	0.0870	0.0975
$wR2$ (all data)	0.1093	0.0854	0.1322
S	1.07	0.97	0.98
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.90/–0.51	0.73/–0.49	1.53/–0.97

33.94 (-Cy, $-CH_2-$), 33.43 ($-OSi(O\text{-}t\text{-}Bu_3)_3$, $-CH_3$), 61.33, 61.51 (cod, $-CH_2-$), 72.56 ($-OSi(O\text{-}t\text{-}Bu_3)_3$, $-OC(CH_3)_3$), 100.27, 100.37, 100.42, 100.53 (cod, =CH-). ^{31}P NMR (C_6D_6) δ: 27.03 (d, $J_{Rh\text{-}P}$ = 143 Hz). ^{29}Si NMR (C_6D_6) δ: –21.53. Anal. calcd. for $RhPSiO_4C_{38}H_{72}$: C 60.46, H 9.61; found: C 60.72, H 9.08.

Crystallization of the complexes

A portion of about 0.05 g of the complex and an amount of dry and deoxygenated C_5H_{12} sufficient to obtain a clear solution were placed in a Schlenk flask. Crystallization was conducted for 10–14 days at –15 °C. A few crystals selected under a microscope were placed in glass capillary tubes of 0.3 mm in diameter and subjected to X-ray diffraction study.

X-ray crystallography

X-ray diffraction data was collected, from the crystals sealed in glass capillaries, on a KUMA KM4CCD diffractometer (18) using graphite-monochromated MoKα radiation (λ = 0.71073 Å). Data collections were performed in six separate runs (a total of 782 frames for **1** and **4**, and 588 frames for **3**) to cover an appropriate part of the reflection sphere. The ω-scan was used, two reference frames were measured after every 50 frames, and they did not show any systematical changes neither in the peak position nor in their intensities. The unit-cell parameters were determined by least-squares treatment of the setting angles of 9625 (**1**), 5103 (**3**), and 5665 (**4**) highest-intensity reflections, chosen from the whole experiment. Lorentz and polarization effects were accounted for (19), and then data were corrected for absorption and merged with SORTAV (20). The structures were solved by direct methods with the SHELXS-97 program (21), and refined with full-matrix least-squares by SHELXL-97 (22). All non-hydrogen atoms, including those from the disordered solvent–pentane molecule in **3,** were refined anisotropically. The positions of hydrogen atoms were generated geometrically and they were refined as a “riding model”. The U_{iso} parameters of hydrogen atoms were set at 1.2 times U_{eq} of the appropriate carrier atom.

A summary of crystal data, data collection and refinement is given in Table 1.

Results and discussion

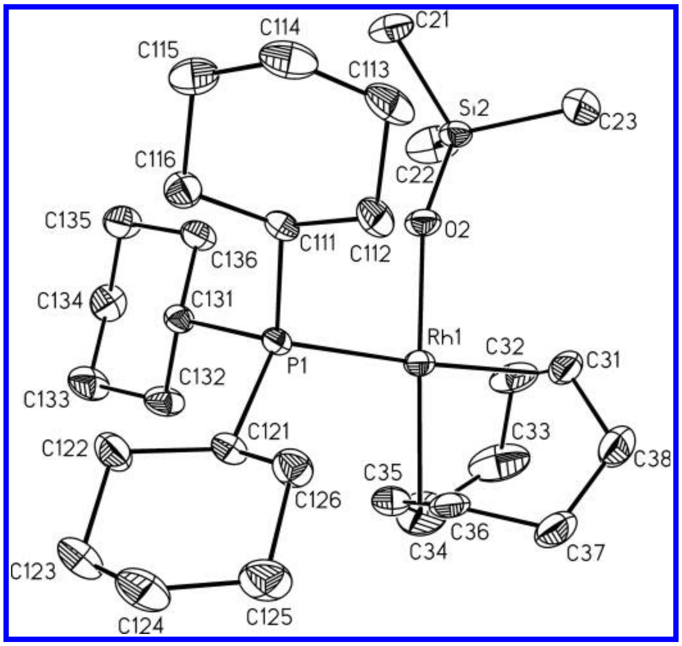
Two types of reactions were used for the synthesis of the rhodium-siloxide complexes:

$$[Rh(cod)(\mu\text{-}OSiMe_3)]_2 + 2PR_3' \xrightarrow[\text{room temp.}]{C_6H_6,\ 2\ h} 2[Rh(cod)(PR_3')(OSiMe_3)]$$

where R′ = Cy, Ph and

$$[Rh(cod)(PCy_3)(Cl)] + NaOSiR_3 \xrightarrow[\text{room temp.}]{C_6H_6,\ 24\ h} [Rh(cod)(PCy_3)(OSiR_3)] + NaCl$$

Fig. 1. Anisotropic displacement representation of complex **1** showing the labelling scheme. Displacement ellipsoids are shown at the 33% probability level and hydrogen atoms are omitted for clarity.



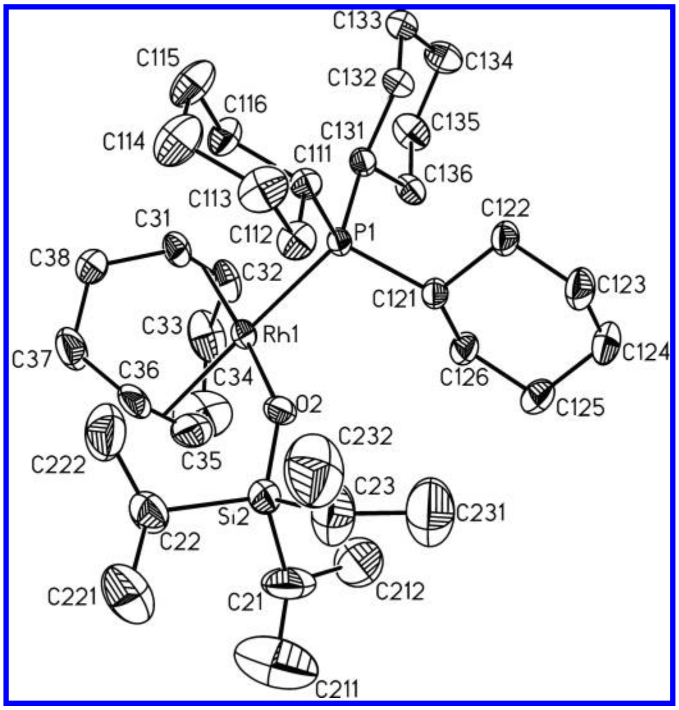
where R = *i*-Pr, O-*t*-Bu. All the rhodium-siloxide products were characterized by ^{1}H, ^{13}C, ^{31}P, and ^{29}Si NMR spectroscopy.

The molecular structures of complexes [Rh(cod)-(PCy$_3$)(OSiMe$_3$)] (**1**), [Rh(cod)(PCy)$_3$(OSi-*i*-Pr$_3$)] (**3**), and [Rh(cod)(PCy)$_3$(OSi(O-*t*-Bu)$_3$)] (**4**) with the atom-numbering scheme are depicted in Figs. 1, 2, and 3, respectively. Selected geometrical parameters are listed in Table 2.

In all three complexes the coordination of rhodium is square planar, providing that the middle points of the cyclooctadiene double bonds are regarded as the coordination sites X1 and X2. This is confirmed by the values of bond angles at rhodium (cf. Table 2) as well as by the least-squares calculation of the mean plane through five points: Rh, X1, X2, O, and P. Maximum deviation from this plane is 0.017(2) Å in **1**, 0.059(5) Å in **3**, and 0.005(2) Å in **4**. The cyclooctadiene double bonds are approximately perpendicular to the central coordination plane.

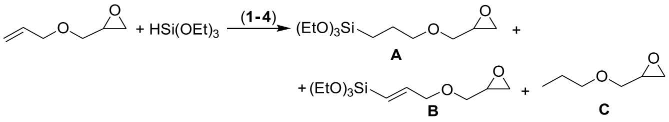
The bond lengths and angles are quite typical. All cyclohexyl rings are slightly distorted chairs, and the conformations of cyclooctadiene rings are close to a C_2 – twist-boat, the minimum energy conformation (23, 24). Despite these similarities there are some quite interesting differences in the overall conformation between alkyl-substituted siloxide complexes **1** and **3** and, on the other side, the alkoxy-substituted siloxide complex **4**. For example, the disposition of the substituents at the Si atom with respect to the O—Si bond can be described as +*sc*,–*sc*, *ap* (Rh-O-Si-C torsion angles approximately +60°, –60°, 180°) in **1** and **3**, while in **4** it is +*ac*,–*ac*, *sp* (Rh-O-Si-O values are close to +120°, –120°, 0°).

Fig. 2. Anisotropic displacement representation of complex **3** showing the labelling scheme. Displacement ellipsoids are shown at the 33% probability level and hydrogen atoms are omitted for clarity.



All the monomeric rhodium-siloxide complexes **1**–**4** were tested in the hydrosilylation of allyl glycidyl ether by triethoxysilane leading to glycidoxypropyltriethoxysilane, which is a commercially important silane coupling agent.

The reaction gives the hydrosilylation product (**A**) with very high yield accompanied by products of the dehydrogenative silylation (**B** + **C**) according to the following scheme:



The effect of the catalyst **1**–**4** concentrations as well as other conditions (temperature and time of the reaction) on the yield of the main product and by-products is compiled in Table 3. Dimeric [Rh(cod)(μ-OSiMe$_3$)]$_2$ (**5**), whose structure (7*b*) and catalytic activity in this reaction (13, 14) was reported previously, is used for comparison.

The order of the activity is as follows:

[Rh(cod)(μ-OSiMe$_3$)]$_2$ ≈ [Rh(cod)(PCy$_3$)(OSiMe$_3$)] ≥
5 **1**
[Rh(cod)(PPh$_3$)(OSiMe$_3$)] ≈ [Rh(cod)(PCy$_3$)(OSi-*i*-Pr$_3$)] >>
2 **3**
[Rh(cod)(PCy$_3$)(OSi(O-*t*-Bu)$_3$)] and can be explained by
4

increasing steric effects of the siloxy group influencing directly the rate of the hydrosilylation process as well as by a complex stereoelectronic effect of the trisubstituted phosphine (**1** ≥ **2**). The latter effect is a result of facile oxygenation and dissociation of PCy$_3$ vs. PPh$_3$ caused mainly by an

Fig. 3. Anisotropic displacement representation of complex **4** showing the labelling scheme. Displacement ellipsoids are shown at the 50% probability level and hydrogen atoms are omitted for clarity.

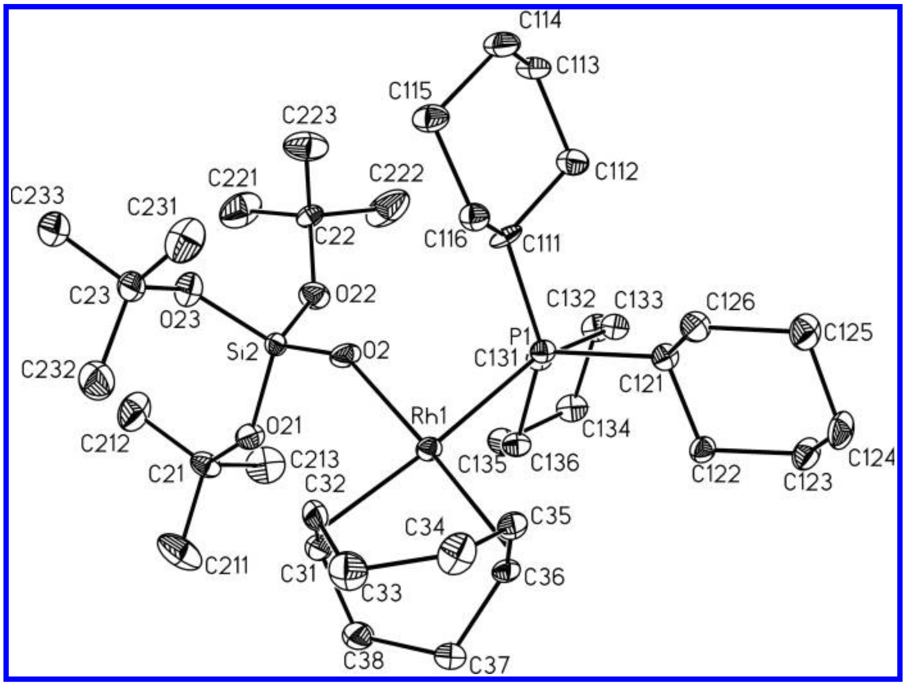


Table 2. Selected bond lengths (Å) and bond angles (°) (X1, X2 denote the middle points of the cyclooctadiene double bonds) with esds in parentheses.

Compound	1	3	4
Bond lengths (Å)			
Rh1—X1	2.086(3)	2.007(5)	2.083(5)
Rh1—X2	1.995(3)	2.110(6)	2.002(4)
Rh1—P1	2.3411(7)	2.3444(15)	2.3609(12)
RH1O2	2.030(2)	2.064(3)	2.065(3)
<P—C>	1.860(6)	1.854(11)	1.859(3)
O2—Si2	1.577(2)	1.593(4)	1.561(3)
Bond angles (°)			
X1-Rh1-X2	86.53(15)	85.6(3)	86.3(2)
X1-Rh1-P1	176.53(11)	178.5(2)	175.46(13)
X1-Rh1-O2	90.84(11)	92.0(2)	90.91(16)
X2-Rh1-P1	96.87(12)	95.08(16)	98.19(14)
X2-Rh1-O2	177.15(13)	174.9(2)	177.2(2)
P1-Rh1-O2	85.77(6)	87.48(10)	84.57(10)
Rh1-O2-Si2	152.70(13)	147.4(2)	143.6(2)

Table 3. The hydrosilylation of allyl glycidyl ether by triethoxysilane catalyzed by rhodium siloxide(I) complexes (**1**–**5**).

	Yield (%)	
Catalyst	**A**	**B + C**
Conditions: 25 °C, [Rh] = 5 × 10^{-3} mol L^{-1}, 15 min		
1	96	4
2	70	2
3	99	—
4	40	2
5*	90	10
Conditions: 25 °C, [Rh] = 10^{-3} mol L^{-1}, 4 h		
1	99	1
2	100	—
3	68	1
4	35	—
5*	98	2
Conditions: 40 °C, [Rh] = 10^{-4} mol L^{-1}, 24 h		
1	98	2
2, (**2***)	99 (98)	1 (2)
5*	99	1
Conditions: 60 °C, [Rh] = 5 × 10^{-5} mol L^{-1}, 1 h		
1, (**1**)	98 (50)	1 (–)
2, (**2**)	41 (4)	Traces
5	98	—

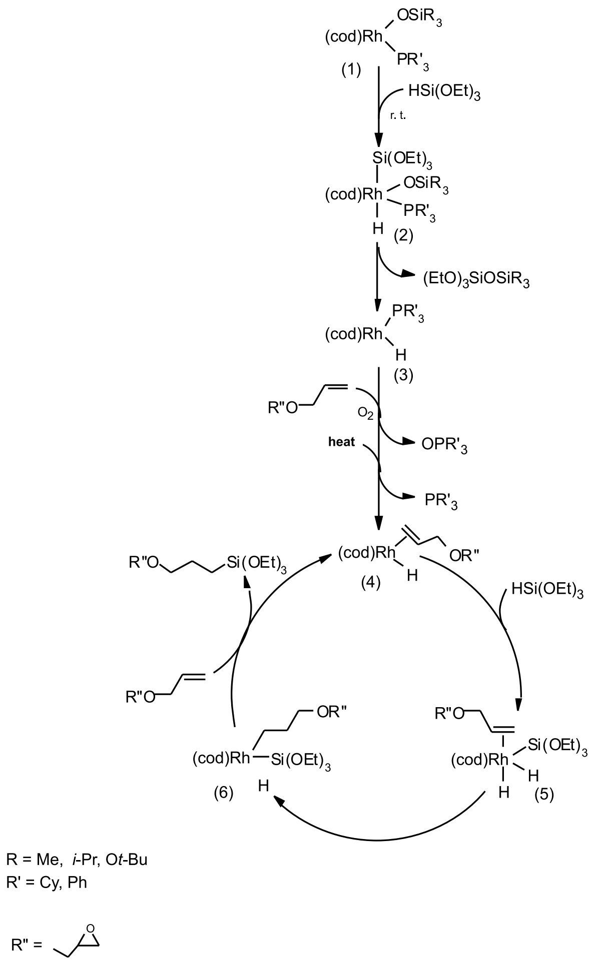
Note: All reactions carried out under the following conditions (except for those designated by *): [HSi(OEt)$_3$]:[ether] = 1:1.5, glass ampoules, air (* indicates reactions carried out in an argon atmosphere).

increase in electron-donor properties of the former phosphine.

Similarly to the hydrosilylation by dimeric rhodium siloxide **5** (25), monomeric phosphine rhodium siloxides (**1**–**4**) undergo an oxidative addition with triethoxysilane followed by elimination of disiloxane according to the mechanistic pathways proposed in Scheme 1.

Preliminary ^{1}H NMR study on the stoichiometric reactions of (1) with triethoxysilane performed in C_6D_6 in room temperature and in air, right away after mixing of the substrate, revealed the presence of several doublets at $\delta \sim -13.35$ and $J_{\text{Rh-H}} \sim 43$ in the spectra to be formed in the mixture of the penta-coordinate complexes similarly to the spectra observed previously in the system – dimeric complex **5**

Scheme 1. Catalysis of hydrosilylation by monomeric rhodium-siloxide phosphine complexes.



(HSi(OEt)$_3$) (7*a*). A rapid elimination of disiloxane $Me_3SiOSi(OEt)_3$ in the reaction mixture observed by GC–MS techniques is a direct evidence of reductive elimination of (2) to yield tetracoordinated complex (3) (see Scheme 1). This reaction occurs even at room temperature.

The very efficient oxygenation of phosphine observed in air vs. dissociation of phosphine in oxygen-free conditions, particularly observed at enhanced temperature (60 °C) (a formation of OPR_3' vs. PR_3' is detected by ^{31}P NMR), is proposed to be responsible for generation of [Rh(cod)(H)(alkene)]. Although no direct evidence was found for (4) by NMR, this 16e hydride rhodium complex with an already coordinated molecule of alkene seems to be a key intermediate in all catalytic transformations involving hydrosilanes, e.g., hydrosilylation, dehydrogenative silylation, silylformylation, etc. The variant of the Chalk and Harrod mechanism (26) involving the insertion of allyl ether into the Rh—Si bond, which could account for slight side reactions of dehydrogenative silylation observed (1% to 2%), is omitted from the scheme for clarity.

Conclusions

Four new monomeric, square-planar rhodium siloxide complexes of the general formula $[Rh(cod)(PR_3')(OSiR_3)]$ where R′ = Cy, Ph, R = Me, *i*-Pr, O-*t*-Bu were synthesized and three of them were structurally characterized.[3]

The complex (**1**) ($[Rh(cod)(PCy)_3(OSiMe_3)]$) appeared to be a very efficient catalyst for hydrosilylation of allyl glycidyl ether occurring in air. All catalytic data and stoichiometric reactivities of (**1**) with triethoxysilane are consistent with a mechanism involving a generation of tetracoordinated Rh-H species (responsible for catalysis).

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References

1. For reviews: (*a*) F.R. Hartley. Supported metal complexes. Reidel, Boston. 1985; (*b*) Y. Iwasawa. (*Editor*). Tailored metal catalysts. Reidel, Boston. 1986; (*c*) P.T. Wolczanski. Polyhedron, **14**, 3335 (1995); (*d*) B. Marciniec and H. Maciejewski. Coord. Chem. Rev. **223**, 301 (2001).
2. A.N. Kornev, T.A. Chesnokova, V.V. Semenov, E.V. Zhezlova, L.N. Zakhonov, L.G. Klapshina, G.A. Domrachev, and V.S. Rusakov. J. Organometal. Chem. **547**, 113 (1997).
3. (*a*) G.A. Siegel, R.A. Bartlett, D. Decker, M.M. Olmsted, and P.P. Power. Inorg. Chem. **26**, 1773 (1987); (*b*) I. Kownacki, M. Kubicki, and B. Marciniec. Polyhedron, **20**, 3015 (2001).
4. A.K. McMullen, T.D. Tilley, A.L. Rheingold, and S.J. Geib. Inorg. Chem. **29**, 2228 (1990).
5. (*a*) J.T. Poulton, K. Folting, W.E. Streib, and K.G. Caulton. Inorg. Chem. **31,** 3190 (1992); (*b*) J. Puga, T.P. Fehlner, B.C. Gates, D. Braga, and F. Greponi. Inorg. Chem. **29**, 2376 (1990); (*c*) T.J. Johnson, K. Folting, W.E. Streib, J.D. Martin, J.C. Huffman, S.A. Jackson, O. Eisenstein, and K.G. Caulton. Inorg. Chem. **34**, 488 (1995).
6. (*a*) G. Palyi, C. Zucchi, U. Ugo, R. Psaro, A. Sironi, and A.J. Vizi-Orosz. J. Mol. Catal. **74**, 51 (1992); (*b*) A.J. Vizi-Orosz, R. Ugo, R. Psaro, A. Sironi, M. Moret, C. Zucchi, F. Ghelti, and G. Palyi. Inorg. Chem. **33**, 4600 (1994).
7. (*a*) B. Marciniec and P. Krzyżanowski. J. Organometal. Chem. **493**, 261 (1995); (*b*) P. Krzyżanowski, M. Kubicki, and B. Marciniec. Polyhedron, **15**, 1 (1996); (*c*) B. Marciniec, P. Krzyżanowski, and M. Kubicki. Polyhedron, **15**, 4233 (1996).
8. L. Marko and A.J. Vizi-Orosz. Trans. Met. Chem. **7**, 216 (1982).
9. (*a*) F.J. Feher and T.L. Tajima. J. Am. Chem. Soc. **116**, 2145 (1994); (*b*) F.J. Feherand and R.L. Blanski. Organometallics, **12**, 958 (1993).

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[3] Supplementary data may be purchased from the Directory of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada (http://www.nrc.ca/cisti/irm/unpub_e.shtml for information on ordering electronically). CCDC 205459 (**1**), 205460 (**3**), and 205461 (**4**) contain the crystallographic data for this manuscript. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

10. (*a*) A. Fukuoka, A. Sato, K. Kodama, M. Hiramo, and S. Komiya. Inorg. Chim. Acta, **294**, 266 (1999); (*b*) J. Pfeiffer, G. Kickelbick, and G. Schubert. Organometallics, **19**, 957 (2000); (*c*) H. Schmidbaur and J. Adlkofer. Chem. Ber. **107**, 3680 (1974).
11. J.L. Herde, J.V. Lambert, and C.V. Senoff. Inorg. Synth. **15**, 18 (1974).
12. B. Marciniec, P. Krzyżanowski, E. Walczuk-Guściora, and W. Duczmal. J. Mol. Catal. **144**, 263 (1999).
13. B. Marciniec, E. Walczuk, P. Błażejewska-Chadyniak, D. Chadyniak, M. Kujawa-Welten, and S. Krompiec. *In* Organosilicon chemistry V — From molecules to materials. Accepted for publication.
14. (*a*) B. Marciniec, P. Błażejewska-Chadyniak, E. Walczuk-Guściora, and M. Kujawa-Welten. Pol. Patent P-351 449, 2001; (*b*) B. Marciniec, D. Chadyniak, P. Pawluć, H. Maciejewski, and P. Błażejewska-Chadyniak. Pol. Patent P-351 451, 2001.
15. (*a*) B. Marciniec, E. Walczuk-Guściora, and P. Błażejewska-Chadyniak. J. Mol. Catal. **160**, 165 (2000); (*b*) B. Marciniec, E. Walczuk-Guściora, and C. Pietraszuk. Organometallics, **20**, 3423 (2001).
16. G. Giordano and R.H. Crabtree. Inorg. Synth. **19**, 218 (1979).
17. M.A. Kulzick, R.T. Price, R.A. Andersen, and E.L. Muetterties. J. Organometal. Chem. **333**, 105 (1987).
18. CRYSALIS. Version 162 [computer program]. KUMA Diffraction, Wrocław, Poland. 2000.
19. CRYSALISRED. Version 162 [computer program]. KUMA Diffraction, Wrocław, Poland. 2000.
20. R.H. Blessing. J. Appl. Crystallogr. **22**, 396 (1989).
21. G.M. Sheldrick. Acta Crystallogr. **A46**, 467 (1990).
22. G.M. Sheldrick. SHELXL97 [computer program]. University of Göttingen, Göttingen, Germany. 1997.
23. F.A.L. Anet and L. Kozerski. J. Am. Chem. Soc. **95**, 3407 (1973).
24. D.N.J. White and M.J. Bovill. J. Chem. Soc., Perkin Trans. 2, 1610 (1977).
25. B. Marciniec, I. Kownacki, M. Kubicki, P. Krzyzanowski, E. Walczuk, and P. Błażejewska-Chadyniak. *In* Perspectives in organometallic chemistry. RSC, Cambridge. 2003. p. 253.
26. A.J. Chalk and J.F. Harrod. J. Am. Chem. Soc. **87**, 16 (1965).

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3. Bogdan Marciniec, Ireneusz Kownacki, Adrian Franczyk, Maciej Kubicki. 2011. Silsesquioxyl rhodium(i) complexes - synthesis, structure and catalytic activity. *Dalton Transactions* **40**:18, 5073. [CrossRef]
4. Sophie Putzien, Oskar Nuyken, Fritz E. Kühn. 2010. Functionalized polysilalkylene siloxanes (polycarbosiloxanes) by hydrosilylation—Catalysis and synthesis. *Progress in Polymer Science* **35**:6, 687-713. [CrossRef]
5. Hong Zhao, Lingfang Zha, Mingzhong Cai. 2010. Synthesis of an MCM-41-supported mercapto rhodium complex and its catalytic behavior in the hydrosilylation of olefins with triethoxysilane. *Reaction Kinetics, Mechanisms and Catalysis* . [CrossRef]
6. Szymon Rogalski, Cezary Pietraszuk, Bogdan Marciniec. 2009. Synthesis of siloxy-modified second generation Hoveyda–Grubbs catalysts and their catalytic activity. *Journal of Organometallic Chemistry* **694**:24, 3918-3922. [CrossRef]
7. Bogdan Marciniec, Karol Szubert, Marek J. Potrzebowski, Ireneusz Kownacki, Hieronim Maciejewski. 2009. Catalysis of Hydrosilylation by Well-Defined Surface Rhodium Siloxide Phosphine Complexes. *ChemCatChem* **1**:2, 304-310. [CrossRef]
8. Bogdan Marciniec, Karol Szubert, Ryszard Fiedorow, Ireneusz Kownacki, Marek J. Potrzebowski, Michał Dutkiewicz, Adrian Franczyk. 2009. Catalysis of hydrosilylation by well-defined rhodium siloxide complexes immobilized on silica. *Journal of Molecular Catalysis A: Chemical* **310**:1-2, 9-16. [CrossRef]
9. Jianbo Zhao, Bing Xie, Guoqing Wang, Shiqiu Song, Yu'an Sun. 2009. Catalytic synthesis of 3-glycidoxypropyltriethoxysilane over silica-supported chitosan-platinum complex. *Reaction Kinetics and Catalysis Letters* **96**:1, 101-108. [CrossRef]
10. Hieronim Maciejewski, Karol Szubert, Bogdan Marciniec, Juliusz Pernak. 2009. Hydrosilylation of functionalised olefins catalysed by rhodium siloxide complexes in ionic liquids. *Green Chemistry* **11**:7, 1045. [CrossRef]
11. Ireneusz Kownacki, Maciej Kubicki, Karol Szubert, Bogdan Marciniec. 2008. Synthesis, structure and catalytic activity of the first iridium(I) siloxide versus chloride complexes with 1,3-mesitylimidazolin-2-ylidene ligand. *Journal of Organometallic Chemistry* **693**:2, 321-328. [CrossRef]
12. Aroop K. RoyA Review of Recent Progress in Catalyzed Homogeneous Hydrosilation (Hydrosilylation) **55**, 1-59. [CrossRef]
13. Ireneusz Kownacki, Bogdan Marciniec, Anna Macina, Sławomir Rubinsztajn, David Lamb. 2007. Catalytic activity of iridium siloxide complexes in cross-linking of silicones by hydrosilylation. *Applied Catalysis A: General* **317**:1, 53-57. [CrossRef]
14. Hieronim Maciejewski, Agata Wawrzyńczak, Michał Dutkiewicz, Ryszard Fiedorow. 2006. Silicone waxes—synthesis via hydrosilylation in homo- and heterogeneous systems. *Journal of Molecular Catalysis A: Chemical* **257**:1-2, 141-148. [CrossRef]
15. Bogdan Marciniec, Hieronim Maciejewski, Karol Szubert, Magdalena Kurdykowska. 2006. Modification of (Poly)Siloxanes via Hydrosilylation Catalyzed by Rhodium Complex in Ionic Liquids. *Monatshefte für Chemie - Chemical Monthly* **137**:5, 605-611. [CrossRef]
16. Ewa Mieczyńska, Anna M. Trzeciak, Józef J. Ziółkowski, Ireneusz Kownacki, Bogdan Marciniec. 2005. Hydroformylation and related reactions of vinylsilanes catalyzed by siloxide complexes of rhodium(I) and iridium(I). *Journal of Molecular Catalysis A: Chemical* **237**:1-2, 246-253. [CrossRef]
17. Piotr Pawluc, Bogdan Marciniec, Ireneusz Kownacki, Hieronim Maciejewski. 2005. Synthesis of phenylene–silylene–ethylene polymers via transition metal complex catalyzed hydrosilylation polymerization. *Applied Organometallic Chemistry* **19**:1, 49-54. [CrossRef]