

DOI:10.1002/ejic.201402212

Ru⁰-Catalyzed Coupling of Vinylboronates with Silanols, Disilanols, and Disiloxanediols: a Selective Route to Borasiloxanes

Dawid Frąckowiak,^[a] Jędrzej Walkowiak,^[b] Grzegorz Hreczycho,^[a] and Bogdan Marciniec^{*[a,b]}

Keywords: Homogeneous catalysis / Borasiloxane / Borylative coupling / Ruthenium / Silanol / Reaction mechanisms

A new highly selective method for the synthesis of borasiloxanes through the O-borylation of silanols, disilanols, and disiloxanediols with vinylboronates in the presence of $\rm Ru^0$ complexes (mainly $\rm Ru_3CO_{12}$) is described. The method leads to the formation of special compounds with a B–O–Si inorganic

Introduction

The silvlative coupling of olefins with vinyl-substituted organosilicon compounds, which we developed in the last two decades as a new, effective catalytic activation of the =C-H bond of olefins and the =C-Si bond of organosilicon compounds (generally occurring in the presence of complexes containing [M]-H and [M]-Si bonds),^[1] has been recently found to be general and is also exhibited by vinyl derivatives of other p-block elements (e.g., boron^[2] and germanium^[3]). This mode of catalytic reactivity has also been successfully extended to the catalytic activation of other sp² carbon atoms, that is, =Caryl-H bonds and sp-hybridized carbon-hydrogen bonds^[4], as well as of the O-H bonds of silanols, alcohols, and boronic acids.^[5,6] Such reactions, catalyzed predominantly by Ru^{II} complexes containing Ru-H bonds, proceed according to the general equation given in Scheme 1.



Scheme 1. General protocol for the activation of C–H and O–H bonds by vinylmetalloids and other hydrogen donors.

Our recent reports have proved the successful use of vinylmetalloid (Si, B, Ge) compounds as new hydrogen acframework. When Ru^0 complexes are used as a catalyst, no vinylboronate homocoupling is observed. A mechanism for this transformation is proposed on the basis of stoichiometric reactions of Ru^0 with triethylsilanol and vinylboronate.

ceptors for *O*-metallation of silanols.^[5,6a] However, some of the reactions catalyzed effectively by Ru–H complexes are not entirely selective (depending on the substrates and catalysts) and yield small amounts of products of the vinylmetalloid homocoupling.

Borasiloxanes are a class of siloxanes with the B-O-Si moiety as a basic unit in their structure. Borasiloxane units are thermally robust but prone to hydrolysis, the extent of which depends on the boron content and the type of substituents at the silicon atoms.^[7] They can be represented by linear oligomeric and polymeric derivatives^[8] as well as cyclic and cage structures.^[9] Borasiloxanes possess a stable inorganic framework, as they are analogues to borosilicates, and this makes them ideal precursors for hybrid organicinorganic materials. Such materials have many potential applications, for example, in the preparation of conjugated polymer sensors based on borasiloxane cages assembled by electrode polymerization of eight-membered borasiloxane rings^[10] and in the synthesis of precursors for supramolecular motifs and networks.^[11] Moreover, borasiloxanes are commonly used as polymer additives for hydraulic fluids, lubricants, antifoaming agents, sealants, and components of heat-resistant adhesives, among many other applications (see ref.^[7]).

Most methods for the synthesis of borasiloxanes are based on condensation reactions of chloroboranes or boronic acids with silanols, silanolates, and chlorosilanes under various conditions (recently, the mechanochemical synthesis of cyclic borasiloxanes has been reported^[12]), often leading to the evolution of dangerous and corrosive byproducts (e.g., HCl) or using air- and moisture-sensitive substrates (namely chloroboranes). Our group has developed a catalytic transformation mediated by hydridoruthenium complexes, which leads to borasiloxanes through

[[]a] Adam Mickiewicz University in Poznan, Faculty of Chemistry, Umultowska 89b, 61-614 Poznan, Poland E-mail: bogdan.marciniec@amu.edu.pl http://www.metalorg.amu.edu.pl/
[b] Adam Mickiewicz University, Centre for Advanced Technologies.

Grunwaldzka 6, 60-780 Poznan, Poland





the coupling of vinylboronates with silanols (see Scheme 1 and ref.^[6a]).

The results from our previous report on the reaction of silanols with vinylgermanes, which is catalyzed selectively by the complex Ru_3CO_{12} ,^[13] prompted us to make use of this general feature of Ru^0 complexes (lack of activity in the homocoupling of vinylmetalloids) in the *O*-metallation of silanols, silanediols, and siloxanediols by vinylboronates. Moreover, we wanted to extend the scope of substrates for the *O*-borylation reaction with dihydroxysilicon derivatives, such as silanediols and siloxanediols. These processes can serve as versatile methods for the synthesis of organometallic species based on borasiloxane (-B-O-Si-O-B-) inorganic frameworks with desired well-defined structures for the precursors of new hybrid inorganic–organic materials.

Results and Discussion

For all the reactions, we chose three vinylboronates (i.e., vinylboronate esters) (Figure 1). Compound I proved to be active in the homocoupling reaction even in the presence of $RuHCl(CO)(PPh_3)_3$ (which was previously reported to be inactive in this process with other vinylboronates).



Figure 1. Vinylboronates: substrates for the O-borylation reaction.

Four Ru^0 complexes, $Ru(CO)_3(PPh_3)_2$, $Ru(CO_2)(PPh_3)_2$, $Ru_3(CO)_{12}$, and Ru(COD)(COT), were tentatively screened in catalytic tests. Only the latter two showed activity in the *O*-metallation reaction (Table 1). The activity of Ru(COD)-(COT) in the coupling reaction was lower than that of $Ru_3(CO)_{12}$. Our recent studies recognized $Ru_3(CO)_{12}$ as an

Table 1. Catalyst screening in a model reaction of vinylboronate (ViB) I with $(Me_3SiO)_3SiOH$.^[a]

Entry	Catalyst	Silanol conversion [%] ^[b]
1	$Ru_3(CO)_{12}$	100
2	$Ru(CO)_2(PPh_3)_3$	0
3	$Ru(CO)_3(PPh_3)_2$	0
4	Ru(COD)(COT)	75

[a] Reaction conditions: [ViB]/[SiOH]/[Ru⁰] = 2:1:0.02, toluene or 1,4-dioxane, 110 °C, 24 h, in a sealed glass tube or Schlenk reactor. [b] Conversion determined by GC. effective and selective catalyst in the *O*-germylation of silanols and proved that it has virtually no activity towards the homocoupling of vinylmetalloids (see ref.^[13]).

To check the efficiency of the $Ru_3(CO)_{12}$ -catalyzed *O*borylation process, a number of silanols, silanediols, and siloxanediols were tested. The reaction catalyzed by $Ru_3(CO)_{12}$ proceeded through the activation of the O–H bond and the elimination of ethylene (Scheme 2).

$$\begin{array}{c} R \\ R - \stackrel{O}{Si-O} \stackrel{!}{\cdot} H \\ R \end{array} + \stackrel{O}{\searrow} \stackrel{O}{\longrightarrow} \frac{2 \text{ mol-\% Ru}_3(CO)_{12}}{\underset{110 \text{ °C}, 24 \text{ h}}{\text{ mol-\% Ru}_3(CO)_{12}}} R \stackrel{R}{-\stackrel{O}{Si-O} - \stackrel{O}{B} \\ \stackrel{O}{\longrightarrow} + =$$

Scheme 2. General reaction protocol for the *O*-borylation of silanols.

Vinylboronates proved to be much more reactive substrates in the *O*-metallation process than vinylgermanes. With the former, the reaction proceeds smoothly with lower catalyst loading (2 mol-%), at slightly lower temperature (110 °C), and a twofold excess of vinylboronate, giving quantitative conversion of silanols to afford borasiloxanes as the only products in high yields (see Table 2).

Table 2. O-Borylation of silanols catalyzed by Ru₃(CO)₁₂.^[a]

Entry	Vinylboronate (ViB)	Silanol	Yield [%]
1	Ι	(Me ₃ SiO) ₃ SiOH (A)	90 ^[b]
2	II	(Me ₃ SiO) ₃ SiOH	100 ^[c]
3	III	(Me ₃ SiO) ₃ SiOH	100 ^[c]
4	I	$Et_3SiOH(\mathbf{B})$	90 ^[b]
5	II	Et ₃ SiOH	100 ^[c]
6	III	Et ₃ SiOH	100 ^[c]
7	Ι	<i>i</i> Pr ₃ SiOH (C)	91 ^[b]
8	II	<i>i</i> Pr ₃ SiOH	100 ^[c]
9	III	<i>i</i> Pr ₃ SiOH	100 ^[c]

[a] Reaction conditions: [ViB]/[SiOH]/[Ru₃(CO)₁₂] = 2:1:0.02, toluene or 1,4-dioxane, 110 °C, 24 h, in a sealed glass tube or Schlenk reactor. [b] Isolated yield. [c] Yield based on GC.

To obtain more complex borasiloxanes, we applied the same conditions to the *O*-borylation of selected silanediols, disilanols, and siloxanediols (Scheme 3, Table 3). A catalytic screening of vinylboronates in the presence of a hydridoruthenium catalyst in a model reaction with diisopropylsilanediol showed the formation of diborylethenes as the main products and small amounts of borasiloxanes. Therefore, dodecacarbonyltriruthenium appeared to be an ideal solution for the selective synthesis of borasiloxanes. Because of the low solubility of silicon substrates in toluene, all reactions were carried out in 1,4-dioxane. Among the selected substrates, only diethylsilanediol and 1,4-bis(hydroxydimethylsilyl)benzene were unreactive towards *O*-borylation, and mainly cyclosiloxanes and polysiloxanes, respectively, were formed. On the other hand, the reaction of vinyl-

$$H \stackrel{\circ}{\stackrel{\circ}{_{\scriptstyle +}}} O \stackrel{\circ}{\stackrel{\circ}{_{\scriptstyle +}}} O \stackrel{\circ}{\stackrel{\circ}{_{\scriptstyle +}}} H + 2 \stackrel{\circ}{\stackrel{\circ}{_{\scriptstyle +}}} \stackrel{\circ}{\stackrel{\circ}{_{\scriptstyle +}}} O \stackrel{\circ}{\longrightarrow} \frac{4 \text{ mol-\% Ru}_3(CO)_{12}}{\text{dioxane, 110 °C, 24 h}} \stackrel{\circ}{\longrightarrow} O \stackrel{\circ}{\stackrel{\circ}{\underset{\scriptstyle +}}} O \stackrel{\circ}{\stackrel{\circ}{\underset{\scriptstyle +}}} \stackrel{\circ}{\longrightarrow} O \stackrel{\circ}{\xrightarrow} + 2 =$$

Scheme 3. General reaction protocol for the O-borylation of silanediols and siloxanediols.



Table 3. O-Borylation of silanediols and disiloxanediol.[a]

Entry	Vinylboronate (ViB)	Silanediol or disiloxanediol	Yield [%] ^[b]
1	Ι	$Et_2Si(OH)_2$	0
2	Ι	1,4-bis(hydroxydimethylsilyl)benzene	0
3	Ι	$i \Pr_2 Si(OH)_2$ (D)	90
4	II	$i Pr_2 Si(OH)_2$ (E)	89
5	III	$i \Pr_2 Si(OH)_2$ (F)	85
6	Ι	$Ph_2Si(OH)_2$	71/29 ^[c]
7	Π	$Ph_2Si(OH)_2$	68/32 ^[c]
8	III	$Ph_2Si(OH)_2$	60/40 ^[c]
9	Ι	$HOSi(iPr)_2OSi(iPr)_2OH$ (G)	85
10	Π	HOSi(<i>i</i> Pr) ₂ OSi(<i>i</i> Pr) ₂ OH (H)	80
11	III	$HOSi(iPr)_2OSi(iPr)_2OH$ (i)	78

[a] Reaction conditions: $[ViB]/[R_2Si(OH)_2]/[Ru_3(CO)_{12}] = 4:1:0.04$, 1,4-dioxane, 110 °C, 24 h, in a sealed glass tube or Schlenk reactor. [b] Isolated yields. [c] Monosubstituted product, determined by GC.

boronates with diisopropylsilanediol gave disubstituted products exclusively in high yields with complete conversion of silanediol. However, when diphenylsilanediol was used, only a mixture of mono- and disubstituted products was obtained. Even with a larger excess of vinylboronates, we could not achieve complete conversion of silanediol to disubstituted borasiloxane.

The functionalization of 1,1,3,3-tetraisopropyldisiloxane-1,3-diol gave full conversion of disiloxanediol to the desired products. In all cases, no products of vinylboronate homocoupling were observed. New borasiloxanes were isolated (see Table 3) and characterized spectroscopically (¹H, ¹³C NMR) and by GC–MS. Non-isolated compounds were identified by GC–MS. To establish a mechanism for the ruthenium(0)-catalyzed O-borylation, we examined an equimolar stoichiometric reaction between triethylsilanol and Ru₃(CO)₁₂, which was carried out in deuterated benzene (Scheme 4) and monitored by ¹H NMR spectroscopy. Triethylsilanol was selected, because its carbonylruthenium derivative is well



Scheme 4. Stoichiometric reaction of Et₃SiOH with Ru₃(CO)₁₂.



Figure 2. Stoichiometric reaction of $Ru_3(CO)_{12}$ with Et_3SiOH (bottom) and bridged hydrido-siloxido complex with vinylboronic pinacol ester (top).



characterized^[14] and appeared to be a potential intermediate species in our transformation.

After heating of the reaction mixture at 100 °C for 12 h in C₆D₆ in a closed Young NMR tube, a new signal of low intensity appeared at $\delta = -12.3$ ppm, which can be arguably assigned to the presence of a bridged hydrido-siloxido complex (μ -H)Ru₃(CO)₁₀(μ -OSiEt₃) – the product of an oxidative addition of silanol to Ru₃(CO)₁₂. The chemical shift of this complex provided in the literature is $\delta = -12.08$ ppm (in CDCl₃). To prove that this complex is an exact catalytic species, we added an equimolar amount of vinylboronate to the reaction mixture. Monitoring by ¹H NMR spectroscopy showed the disappearance of the signal at $\delta = -12.3$ ppm, and the evolution of molecular ethylene was observed (singlet at $\delta = 5.25$ ppm) (Figure 2, Scheme 5).



Scheme 5. Stoichiometric reaction of a bridged hydrido-siloxido complex with vinylboronic pinacol ester.

The GC–MS analysis of the reaction mixture showed only one product, the expected borasiloxane, and the mass spectrum displayed a molecular ion with m/z = 258, which is in agreement with the analysis of an isolated compound.

On the basis of the experimental data, we propose a mechanism of the catalytic borylation of silanols in the presence of $Ru_3(CO)_{12}$ (Scheme 6).



Scheme 6. Proposed catalytic cycle for the $Ru_3(CO)_{12}$ -catalyzed *O*-borylation of silanols. Pin = pinacol.

The catalytic cycle involves the oxidative addition of silanol to $Ru_3(CO)_{12}$ and the formation of a cluster hydridosiloxido complex. This complex undergoes insertion of vinylboronate to the Ru–H bond with a subsequent β -boryl transfer and the elimination of molecular ethylene. The obtained borylsiloxido complex undergoes reductive elimination, and a borasiloxane is formed.

Conclusions

We report a new catalytic route for the effective *O*-borylation of silanols, silanediols, and disiloxanediols with vinylboronate esters in the presence of $Ru_3(CO)_{12}$ [contrary to hydridoruthenium(II) catalysts] for the highly selective synthesis of borasiloxanes, compounds with a B–O–Si inorganic framework. This process can be extended to the synthesis of hybrid borasiloxane polymers. The *O*-borylation of dihydroxy organosilicon compounds with divinyl-substituted boronates is now under investigation.

Catalytic and stoichiometric studies of an Ru^0 complex with silanols and vinylboronate allowed us to propose a rational mechanism for the *O*-borylation process.

Experimental Section

General: ¹H NMR (300 MHz) and ¹³C NMR (75 MHz) spectra were recorded with a Varian XL 300 MHz spectrometer in CDCl₃ (or C_6D_6) solution. Chemical shifts (δ) are reported in ppm with reference to the residual solvent peak (CHCl₃) for ¹H and ¹³C. Gas chromatographic (GC) analyses were performed with a Varian 3300 with a DB-5 fused silica capillary column (30 m \times 0.15 mm) and a thermal conductivity detector (TCD). Mass spectra of the monomers and products were obtained by GC-MS analyses [Varian Saturn 2100 T, equipped with a BD-5 capillary column (30 m) and an ion-trap detector]. Elemental analyses were carried out with a Vario EL III instrument (Elementar GmbH). Column chromatography was performed with silica gel 60 (70-230 mesh, Fluka). Toluene was dried by distillation from sodium/potassium alloy; dioxane was purified and distilled from Na/benzophenone; hexane was distilled from calcium hydride. All solvents were purified under argon. Dichlorodiethylsilane, chlorotriisopropylsilane, dichlorodiisopropylsilane, chlorotris(trimethylsiloxy)silane and 1,4-bis(hydroxydimethylsilyl)benzene were purchased from ABCR and used as received. Ru₃(CO)₁₂, diphenylsilanediol, tributylchlorostannane, triethylamine and 4,4,5,5-tetramethyl-2-vinyl-1,3,2-dioxaborolane (I) were purchased from Sigma-Aldrich. Diethylsilanediol,^[15] diisopropylsilanediol,^[16] and 1,3-dihydroxy-1,1,3,3-tetraisopropyldisiloxane^[17] were prepared according to methods reported in the literature. 2-Vinyl-1,3,2-dioxaborinane (II) and 2-vinyl-1,3,2-dioxaborolane (III) were synthesized according to literature procedures with some modifications.^[18] Diphenylsilanediol was purified by recrystallization. Triethylamine was dried with CaH₂.

General Procedure for the *O*-Borylation Reaction: $Ru_3(CO)_{12}$ (2 mol-% for silanols, 4 mol-% for silanediols and disiloxanediol) was placed in a glass ampoule or small Schlenk reactor, and a small portion of toluene or dioxane was added. Then, the Si–OH substrate, vinylboronate, and the rest of the solvent were added. The reaction mixture was heated at 110 °C in an oil bath for for 24 h. The progress of the reaction was completed, all volatiles were removed under reduced pressure, and the crude substrate was purified from the catalyst on a short silica column with hexane or hexane/ethyl acetate (1:1) as eluents.



Procedure for the Stoichiometric Reactions: A Young NMR tube filled with argon was charged with C_6D_6 (0.5 mL), triethylsilanol (0.01 mL), and $Ru_3(CO)_{12}$ (18 mg). The mixture was heated to 100 °C for 12 h, and then (after NMR examination) 4,4,5,5-tet-ramethyl-2-vinyl-1,3,2-dioxaborolane was added, and the resulting mixture was heated at 100 °C for additional 12 h. The resulting mixture was examined by ¹H NMR spectroscopy and GC–MS analyses.

Analytical Data for Selected Products

(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)tris(trimethylsilyl) Orthosilicate (A): ¹H NMR: $\delta = 0.11$ (s, 27 H), 1.22 (s, 12 H) ppm. ¹³C NMR: $\delta = 1.4$, 24.7, 82.2 ppm. C₁₅H₃₉BO₆Si₄ (438.19): calcd. C 41.07, H 8.96, B 2.46, O 21.89, Si 25.61; found C 40.97, H 8.92, B 2.40, O 21.82, Si 25.56. MS (EI): *m*/*z* (%) = 423 (100), 365 (5), 307 (35), 281 (37), 267 (65).

Triethyl[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy]silane (B): ¹H NMR: δ = 0.62 (t, 9 H), 0.94 (q, 6 H), 1.21 (s, 12 H) ppm. ¹³C NMR: δ = 5.3, 6.4, 24.5, 81.9 ppm. C₁₂H₂₇BO₃Si (258.18): calcd. C 55.81, H 10.54, B 4.19, O 18.59, Si 10.88; found C 55.76, H 10.49, B 4.13, O 18.52, Si 10.79. MS (EI): *m*/*z* (%) = 243 (20), 229 (5), 187 (45), 147 (90), 83 (100).

Triisopropyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxylsilane (C): ¹H NMR (300 MHz, CDCl₃): δ = 1.06 (br., 21 H), 1.22 (s, 12 H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 12.3, 17.6, 24.5, 76.5, 77.0, 77.4, 81.9 ppm. C₁₅H₃₃BO₃Si (300.23): calcd. C 59.99, H 11.08, B 3.60, O 15.98, Si 9.35; found C 59.92, H 10.98, B 3.55, O 15.91, Si 9.28. MS (EI): *m*/*z* (%) = 331 (5), 301 (50), 285 (35), 257 (45), 215 (40).

Diisopropylbis[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxylsilane (D): ¹H NMR (300 MHz, CDCl₃): δ = 1.00 (14 H), 1.22 (s, 12 H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 12.47, 16.55, 24.53, 82.29 ppm. C₁₈H₃₈B₂O₆Si (400.26): calcd. C 54.02, H 9.57, B 5.40, O 23.99, Si 7.02; found C 53.97, H 9.51, B 5.35, O 23.93, Si 6.96. MS (EI): *m/z* (%) = 357 (5), 300 (25), 275 (25), 259 (100), 147 (5).

Bis[(1,3,2-dioxaborinan-2-yl)oxyldiisopropylsilane (E): ¹H NMR (300 MHz, CDCl₃): δ = 1.02 (14 H), 1.87 (br., 2 H), 4.04 (t, 3 H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 12.49, 16.58, 27.5, 62.9 ppm. C₁₂H₂₆B₂O₆Si (316.17): calcd. C 45.60, H 8.29, B 6.84, O 30.37, Si 8.89; found C 45.57, H 8.23, B 6.79, O 30.32, Si 8.81.

Bis[(1,3,2-dioxaborolan-2-yl)oxyldiisopropylsilane (F): ¹H NMR (300 MHz, CDCl₃): δ = 1.06 (14 H), 4.19 (s, 4 H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 12.45, 16.54, 64.70 ppm. C₁₀H₂₂B₂O₆Si (288.14): calcd. C 41.71, H 7.70, B 7.51, O 33.33, Si 9.75; found C 41.68, H 7.65, B 7.48, O 33.29, Si 9.70.

1,1,3,3-Tetraisopropyl-1,3-bis[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxyldisiloxane (G): ¹H NMR (300 MHz, CDCl₃): $\delta = 1.02$ (m, 4 H), 1.21 (s, 24 H), 1.27 (d, 24 H) ppm. ¹³C NMR (75 MHz, CDCl₃): $\delta = 12.82$, 16.72, 24.39, 82.15 ppm. C₂₄H₅₂B₂O₇Si₂ (530.34): calcd. C 54.34, H 9.88, B 4.08, O 21.11, Si 10.59; found C 54.30, H 9.82, B 4.02, O 21.08, Si 10.52. MS (EI): *m/z* (%) = 487 (5), 415 (15), 345 (25), 305 (70), 277 (10).

1,3-Bis[(1,3,2-dioxaborinan-2-yl)oxy]-1,1,3,3-tetraisopropyldisiloxane (H): ¹H NMR (300 MHz, CDCl₃): δ = 1.01 (m, 4 H), 1.28 (d, 24 H), 1.9 (m, 2 H), 4.03 (t, 4 H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 12.80, 16.69, 27.1, 62.6 ppm. C₁₈H₄₀B₂O₇Si₂ (446.25): calcd. C 48.44, H 9.03, B 4.84, O 25.09, Si 12.59; found C 48.39, H 8.95, B 4.79, O 24.99, Si 12.54.

1,3-Bis[(1,3,2-dioxaborolan-2-yl)oxy]-1,1,3,3-tetraisopropyldisiloxane (I): ¹H NMR (300 MHz, CDCl₃): δ = 1.00 (m, 4 H), 1.24 (d, 24 H), 4.17 (s, 4 H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 12.80, 16.69, 64.4 ppm. C₁₆H₃₆B₂O₇Si₂ (418.22): calcd. C 45.95, H 8.68, B 5.17,O 26.78, Si 13.43; found C 45.90, H 8.62, B 5.09, O 26.71, Si 13.38.

Acknowledgments

This work was supported by a project of the National Science Centre ("Maestro", UMO 2011/02/A/ST5/00472).

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Received: March 21, 2014 Published Online: June 3, 2014