

Application of Green Solvents: PEG and $scCO_2$ in the Mono- or Biphase Catalytic Systems for the Repetitive Batch Coupling of Vinylsilanes with Vinyl Boronates toward 1-Boryl-1-silylethenes

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ABSTRACT: A new method for the repetitive batch silylative coupling (trans-silylation) of vinylsilanes with vinyl boronates in the presence of $Ru(CO)Cl(H)(PCy_3)_2$ immobilized in poly(ethylene glycols) (PEGs) has been developed. Three PEGs (PEG600, PEG2000, and MPEG2000) with different molecular weights and end groups (MW = 600–2000) were tested as solvents and immobilization media, while an aliphatic solvent (*n*-hexane or *n*-heptane) or supercritical CO_2 was used for product extraction. By applying 2 mol % of the Ru–H catalyst, it was possible to carry out up to 15 complete runs, with the predominant formation of 1-boryl-1-silylethenes. This immobilization strategy permitted for catalyst reuse and obtaining higher TON values (approximately 660–734) compared to the reaction in conventional solvents (~50). Detailed kinetic studies of the most effective catalytic system were performed to determine catalyst activity and stability. Moreover, the reactions were carried out in an MPEG2000/ $scCO_2$ biphasic system, positively influencing the process sustainability.



- High selectivity and stability
- Reusable catalytic system
- High TON values
- Detailed kinetic studies

INTRODUCTION

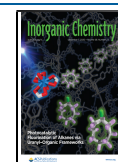
Unsaturated derivatives of metalloids, such as boryl, silyl, stannyl, and germlysubstituted olefins, are useful intermediates in the synthesis of organic compounds with defined structures and selectivities.^{1–4} Such p-block element groups attached to C sp^2 or C sp atoms can easily be transformed into products possessing various functionalities (e.g., halogen, amine, and carbonyl groups) or used in coupling reactions (Suzuki, Hiyama, or Stille), leading to the formation of new C–C bonds.^{1b,2b,c,3a,5} Because of their high reactivity and air and moisture stability, boryl- and silyl-substituted compounds are often the reagents of choice. Olefins substituted with both silyl and boryl functionalities constitute a special class of such compounds. These can have selective functionalization based on the different reactivities of these metalloids. They can be synthesized by various catalytic methods, such as the hydroboration of silyl-substituted alkynes,⁶ metathesis,⁷ the silaborylation of alkynes,⁸ or silylative coupling (trans-silylation) reactions.⁹ Most of these transformations require the application of a molecular catalyst and proceed as homogeneous processes. The silylative coupling reaction of vinylsilanes with olefins (also vinyl boronates), which was discovered at the same time by Wakatsuki¹⁰ and Marciniec,¹¹ occurs via catalytic activation of the C–Si bond in vinylsilane and the C–H bond in olefin. When vinyl boronate is used as an olefin, the formation of 2-boryl-1-silylethene or 1-boryl-1-silylethene with the simultaneous evolution of ethylene as a byproduct occurs.^{3a,12} This process, which is catalyzed by hydride Ru(II) complexes, especially $Ru(CO)Cl(H)(PCy_3)_2$ and $Ru(CO)Cl(H)(PPh_3)_3$, is temperature-tunable. At 0 °C,

predominantly *geminal* 1-boryl-1-silylethene is formed, while at elevated temperatures (>60 °C), (*E*)-2-boryl-1-silylethene is the most common product.^{9,12c} The problems with the molecular catalysts' stability and activity, which are predominantly sacrificed during the separation stage, were the reasons for not using homogeneous processes on a large production scale.

To avoid the homocoupling of vinylsilane, less-reactive vinyl boronate is used in excess. Nevertheless, bis(boryl)ethene is still formed as a byproduct in small amounts in competitive borylative coupling. The silylative coupling reaction allows the synthesis of various borylsilylethenes. Some of them, especially *geminal* products, cannot be formed in metathesis or hydroboration reactions. The method uses commercially available and easy-to-handle reagents and catalysts but has some drawbacks. The reaction occurs with high catalyst loading (≥ 2 mol % Ru catalyst), applying toxic solvents such as benzene to ensure the homogeneity of the process. Additionally, the application of typical organic solvents causes problems for catalyst reuse and recycling and product separation from the Ru complex. Therefore, the TON values are low.^{12a}

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To intensify the process in terms of productivity and to reduce catalyst content in the postreaction mixture, several papers were reported. These describe Ru–H catalyst immobilization and recycling in a various green solvents [e.g., PEGs, ionic liquids (ILs), and supercritical CO₂ (scCO₂)]. These systems allowed the catalyst to be reused several times without any significant changes in its activity and stability.^{6,13} Moreover, no significant Ru leaching was observed. Ammonium, pyridinium, or imidazolium ILs with various anions were also used for Ru–H catalyst immobilization in the homocoupling of vinylsilanes. 1,2-Bis(silyl)ethene was obtained in high yield with high selectivity, while the catalyst showed stable activity for up to 12 cycles for dimethylphenylvinylsilane and 10 cycles for methylbis(trimethylsiloxy)vinylsilane.¹⁴

Their properties, which are similar to those of ILs, their ability to dissolve transition-metal molecular catalysts, and their very low toxicity during use and production make the application of PEGs attractive for catalytic processes and the immobilization of molecular catalysts.^{6a,15} Various catalytic reactions, such as dehydrogenative arylations,¹⁶ oxidation,¹⁷ Pd coupling,¹⁸ the addition of CO₂ to epoxides,¹⁹ hydrogenation,²⁰ and dimerization²¹ were carried out in different PEGs, which can act as a solvent or medium for catalyst immobilization or nanoparticle stabilization.^{15,22} Additionally, these solvents are nonvolatile and nonflammable, which increases the safety of the process; they are stable in alkaline or acidic solutions, widely available, and relatively cheap when compared to ILs. They are very soluble in water and in many organic solvents, including toluene, dichloromethane, and acetone. However, their miscibility with hexane, heptane, cyclohexane, and diethyl ether is limited and depends on the molecular weight of the polymer.^{23,24} Therefore, these typical organic solvents can be used in a biphasic system or just for product extraction when the process is finished. Combining PEG, used for immobilization of the catalyst and as a reaction medium, with another nonpolar solvent for product extraction or the application of a biphasic system opens the possibility for catalyst recycling. This latter method is particularly attractive if it is combined with scCO₂, which is commonly considered to be a green solvent. The method permitted the effective extraction of products when they are soluble in this solvent and intensified the process according to its productivity by the application of repetitive batch or continuous flow processes.²⁵

The aim of this work was to examine the silylative coupling of vinylsilanes with vinyl boranates in various poly(ethers), allowing catalyst immobilization. This was due to the growing interest in improving reaction conditions in terms of their cost and environmental impact as well as process sustainability, and the aim of this work was to examine the silylative coupling of vinylsilanes with vinyl boranates in various poly(ethers), allowing catalyst immobilization. Three different PEGs, a conventional organic solvent (toluene) reaction under neat conditions (without solvents), and a biphasic solvent system PEG/scCO₂ were compared to find the best system for obtaining the products with high selectivity and yield and to intensify process productivity by carrying out the reaction under repetitive batch conditions (Figure 1). Moreover, the effective immobilization of the expensive Ru catalyst and the low price of PEG will reduce the economic factors of this process. Such a simple methodology for molecular catalyst immobilization and the low reactivity of PEGs in chemical transformation makes this method versatile. It can be applied to many catalytic trans-

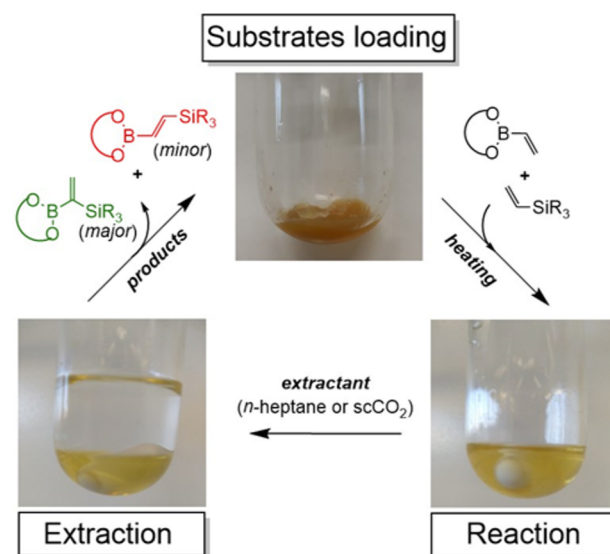


Figure 1. Repetitive batch silylative coupling of vinyl boronates (**1a** and **1b**) with vinylsilanes (**2a** and **2b**) catalyzed by Ru(CO)Cl(H)(PCy₃)₂ (**A**) immobilized in PEG.

formations, which are carried out under homogeneous conditions.

EXPERIMENTAL SECTION

General Procedure for the Catalytic Silylative Coupling Reaction. *In Toluene.* In a typical test, the syntheses were carried out in a dried and evacuated (vacuum/argon) 25 mL Schlenk vessel with a magnetic stirring bar under an argon atmosphere. Ruthenium catalyst Ru(CO)Cl(H)(PCy₃)₂ (**A**) (4.64 mg, 6.4 μmol) was dissolved in dried and degassed toluene (1.28 mL). Then vinylsilane [0.32 mmol; dimethylphenylvinylsilane (**2a**), trimethylvinylsilane (**2b**), triethoxyvinylsilane (**2c**), methylbis(trimethylsiloxy)vinylsilane (**2d**), or dimethoxymethylvinylsilane (**2e**)] and vinyl boronate [0.64–1.28 mmol; 4,4,6-trimethyl-2-vinyl-1,3,2-dioxaborinane (**1a**) or 4,4,5,5-tetramethyl-2-vinyl-1,3,2-dioxaborolane (**1b**)] were added. The vessel was held for 24 h at 80 °C, and the composition of the reaction mixture was determined by GC and GC–MS analyses.

Under Solvent-Free Conditions. In a typical test, the syntheses were carried out according to the above procedure, but the catalyst was soluble in the reagent solution.

In PEG600, PEG2000, and MPEG2000. In a typical test, the syntheses were carried out in a dried and evacuated (vacuum/argon) 25 mL Schlenk vessel with PEG (1.28 g, PEG 600, PEG2000, or MPEG2000) and a magnetic stirring bar under an argon atmosphere. Ruthenium catalyst Ru(CO)Cl(H)(PCy₃)₂ (**A**) (4.64 mg, 6.4 μmol) was added and mixed with PEG at room temperature (PEG600), 60 °C (PEG2000), or 50 °C (MPEG2000). Then, vinylsilane (0.32 mmol, **2a–e**) and vinyl boronic acid (0.64–1.28 mmol, **1a–b**) were added, and the reaction mixture was held at 80 °C for 6–24 h. After the mixture was cooled, the products and unreacted reagents were quantitatively extracted with deoxygenated and dried *n*-hexane or *n*-heptane (3 × 2 mL), while the ruthenium catalyst remained in PEG in the vessel. The residue of the solvent was evaporated under vacuum conditions and refilled with a new portion of the reagent. The composition of the extracted reaction mixture in each batch was determined by GC and GC–MS analyses. Catalyst leaching was analyzed using ICP–MS.

In the MPEG2000/scCO₂ System. In a typical test, to the high-pressure stainless steel autoclave reactor (10 mL) equipped with sapphire windows and connected to a Schlenk line, dried MPEG2000 (1.28 g) and Ru(CO)Cl(H)(PCy₃)₂ (**A**) (4.64 mg, 6.4 μmol) were added under an argon atmosphere and stirred for 1 h at 50 °C. Then, vinylsilane (0.32 mmol (**2a–b**)) and vinyl boronic acid pinacol ester

Scheme 1. Silylative Coupling of Vinyl Boronates (1a and 1b) with Vinylsilanes (2a–e) Catalyzed by Ru–H Complexes A and B

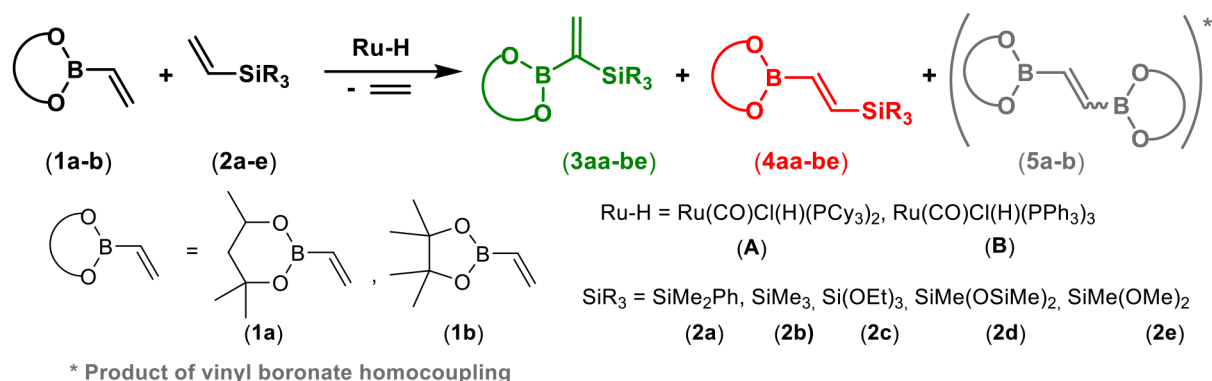


Table 1. Optimization of the Silylative Coupling of Vinyl Boronate (1a) with Vinylsilane (2a) Catalyzed by Ru Complexes A and B in Toluene under Solvent-Free Conditions and in PEG600, PEG2000, and MPEG2000

entry ^a	Ru	molar ratio (Ru)/(2a)/(1a)	solvent	conversion of 2a [%] ^b	selectivity of 3aa/4aa [%] ^c	% of 5a in the postreaction mixture ^d
1	A	2 × 10 ⁻² :1:2	toluene	91	42/58	27
2		2 × 10 ⁻² :1:2	solvent-free	86	68/32	8
3		2 × 10 ⁻² :1:2	PEG600	76	100/0	0
4		2 × 10 ⁻² :1:2	PEG600	78 ^e	100/0	0
5	B	2 × 10 ⁻² :1:2	PEG600	57	90/10	0
6	A	2 × 10 ⁻² :1:3	PEG600	86	89/11	0
7		2 × 10 ⁻² :1:4	PEG600	96	79/21	<1
8	A ^f	2 × 10 ⁻² :1:4	PEG600	95	69/31	<1
9	A	2 × 10 ⁻² :1:2	PEG2000	70	100/0	<1
10		2 × 10 ⁻² :1:4	PEG2000	94	69/31	<1
11		2 × 10 ⁻² :1:2	MPEG2000	73	100/0	0
12		2 × 10 ⁻² :1:4	MPEG2000	93	91/9	<1

^a80 °C, argon atmosphere, toluene (0.25 M) or PEG (1.28 g), 24 h. ^bDetermined by GC and GC–MS analyses. ^cDetermined by GC, GC–MS, and ¹H NMR analyses. ^dThe byproduct formed in the side homocoupling of vinyl boronates. In the table, the % amount refers to the composition of the whole postreaction mixture. ^eAfter 36 h. ^fAddition of 10 mol % CuCl.

(0.64 mmol (1b)) were added, and the reactor was pressurized with CO₂ to 55 bar, heated to 80 °C, and pressurized to the required pressure (approximately 170–190 bar). After 3 h, the reactor was cooled to 40 °C and the products were extracted in a stream of CO₂ (160–180 bar of CO₂, 8 mL/min, 35 min) into a small amount (10 mL) of *n*-heptane to avoid product loss during extraction. Afterward, the reactor was refilled with argon, and new substrate loading was added. The reactions and extractions were performed according to the conditions described above. The extracts were evaporated, weighed, and characterized using GC–MS analysis.

Kinetic Examination. The conversion of substrates was calculated using the internal standard method. Kinetic measurements were carried out in a dried and evacuated (vacuum/argon) 100 mL Schlenk vessel with MPEG2000 (20 g) and a magnetic stirring bar under an argon atmosphere. Ruthenium catalyst Ru(CO)Cl(H)(PCy₃)₂ (A) (72.3 mg, 0.0995 mmol) was added and mixed with MPEG2000 at 80 °C. The mixture of vinylsilane 2a (0.80 g, 4.9 mmol), vinyl boronic acid 1a (3.04 g, 19.7 mmol), and dodecane as an internal standard (20% of reagents volume) was prepared in a separate vessel, and sample *t*₀ was taken. The reagents were added to the already heated system of catalyst A immobilized in MPEG2000. GC analyses were carried out after 0.25, 0.5, 0.75, 1, 1.25, 1.5, 1.75, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, 6, 7, 8, 9, and 10 h in the following way: 50 μL of the reaction mixture was taken under argon and placed in a GC vial, and then 1 mL of *n*-hexane was added for the extraction of reagents from MPEG2000. The GC vial was cooled, and then the solution was decanted and analyzed. After 10 h, the reaction mixture was cooled, and the products and unreacted reagents were quantitatively extracted with deoxygenated and dried *n*-hexane (3 × 20 mL), while the ruthenium catalyst remained in PEG in the vessel. The residue of the solvent was evaporated under vacuum conditions

and refilled with a new portion of the reagent. This portion was progressively smaller each time since 1 mL (20 samples × 50 μL) of reaction mixture per batch was used to carry out GC analysis.

RESULTS AND DISCUSSION

In our studies, we used poly(ethylene glycols) with different molecular weights [PEG600, PEG2000, and MPEG2000 poly(ethylene glycol) modified with the methoxy groups at the ends of the chains] for catalyst immobilization and as solvents in the silylative coupling of various vinylsilanes [dimethylphenylvinylsilane (2a), trimethylvinylsilane (2b), triethoxyvinylsilane (2c), methylbis(trimethylsiloxy)vinylsilane (2d), dimethoxymethylvinylsilane (2e)] with two vinyl boronates [4,4,6-trimethyl-2-vinyl-1,3,2-dioxaborinane (1a); 4,4,5,5-tetramethyl-2-vinyl-1,3,2-dioxaborolane (1b)] (Scheme 1). All reagents and solvents were commercially available. Ruthenium hydride complexes Ru(CO)Cl(H)(PCy₃)₂ (A) and Ru(CO)Cl(H)(PPh₃)₃ (B), which have previously been reported to be the most active catalysts in silylative coupling reactions, were used in the transformations that are the subject of this study.^{12a,c}

In previous reports on the silylative coupling of vinyl boronates, other noncommercially available organoboron compounds were used as reagents, namely, 2-vinyl-1,3,2-dioxaborinane and 2-vinyl-1,3,2-dioxaborolane. Therefore, we initially tested the influence of the substrate structure (1a and 2b) on process selectivity using toluene as the solvent. The

Table 2. Silylative Coupling of Vinyl Boronates (1a and 1b) with Vinylsilanes (2a–e) Catalyzed by the Ru Complex (A) in Toluene and in MPEG2000

entry ^a	ViB (1)	ViSi (2)	molar ratio (Ru)/(2)/(1)	solvent	conversion of 2 [%] ^b	selectivity of 3/4 [%] ^c	% of 5 in the postreaction mixture ^d
1	1a	2a	2 × 10 ⁻² :1:4	toluene	100	45/58	26
2				MPEG2000	93	91/9	<1
3	1b	2a	2 × 10 ⁻² :1:4	toluene	89	57/43	21
4				MPEG2000	90	90/10	<1
5	1a	2b	2 × 10 ⁻² :1:2	toluene	100	47/53	26
6				MPEG2000	100	89/11	<1
7	1b	2b	2 × 10 ⁻² :1:2	toluene	99	58/42	30
8				MPEG2000	99	88/12	<1
9	1a	2c	2 × 10 ⁻² :1:4	toluene	0	0/0	28
10				MPEG2000	60 ^e	75/25	2
11	1b	2c	2 × 10 ⁻² :1:4	toluene	0	0/0	19
12				MPEG2000	50 ^e	75/25	<1
13	1a	2d	2 × 10 ⁻² :1:4	toluene	0	0/0	15
14				MPEG2000	54 ^e	57/43	23
15	1b	2d	2 × 10 ⁻² :1:4	toluene	0	0/0	28
16				MPEG2000	55 ^e	57/43	20
17	1a	2e	2 × 10 ⁻² :1:4	toluene	0	0/0	45
18				MPEG2000	45 ^e	87/13	0
19	1b	2e	2 × 10 ⁻² :1:4	toluene	0	0/0	43
20				MPEG2000	59 ^e	75/25	0

^a80 °C, argon atmosphere, toluene (0.25 M) or PEG (1.28 g), 24 h. ^bDetermined by GC and GC–MS analyses. ^cDetermined by GC, GC–MS, and ¹H NMR analyses. ^dThe byproduct formed in the side homocoupling of vinyl boronates. In the table the % amount refers to the composition of the whole postreaction mixture. ^eAfter 96 h.

reactions were carried out at 80 °C, because elevated temperatures are necessary for the dissolution of most of the PEGs, which are solid under ambient conditions. This is discussed later in this article.

The reagents were used in the ratio (A or B)/(2)/(1) = 2 × 10⁻²:1:2, and the process was carried out for 24 h in an inert atmosphere. The reagent conversions and product yields were monitored by GC and GC–MS analyses, while the selectivity was additionally determined by ¹H NMR. When 2a and 2b were used as reagents, three different products in similar amounts were formed: 1-boryl-1-silylethene (3), (*E*)-2-boryl-1-silylethene (4), and 1,2-bis(boryl)ethene (5). 5 is a byproduct of vinyl boronate homocoupling used in excess (Scheme 1). The high conversion of reagents was observed only when Ru(CO)Cl(H)(PCy₃)₂ (A) was used (Table 1, entries 1 and 2). For Ru(CO)Cl(H)(PPh₃)₃ (B), desired products (3aa) and (4aa) were formed in small amounts due to a low conversion of 2a (65%).

Marciniec et al. reported that the addition of CuCl to the catalytic system facilitated the dissociation of the phosphine ligand and the formation of an active form of the complex, which accelerated the reaction.^{9,12b} The addition of 10 mol % CuCl to the reactions carried out in PEGs had a negative effect on catalyst immobilization in these solvents. The complex was washed out during product extraction with *n*-hexane or *n*-heptane. This was indicated by the yellow color of the extract. Unexpectedly, the addition of CuCl to the reaction system completely changed its stability during the extraction process (Table 1, entry 8). Therefore, no phosphine scavenger was used for the further processes in PEGs.

We also attempted to carry out a silylative coupling reaction in a solvent-free environment under the same reaction conditions. In this case, three products were obtained as well. However, the geminal isomer (3aa) predominated, with a 68% yield, as calculated by GC (Table 1, entry 2). Surprisingly, the side

reaction of borane homocoupling was less effective, and only 8% of product 5a was observed in the reaction mixture. Using a traditional organic solvent or solvent-free conditions, the process selectivity was very poor, even worse than previously reported by Marciniec et al. for the coupling of vinylsilanes (2a and 2b) with 2-vinyl-1,3,2-dioxaborinane and 2-vinyl-1,3,2-dioxaborolane. This shows that both the reaction conditions and the reagent type influence the process selectivity.^{12b} Moreover, the homogeneous character of the process did not permit for catalyst recycling, as the postreaction workup is complicated and leads to the total deactivation of the catalyst. There were excellent results with the hydroboration of alkynes and the borylative coupling of olefins with vinyl boronates in PEGs, catalyst recycling, stability, and high accumulative TON values, obtained after several repetitive batches.^{6a} Bearing this in mind, we decided to investigate analog systems based on the Ru–H complexes immobilized in PEGs in the silylative coupling of vinyl boronates (1a and 1b) with the selected vinylsilanes (2a and 2b).

The catalytic system was prepared by the dissolution of Ru complex (A) or (B) in PEG600, PEG2000, or MPEG2000 at 80 °C. We carried out optimization tests to determine whether a change in solvent influences the catalyst activity in the reaction of vinyl boronate (1a) with dimethylphenylvinylsilane (2a). When a homogeneous solution was formed, the reagents were added and the reaction was carried out for 24 h, the time considered necessary for the total conversion of vinylsilane (2a) under conventional conditions using toluene as a solvent. The application of the Ru(CO)Cl(H)(PPh₃)₃ complex (B) did not show sufficient activity in PEGs (Table 1, entry 5); therefore, for further investigations, Ru(CO)Cl(H)(PCy₃)₂ (A) was used.

Initially, a 2-fold molar excess of vinyl boronate (1a) was applied to prevent vinylsilane (2a) homocoupling, and only ~70% vinylsilane conversion was obtained. Unexpectedly, the selectivity of the processes toward the synthesis of the geminal

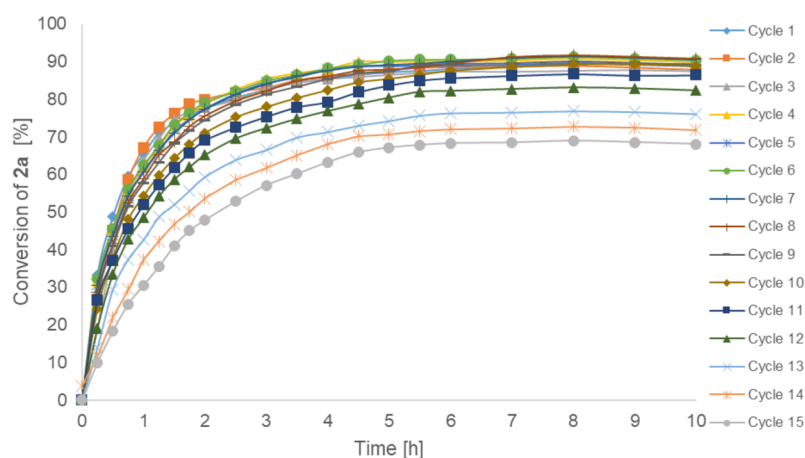


Figure 2. Kinetic examination of $\text{Ru}(\text{CO})\text{Cl}(\text{H})(\text{PCy}_3)_2$ catalyst (A) immobilized in **MPEG2000** in the silylative coupling of **1a** with **2a** at 80°C . Molar ratio (A)/(2)/(1) = 2×10^{-2} :1:4. The reaction was monitored by GC analysis.

isomer was excellent in **PEG600**, **PEG2000**, and **MPEG2000**. Product **3aa** was formed exclusively (Table 1, entries 3, 9, and 11). On the basis of our experiments in toluene or without a solvent as well as the results of research in the previously described reports, the silylative coupling of vinyl boronate under elevated temperatures in organic solvents had poor selectivity. Therefore, our results seem to be very promising. Extending the reaction time by 12 h did not significantly change the yield of product **3aa** (Table 1, entry 4). The total conversion of vinylsilane (**2a**) was obtained when the reagent's molar ratio was (1)/(2) = 4:1, but the selectivity decreased. The formation of the *E* isomer (**4aa**) was also observed in the reaction mixture. However, the regioselectivity of the process was still much higher than in toluene or without solvent. Moreover, for all reactions carried out in PEGs, the side reaction of vinyl boronate homocoupling was not detected, or bis(boryl)ethene (**5a**) was formed in only residual amounts.

The different reactivity of vinylsilane (**2a**) in PEGs prompted us to determine whether other vinylsilanes (**2b–e**) would be reactive in the silylative coupling with vinyl boronates (**1a** and **1b**). Complex **A** and **MPEG2000** were applied in this transformation since this solvent was one of the most effective (high conversion and selectivity) in the reaction with **2a**.

Surprisingly, the silylative coupling of vinylsilanes with alkoxy and siloxy substituents (**2c–e**) with **1a** and **1b** in **MPEG2000** occurred, while in toluene no borylsilyl ethenes were observed in the reaction mixtures. In these cases, only the homocoupling of vinyl boronates (**5a** or **5b**) occurred (Table 2, entries 9, 11, 13, 15, 17, 19). It is assumed that poly(ethers) accelerate the silylative coupling reaction or slow down the vinyl boronate homocoupling.

The reactivity of alkoxy silanes (**2c–e**) with vinyl boronates was definitely lower than for vinylalkylsilanes (**2a** and **2b**). Even extending the reaction time to 96 h was not sufficient to obtain the total conversion of silanes (Table 2, entries 10, 12, 14, 16, 18, 20).

Therefore, it can be assumed that the solvent has a significant influence on the course of the process, its selectivity, and product yields. We are currently trying to determine this phenomenon by applying computational methods based on the DFT calculations. Detailed studies on the mechanism of the reaction in various solvents, at various temperatures, and with different reagents will be the subject of a separate publication.

The activity of the catalyst (**A**) in PEGs and the limited solubility of PEGs in *n*-hexane or *n*-heptane used for product extraction encouraged us to examine the possibility of catalyst reuse and of carrying out the process in repetitive batch mode.

To check the stability of $\text{Ru}(\text{CO})\text{Cl}(\text{H})(\text{PCy}_3)_2$ (**A**) immobilized in PEG, kinetic studies were carried out. Therefore, to answer the question on the process rate in subsequent batches, one of the best systems based on 2 mol % $\text{Ru}(\text{CO})\text{Cl}(\text{H})(\text{PCy}_3)_2$ (**A**) dissolved in **MPEG2000** was chosen and tested in the reaction of **2a** with **1a**. The conversion of vinylsilane **2a** was monitored in time by GC analysis using the internal standard method. (For details, see the [Experimental Section](#).) Direct kinetic measurements using GC, NMR, or FTIR techniques were difficult to conduct since the reaction was carried out in nonvolatile **MPEG2000** solvent. The samples required the extraction of products from **MPEG2000** with *n*-hexane prior to the GC analysis.

The process was carried out under previously optimized conditions at 80°C . There was no significant difference between the results obtained for the first six cycles, in which >85% conversion of **2a** was observed after 6 h (Figure 2). Additionally, the highest activity of the system was observed within the first 2 h of the process, whereas more than 70% of vinylsilane was consumed. Afterward, the kinetic curve became flattened, and after 6 h, the conversion of silane **2a** and the yields of products **3aa** and **4aa** did not change significantly. It clearly showed that the process in PEG occurred faster than in traditional solvents, and the reaction time can be notably reduced. This information is important for our future goal of transferring the process from a batch to a continuous flow system because the residence times of reagents in the reactor might be reduced by up to 4-fold. The decrease in the reaction rate was noticed in cycles 7–10.

A distinct decrease in catalyst activity was noted from cycle 11. After the first 2 h, the silane conversion was 8% lower than in cycle 1 (69.1 vs 77.1%). The conversion of vinylsilane was 68% in the last run after 6 h, which is approximately 20% lower than that obtained after the same time in cycles 1–10. The kinetic plot (Figure 2) clearly showed that the catalyst was the most active in the first 2 h, while its stability was constant in cycles 1–6. (See the [Supporting Information](#) for the tabular presentation of the results.) A slow decrease in the following cycles might be caused by catalyst leaching or its deactivation caused by the impurities in reagents and solvents used for extraction or sensitivity toward oxygen and moisture, which might be

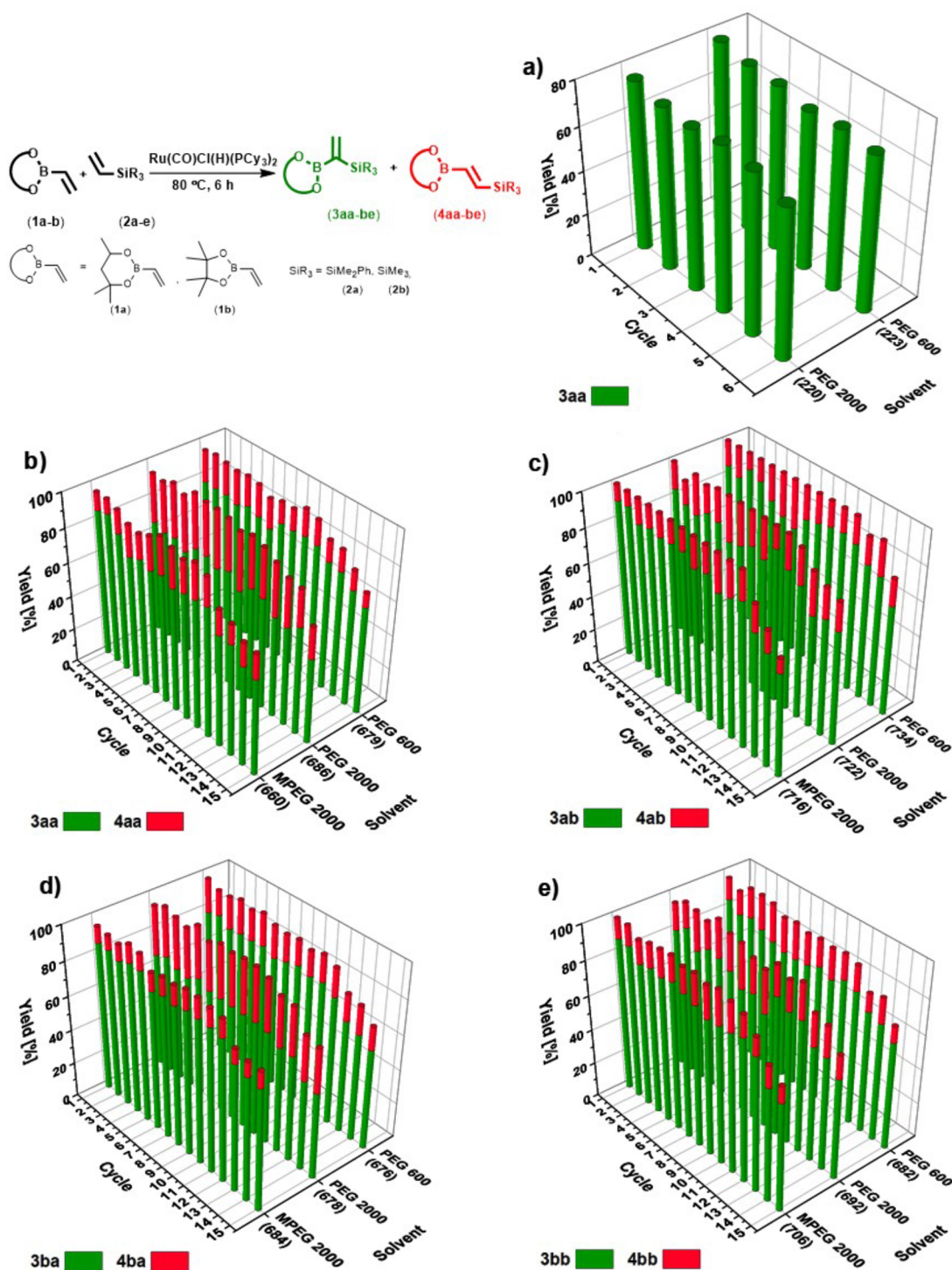


Figure 3. Product yields of (3) and (4) in the silylative coupling of (1a and 1b) with (2a and 2b) at 80 °C after 6 h catalyzed by the Ru complex (A, 2 mol %) carried out in PEG600, PEG2000, and MPEG2000 in repetitive batch mode. (a) (1a)/(2a) = 2:1. (b) (1a)/(2a) = 4:1. (c) (1a)/(2b) = 2:1. (d) (1b)/(2a) = 4:1. (e) (1b)/(2b) = 2:1. Accumulative TON values are presented in parentheses.

introduced into the reactor during extraction or reagent loading. These kinetic studies clearly showed that the reaction time might be reduced to 6 h using PEG as a solvent. Because of the high cost of the kinetic experiments, which required the application of huge amounts of reagents and a catalyst, other repetitive batch experiments were calculated after 6 h. This time was determined to be sufficient for the almost quantitative

conversion of vinylsilane and was presented traditionally as bar graphs (Figure 3).

To determine the product yields after each batch, the reaction mixture was cooled, and the products were extracted with *n*-hexane or *n*-heptane (3 × 2 mL). They were then subjected to analysis by GC, GC–MS, and NMR. *n*-Heptane, which is clearly a less toxic solvent, was preferred in the extraction procedure. We tested the most effective silylative coupling of 1a with 2a

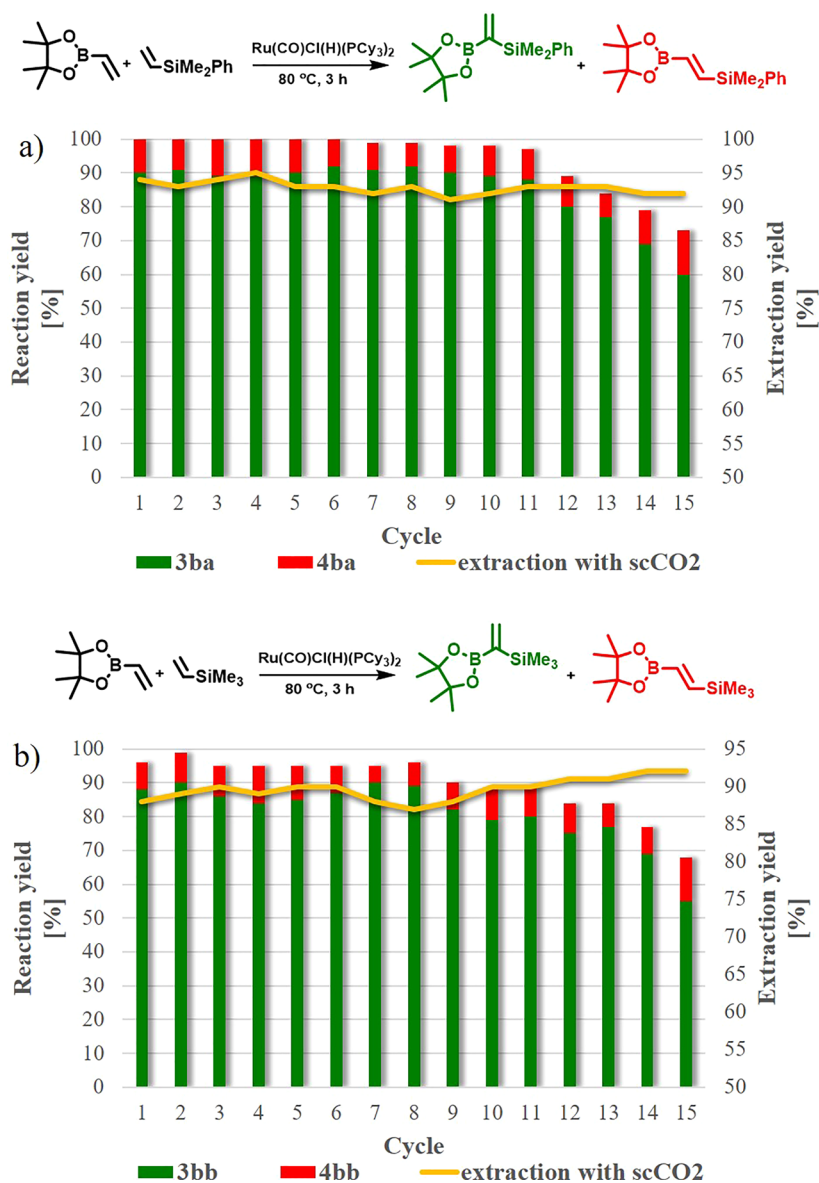


Figure 4. Reaction and extraction yields for repetitive batch silylative coupling of **2a** (a) and **2b** (b) with **1b** catalyzed by the Ru(CO)Cl(H)(PCy₃)₂ (**A**) at 80 °C, 3 h, carried out in MPEG2000/scCO₂ system. Molar ratio (A):(2):(1) = 2 × 10⁻²:1:2.

under repetitive batch conditions using two different molar ratios of reagents: 2:1 or 4:1 in PEG600, PEG2000, and MPEG2000 (Figure 3a, b, d). For the smaller excess of **1a**, the selectivity of the process was excellent in subsequent batches. However, the conversion of vinylsilane was not completed. Increasing the molar ratio of **1a** enabled almost complete vinylsilane **2a** conversion, but the postreaction mixture contained not only desired product **3aa** but also **4aa** (Figure 3b), and traces of vinyl borane homocoupling product **5a**. The selectivity was still much higher than that obtained in toluene or in a solvent-free environment. The catalyst was active for up to 15 cycles. A slow decrease in product yield was observed in subsequent repetitive batches. There was no significant difference among the applications of all three PEGs. It is important to emphasize that process manipulations (reaction, extraction, and reagent loading) must be carried out under an argon atmosphere to prevent catalyst deactivation by oxygen. The selected extracts were analyzed by ICP–MS to determine catalyst leaching and system stability. The Ru content in an

extract from a single batch was very low (approximately 0.2–1.4% of initial Ru loading). This shows the efficiency of the immobilization method. Moreover, the application of an aliphatic nonpolar solvent for extraction did not affect catalyst activity and enabled its retention in PEG.

The results proved the possibility of conducting the silylative coupling reactions in green media such as PEGs, and therefore positively influenced process economy by reusing the catalyst. The calculated accumulative TONs for these processes (686, 679, 660 for PEG600, PEG2000 and MPEG2000 respectively) clearly confirmed the system's activity and recyclability. The same catalyst loading converted a much higher number of vinylsilane moles compared to the processes carried out in toluene, for which catalyst reuse was impossible (TON = 50).

When trimethylvinylsilane (**2b**) was used, the (A):(2b):(1a) = 2 × 10⁻²:1:2 was sufficient to obtain the total conversion of vinylsilane in subsequent repetitive batches. The product's selectivity was almost the same as for (**2a**) and the system was active for 14–15 cycles (Figure 3. c). There was no difference in

product distribution or catalyst leaching. The accumulative TON values were 734, 722, and 716 for PEG600, PEG2000 and MPEG2000, respectively.

Similar results were obtained for the repetitive batch silylative coupling of vinylpinacolborane (**1b**) with vinylsilanes (**2a–b**). For both processes, regardless of the vinylsilane and PEG used, high reagent conversion and product yields were obtained for the formation of **3ba** or **3bb** (Figure 3 d, e). Each chosen system based on the ruthenium catalyst (**A**) immobilized in PEG was recycled several times, without a visible decrease in its activity (see Supporting Information for tabular presentation of the results). The method developed has the potential to lower the cost of the process, through minimizing catalyst consumption and achieving higher selectivity of 1-boryl-1-silylethene (**3**).

On the basis of these results, the best catalytic system for each reaction was chosen to carry out the reaction in a larger 1-g scale. The aim was to isolate the products for spectral analysis and confirm their structures via ¹H NMR.

In the final stage of our investigation, we verified the possibility of applying the biphasic solvent system PEG/scCO₂ in coupling reactions. On the basis of the results obtained for silylative coupling in the monophasic system and kinetic studies, we chose the reaction of **2a** and **2b** with **1b** in MPEG2000 for further research. The process was carried out in 3 h at 80 °C under 170–190 bar of CO₂ (Figure 4).

All reactions were performed in stainless steel high pressure 10 mL autoclaves. As with the monophasic system, a silylative coupling of **2a** with **1b** resulted in very high reaction and extraction (40 °C 160–180 bar of CO₂, 8 mL/min, 35 min) yields up to the 11th cycle. Subsequently, a gradual decrease in reaction yield was observed. The calculated TON value was comparable with the value calculated for the monophasic system (708 vs. 716). For repetitive batch silylative coupling of **2b** with **1b**, high reaction yields were observed until the eighth cycle. Contrary to the reaction of **2a** with **1b**, the lower extraction yields were observed probably due to the presence of phenyl ring in the product structure, which could slightly decrease product solubility in scCO₂. Nevertheless, high accumulative TON values for this reaction were also observed (673). The ruthenium content for selected runs was lower comparing to aliphatic solvent extraction (approximately 0.1–0.4% vs. 0.2–1.4% of initial Ru loading). This shows the high stability of the catalytic system. It is worth emphasizing that in the case of applying scCO₂, high conversions of **2a** and **2b** were observed even with a 2-fold excess of vinyl boronate **1b**. Moreover, scCO₂ lowers the viscosity of PEG, increasing the reaction rate of the process (after 3 h the silane was completely consumed in the first 8 runs).

CONCLUSIONS

An effective, new system was developed for the repetitive batch silylative coupling of vinylsilanes with vinyl boronates based on the application of 2 mol % of Ru(CO)Cl(H)(PCy₃)₂ immobilized in poly(ethylene glycols) or PEG/scCO₂ biphasic system. PEGs with different molecular weights and ending groups – PEG600, PEG2000, MPEG2000 – enabled the effective immobilization of the catalyst and also an increase in the process selectivity with the formation of 1-boryl-1-silylethenes (**3**) as the main products. The reaction time was also significantly reduced. The best results were obtained when dimethylphenylvinylsilane (**2a**) and trimethylvinylsilane (**2b**) were used as silylative agents. Under optimized reaction conditions, it was possible to carry out more than 15 complete

runs, with no significant loss of system activity, for Ru–H immobilized in all applied PEGs. Moreover, catalyst leaching was at a low level. This was calculated on the basis of ICP–MS analysis (less than 1.6% of initial Ru loading in the selected runs, when heptane was used for extraction and <0.4% by applying scCO₂). The repetitive batch silylative coupling of vinyl boronates presented here allowed the conversion of a much larger amount of reagents in comparison to the conventional process in a volatile organic solvent. The accumulative TON was approximately 660–734, which shows high system stability, activity, and productivity. The catalyst stability was determined in the kinetic studies. These clearly showed that its constant activity was observed within the first 6 runs, after which its slow and gradual deactivation was observed. Currently, we are working on the explanation of the process mechanism based on the DFT calculations. This research has clearly shown that applying green solvents such as PEGs and PEG/scCO₂ for silylative coupling reactions enables expensive transition-metal catalysts to be reduced and lowers the consumption of organic solvents when carrying out the reactions under homogeneous conditions, making the process more sustainable. Simplification of the separation procedure by applying scCO₂ extraction, as well as the shorter reaction time, provides good prospects for carrying out silylative coupling reactions under continuous flow processes with the integrated separation strategy and low residence times.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c02796>.

Product characterization and information about repetitive batch processes (Ru leaching, tabular results of the batches, and extraction effectiveness) (PDF)

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Notes

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