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Ru-Catalyzed Repetitive Batch Borylative Coupling of Olefins in Ionic Liquids or Ionic Liquids/scCO₂ Systems

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Abstract: The first, recyclable protocol for the selective synthesis of (*E*)-alkenyl boronates via borylative coupling of olefins with vinylboronic acid pinacol ester in monophasic (cat@IL) or biphasic (cat@IL/scCO₂) systems is reported in this article. The efficient immobilization of [Ru(CO)Cl(H)(PCy₃)₂] (1 mol%) in [EMPy][NTf₂] and [BMIm][OTf] with the subsequent extraction of products with *n*-heptane permitted multiple reuses of the catalyst without a significant decrease in its activity and stability (up to 7 runs). Utilization of scCO₂ as an extractant enabled a significant reduction in the amount of catalyst leaching during the separation process, compared to extraction with *n*-heptane. Such efficient catalyst immobilization allowed an intensification of the processes in terms of its productivity, which was indicated by high cumulative TON values (up to 956) in contrast to the traditional approach of applying volatile organic solvents (TON = ~50–100). The reaction was versatile to styrenes with electron-donating and withdrawing substituents and vinylcyclohexane, generating unsaturated organoboron compounds, of which synthetic utility was shown by the direct transformation of extracted products in iododeborylation and Suzuki coupling processes. All synthesized compounds were characterized using ¹H, ¹³C NMR and GC-MS, while leaching of the catalyst was detected with ICP-MS.

Keywords: homogeneous catalysis; ionic liquids; supercritical CO₂; borylative coupling; catalyst recycling; green chemistry; ruthenium catalyst; vinyl boronates; organoboron compounds

1. Introduction

Homogeneous catalysis has remained a key part of chemistry for several decades and is a powerful tool in the synthesis of valuable compounds. The high activity and selectivity of molecular catalysts under mild reaction conditions, the lack of diffusion barriers in comparison to heterogeneous systems, and the variability of their electronic and steric properties tuned by the proper design and choice of ligands and metal centers lead to their application in the chemical industry in the production of advanced polymers and fine chemicals [1,2]. On the other hand, homogeneous conditions generate notable problems in recovery and reuse of catalysts, which are mostly based on expensive noble transition metals (TM), for example, rhodium, iridium, platinum, palladium, or ruthenium. To obtain high TON values and the proper process selectivity, this precious catalyst is often sacrificed within the separation process. Moreover, homogeneous conditions require a considerable amount of volatile organic solvent to dissolve all reaction components: reagents and catalysts. Such an approach generates problems with the process economy resulting from the high solvent consumption within the process

and separation but also influences toxicological and environmental aspects. As a consequence of these drawbacks, new more sustainable methods for the synthesis of advanced organic and organometallic molecules by the application of environmentally benign solvents and/or catalyst immobilization and recycling are continuously being developed in academia and industry [3–8].

Ionic liquids (ILs) constitute an interesting green alternative to typical organic solvents because of their unique properties, such as incombustibility, negligible vapor pressure and abilities for the dissolution of many inorganic, organic and organometallic compounds. As a result of their physicochemical properties, ILs have immense structural variability which results in a wide range of their applications, for example, lubricants [9,10], solar cells [11,12], biomass processing [13,14] and solvents in chemical syntheses [15–17]. Their affinity to TM-complexes, as well as their high polarity, mean that ILs are frequently used in catalysis as a typical solvent, ligand source or even the catalyst itself. Moreover, ILs can also be used for catalyst immobilization, very often without any interference in its structure, and therefore without affecting its initial activity.

An efficient immobilization of the catalyst in IL and a properly designed product separation strategy significantly reduce metal leaching into the final product and allow for the recycling of the expensive TM-complex. This can be achieved by the extraction of products from the ionic phase through organic solvents or more preferably, supercritical CO₂ (scCO₂) [18]. Combining ILs and scCO₂ permits the development of an approach benefitting from the advantages of both homogeneous and heterogeneous catalysis, i.e., (i) high catalyst activity, selectivity, and stability, (ii) solvent (IL) and catalyst recyclability (iii) enhanced productivity and (iv) product separation simplicity. Moreover, the presence of scCO₂ significantly reduces the viscosity of ILs facilitating mass transfer, increasing the reaction rate and allows for effective extraction of the products by compressed CO₂ from ILs [19].

There are a lot of examples of ILs and scCO₂ being used as benign, eco-friendly alternative solvents in many catalytic processes such as hydrogenations [20,21], oxidations [22], hydroformylations [23], Pd-catalyzed C–C bond-forming couplings [24], hydrometallations [25–27] or silylative coupling [28]. These solvents permit catalyst immobilization in liquid or solid-state, and processes to be carried out under repetitive batch and continuous flow methods. Our group also has experience in the application of green solvents (ILs, scCO₂, PEGs) in designing sustainable protocols for the synthesis of organoboron and organosilicon compounds by the immobilization of the molecular catalyst and their recycling [29–35].

Due to their low toxicity, high reactivity under specified reaction conditions, and ease of handling, these organometallic compounds are valuable synthons in many chemical transformations, for example, Suzuki or Hiyama couplings [36,37] or halodemetalations [34,38]. Most of the organosilicon and organoboron compounds are produced under homogeneous conditions, with the use of TM-complexes as catalysts, thus searching for efficient and more sustainable protocols for their preparation is of great importance.

The utilization of ILs and/or scCO₂ for the synthesis of unsaturated organoboron compounds is poorly explored. Up to date, only three reports focusing on the catalytic hydroboration of alkynes in these solvents have been described [30,31,39]. Because of the challenging regio- and stereoselectivity control of the catalytic hydroboration of alkynes, the exclusive formation of one isomer was difficult to achieve, despite the good or very good recyclability and stability of catalytic systems. In contrast to the catalytic hydroboration of alkynes, borylative coupling (trans-borylation) of vinyl boronates with olefins, especially styrene derivatives, in the presence of ruthenium hydride catalysts, smoothly leads to the exclusive formation of (*E*)-alkenyl boronates [40].

In continuation of our studies on the application of green solvents in the synthesis of unsaturated organoboron compounds, herein, we would like to report the first application of ILs and the Ru-H catalyst [Ru(CO)Cl(H)(PCy₃)₂] in the monophasic ([Ru(CO)Cl(H)(PCy₃)₂]@ILs) or biphasic ([Ru(CO)Cl(H)(PCy₃)₂]@ILs/scCO₂) recyclable borylative coupling of vinylboronic acid pinacol ester with olefins (Scheme 1). The presented method is an interesting variant of traditional protocols through

(i) the ability of catalysts and ILs to recycle, (ii) product separation simplicity, (iii) the high productivity and stability of the systems.

Scheme 1. Ionic liquids-based recyclable protocols for the synthesis of unsaturated organoboron compounds.

2. Results and Discussion

2.1. Reaction and Extraction Conditions Screening

The studies were initiated by an investigation of the borylative coupling of vinylboronic acid pinacol ester (**1**) with styrene (**2a**) as a model reaction performed in several ILs based on pyrrolidinium ([EMPyr]⁺) or 1-butyl-3-methylimidazolium ([BMIm]⁺) cations and various inorganic and organic anions (Figure 1). Most of them were successfully applied in TM-catalyzed transformations [16]. Borylative coupling is a catalytic reaction which occurs in the presence of Ru-H catalysts with the activation of the C–B bond in vinyl boronates and the C–H bond in olefins or O–H bond in alcohols, silanols or boronic acids furnishing boryl-substituted olefins, boronic esters, borasiloxanes or boroxanes respectively, with the simultaneous evolution of ethylene [29,40–43].

Figure 1. Model reaction of **1** with **2a** used for the conditions screening. Pyrrolidinium and imidazolium-based ionic liquids used as solvents and catalyst immobilization media.

For the initial ionic liquids screening, we applied slightly more rigorous reaction conditions if compared to the traditional approach of utilizing volatile organic solvents (a higher process temperature to ensure good homogeneity of the reaction mixture). [Ru(CO)Cl(H)(PCy₃)₂] was used as a catalyst, which was previously described as the most effective in this transformation. In all pyrrolidinium-based ionic liquids, a conversion of **1** was over 90% (Table 1, entry 1–4). The complete conversion of **1** was observed only for [EMPyr][NTf₂]. In general, a higher conversion of **1** was observed for pyrrolidinium cations with ethyl substituents. When butyl groups were attached to the pyrrolidinium cation,

the product yield was slightly lower. Simultaneously, the application of trifluoromethanesulfonate anion ($[\text{OTf}]^-$) resulted in the lower conversion of substrates than for bis(trifluoromethylsulfonyl)imide anion ($[\text{NTf}_2]^-$).

Table 1. Borylative coupling of vinylboronic acid pinacol ester (**1**) with styrene (**2a**) in the presence of $[\text{Ru}(\text{CO})\text{Cl}(\text{H})(\text{PCy}_3)_2]@IL$ —IL screening. IL—Ionic liquids.

Entry	Ionic Liquid	Conversion of 1 [%] ^a	Yield of 3a [%] ^b
1	$[\text{EMPyr}][\text{OTf}]$	95	95
2	$[\text{EMPyr}][\text{NTf}_2]$	100	100
3	$[\text{BMPyr}][\text{OTf}]$	91	91
4	$[\text{BMPyr}][\text{NTf}_2]$	93	93
5	$[\text{BMIm}][\text{NTf}_2]$	97	97
6	$[\text{BMIm}][\text{OTf}]$	100	100
7	$[\text{BMIm}][\text{PF}_6]$	88	88
8	$[\text{BMIm}][\text{BF}_4]$	54	54
9	$[\text{BMIm}]\text{Cl}$	trace	n.d

Reaction conditions: $[\text{Ru-H}]:\mathbf{1}:\mathbf{2a} = 0.03:1:4$, 130 °C, ionic liquid (1 g), inert atmosphere. ^a Determined by GC-MS.

^b Determined by GC-MS and ^1H NMR.

Borylative coupling of **1** with **2a** in 1-butyl-3-methylimidazolium-based ionic liquids with $[\text{OTf}]^-$ or $[\text{NTf}_2]^-$ anions occurred smoothly with very high yields with the formation of the desired product **3a** and excellent selectivity (Table 1, entry 5–6). In contrast to pyrrolidinium cation, the quantitative conversion of **1** was observed for $[\text{OTf}]^-$ anion. Lower yields were observed when moisture-sensitive anions such as hexafluorophosphate ($[\text{PF}_6]^-$) or tetrafluoroborate ($[\text{BF}_4]^-$) were used (Table 1, entry 7–8). The presence of traces of water in those ILs probably caused partial deactivation of the moisture-sensitive catalyst. When $[\text{BMIm}]\text{Cl}$ was used as a solvent and immobilization medium, no conversion of **1** was noticed. This can be explained by the strong coordination ability of chloride anion to the metal center of the catalyst, and inhibition of its activity. This observation is in agreement with previous reports [28,30].

$[\text{EMPyr}][\text{NTf}_2]$ and $[\text{BMIm}][\text{OTf}]$, which ensured the complete conversion of **1** (Table 1, entry 2 and 6), were chosen for further reaction conditions screening. We optimized parameters crucial for obtaining the highest reaction yield, i.e., temperature, time, the molar ratio of substrates, as well as catalyst loading (Table 2). Initially, for $[\text{EMPyr}][\text{NTf}_2]$, the high catalyst loading of $[\text{Ru}(\text{CO})\text{Cl}(\text{H})(\text{PCy}_3)_2]$ (3 mol%) was maintained while the other parameters were tuned. The quantitative yields of **3a** were observed above 110 °C. The same results were noticed when the time of the reaction was reduced from 24 to 6 h. Moreover, only a 1.5-fold excess of **2a** towards **1** was necessary to get a full conversion of **1**. In the final stage of optimization studies in $[\text{EMPyr}][\text{NTf}_2]$, the influence of catalyst loading on reaction efficiency was determined. It was found that 1 mol% of $[\text{Ru}(\text{CO})\text{Cl}(\text{H})(\text{PCy}_3)_2]$ is essential for achieving a very high reaction yield (Table 2, entry 12). Although the application of the equimolar ratio of substrates resulted in a complete conversion of **1**, the presence of a homocoupling product of **1** was observed (Table 2, entry 14). Therefore, a small excess of olefin is essential for the elimination of the side-homocoupling reaction of vinyl boronate. Replacement of ruthenium hydride catalyst with coordinated PCy_3 ligand to $[\text{Ru}(\text{CO})\text{Cl}(\text{H})(\text{PPh}_3)_3]$ leads to a lower conversion of **1** and the formation of undefined by-products (Table 2, entry 15).

Based on the most effective reaction conditions in $[\text{EMPyr}][\text{NTf}_2]$, borylative coupling of **1** with **2a** in $[\text{BMIm}][\text{OTf}]$ was determined. Similar to pyrrolidinium-based IL, the reaction in $[\text{BMIm}][\text{OTf}]$ should be performed at least at 110 °C for 6 h with a slight excess of **2a** towards **1** and 1 mol% of $[\text{Ru}(\text{CO})\text{Cl}(\text{H})(\text{PCy}_3)_2]$, to achieve the best process efficiency (Table 2, entry 16). It is worth emphasizing that the application of ILs as a solvent enhances reaction rate compared to an analogous reaction performed in poly (ethylene glycol), another green solvent with similar properties to ILs [29]. The same phenomenon has already been observed by us during studies on the catalytic hydroboration of alkynes in $\text{Ru}(\text{CO})\text{Cl}(\text{H})(\text{PPh}_3)_3@IL$ s systems [30].

Table 2. Reaction conditions screening for borylative coupling of **1** with **2a** in the presence of immobilized [Ru(CO)Cl(H)(PCy₃)₂]@[EMPyr][NTf₂] or @[BMIm][OTf].

Entry	Ionic Liquid	Temperature [°C]	Time [h]	1:2a [mol]	Catalyst Loading [mol%]	Conversion of 1 [%] ^a	Yield of 3a [%] ^b
1	[EMPyr][NTf ₂]	120		1:4	3	100	100
2	[EMPyr][NTf ₂]	110	24	1:4	3	100	100
3	[EMPyr][NTf ₂]	100	24	1:4	3	96	96
4	[EMPyr][NTf ₂]	80	24	1:4	3	88	88
5	[EMPyr][NTf ₂]	110	18	1:4	3	100	100
6	[EMPyr][NTf ₂]	110	6	1:4	3	100	100
7	[EMPyr][NTf ₂]	110	3	1:4	3	94	94
8	[EMPyr][NTf ₂]	110	6	1:3	3	100	100
9	[EMPyr][NTf ₂]	110	6	1:2	3	100	100
10	[EMPyr][NTf ₂]	110	6	1:2	2	100	100
11	[EMPyr][NTf ₂]	110	6	1:1.5	2	100	100
12	[EMPyr][NTf ₂]	110	6	1:1.5	1	100	100
13	[EMPyr][NTf ₂]	110	6	1:1.5	0.5	93	93
14	[EMPyr][NTf ₂]	110	6	1:1	1	100	83 ^c
15 ^d	[EMPyr][NTf ₂]	110	6	1:1.5	1	46	37 ^e
16	[BMIm][OTf]	110	6	1:1.5	1	100	100
17	[BMIm][OTf]	80	6	1:1.5	1	53	53
18	[BMIm][OTf]	110	3	1: 1.5	1	91	91
19	[BMIm][OTf]	110	6	1:1	1	100	88 ^c
20 ^d	[BMIm][OTf]	110	6	1: 1.5	1	41	33 ^e
21	[BMIm][OTf]	110	6	1: 1.5	0.5	89	89

^a Determined by GC-MS analysis. ^b Determined by GC-MS and ¹H NMR analyses. ^c Homocoupling of **1** was observed. ^d 1 mol% of [Ru(CO)Cl(H)(PPh₃)₃] was used as a catalyst. ^e Undefined side products were observed.

Among many possibilities for the separation of products from the homogeneous reaction mixture, extraction seems to be a fast and efficient method. The extractant should dissolve the reaction products well, not mix with an ionic liquid to prevent leaching of the catalyst, as well as not inhibiting or deactivating the catalyst. The right choice is crucial for the ability to reuse the catalytic system. To find the most appropriate medium for product extraction, we examined several organic solvents and scCO₂ (Table 3). Non-polar aliphatic hydrocarbons (*n*-hexane or *n*-heptane) are completely immiscible with [EMPyr][NTf₂] and [BMIm][OTf], and during the extraction, the two phases were observed. The extractant (upper) phase was transparent or pale yellow. Application of more polar solvents such as toluene, dichloromethane or tetrahydrofuran resulted in partial or complete dissolution of the catalytic systems regardless of the ionic liquid used.

Table 3. Extractant screening.

Entry	Solvent	[EMPyr][NTf ₂]	[BMIm][OTf]
1 ^a	<i>n</i> -Hexane	—	—
2 ^a	<i>n</i> -Heptane	—	—
3 ^a	Toluene	+	+
4 ^b	Dichloromethane	+	+
5 ^a	Tetrahydrofuran	+	+
6 ^c	Supercritical CO ₂	—	—

Extraction conditions: 3 × 5 mL of the solvent at ^a 60 or ^b 40 °C. ^c 160–180 bar of CO₂ at 40 °C, 8 mL/min, 45 min). (–) Biphasic system. (+) Monophasic system or catalyst leaching from IL.

Similar to aliphatic hydrocarbons, ScCO₂ creates a biphasic solvent system with [EMPyr][NTf₂] and [BMIm][OTf]. Additionally, it is known that scCO₂ is partially soluble in ILs, lowering their viscosity, while ILs are not soluble in this supercritical fluid. Therefore, such a biphasic system is suitable for carrying out the reaction/extraction process [44]. Based on extractant screening for further

experiments, *n*-heptane (lower neurotoxicity than *n*-hexane) and *sc*CO₂ were chosen as solvents for product extraction from the post-reaction mixtures.

2.2. Scope of Substrates Investigations

Having optimized the reaction and extraction conditions in hand, we have studied a scope of olefins, mainly electron-deficient, neutral or donating styrenes, in borylative coupling with **1** in [BMIm][OTf] (Table 4). The reaction of **1** with bromo-(**2b**) or fluoro-substituted (**2c**) styrenes in *para* position led to (*E*)-alkenyl boronates with high yields (Table 4, entry 2–3). Application of electron-withdrawing groups such as –CF₃ (**2d–e**) also gave an excellent conversion of **1**. Trans-borylation of **1** with a weakly donating –CH₃ groups in *meta* (**2f**) or *para* (**2g**) positions resulted in the desired products **3f** and **3g** with very good isolation yields (Table 4, entry 6–7). However, the utilization of the sterically hindered alkyl group –C(CH₃)₃ (**2h**) gave a lower conversion of **1**. A similar result was noticeable when the electron-donating –OCH₃ group (**2i**) was applied. We also examined the reactivity of vinylcyclohexane (**2j**) in borylative coupling with **1**. After 6 h, **3j** was observed with a very high yield (Table 4, entry 10).

Table 4. Borylative coupling of **1** with a various olefins **2a–j** in Ru(CO)Cl(H)(PCy₃)₂@[BMIm][OTf] in optimized reaction and extraction conditions.

Entry	Olefin	2	Product	3	Conversion of 1 [%] ^a	Extraction Yield [%] ^b	Isolation Yield [%] ^c
1		a		a	100	94 ^d 90 ^e	81
2		b		b	99	91 ^d 88 ^e	77
3		c		c	99	90 ^d 91 ^e	78
4		d		d	100	93 ^d 94 ^e	83
5		e		e	99	90 ^d 92 ^e	81
6		f		f	100	93 ^d 91 ^e	79
7		g		g	98	84 ^d 81 ^e	69
8		h		h	93	81 ^d 77 ^e	73
9		i		i	89	74 ^d 75 ^e	71
10		j		j	100	95 ^d 96 ^e	87

Reaction conditions: [Ru-H]:**1**:**2a–j** = 0.01:1:1.5, 110 °C, 6 h, 1g [BMIm][OTf], inert atmosphere.

Extraction conditions: 3 × 5 mL of the *n*-heptane at 60 °C or 160–180 bar of CO₂ at 40 °C, 8 mL/min, 45 min.

^a Determined by GC-MS. ^b Calculated on total amount of reagents. ^c After *n*-heptane extraction; calculated on a theoretical mass of the product. ^d *n*-Heptane extraction. ^e Supercritical CO₂ extraction.

Simultaneously, the efficiency of extraction for different products of **3** was investigated. *n*-Heptane (3×5 mL at 60°C) or scCO_2 (160–180 bar of CO_2 at 40°C , 8 mL/min, 45 min) were applied as extractants. Very high extraction yields (over 90%) using *n*-heptane were obtained for most of the products (**3a–f**, **3j**). Similar results were achieved for the product extraction with scCO_2 . It is worth noticing that when CO_2 -philic groups such as $-\text{F}$ or $-\text{CF}_3$ were attached to the phenyl rings (**3c–e**), the extraction yields in scCO_2 were slightly higher (Table 4, entry 3–5). The extraction of product **3j** with a cyclohexyl ring was almost quantitative due to its good affinity to both extractants.

2.3. Repetitive Batch Borylative Coupling in the Monophasic Solvent System— $[\text{Ru}(\text{CO})\text{Cl}(\text{H})(\text{PCy}_3)_2]@\text{ILs}$

A key objective of our research was to develop an efficient and more sustainable protocol for the synthesis of (*E*)-alkenyl boronates via borylative coupling of vinyl boronates with olefins in ILs. Having optimized the process (reaction and extraction) conditions, as well as the information on the reactivity of olefins (**2a–j**), we verified the possibility of catalytic system recycling after each run using $[\text{BMIm}][\text{OTf}]$ and $[\text{EMPyrr}][\text{NTf}_2]$ as solvents. For repetitive batch borylative coupling of **1** with olefins, **2a**, and **2d** were chosen as reagents due to their excellent reaction and extraction yields. Trans-borylation of **1** with **2a** in $[\text{BMIm}][\text{OTf}]$ and $[\text{EMPyrr}][\text{NTf}_2]$ (Figure 2a,b) gave a final product **3a** with very high yields up to the sixth run. For both ionic liquids, a gradual decrease in the reaction yield in the seventh up to the 10th cycle was observed. A higher extraction yield for extractant-soluble components (**3a** and excess or unreacted substrate) was noticed when *n*-heptane was used. Moreover, the cumulative turnover number (cTON) was several times higher than in the classical approach, utilizing volatile organic solvents (930–948 vs. approx. 50–100).

Figure 2. Repetitive batch borylative coupling of **1** with **2a** in $[\text{BMIm}][\text{OTf}]$ (a) and $[\text{EMPyrr}][\text{NTf}_2]$ (b) or **1** with **2d** in $[\text{BMIm}][\text{OTf}]$ (c) and $[\text{EMPyrr}][\text{NTf}_2]$ (d) under optimized reaction ($[\text{Ru-H}]:1:2\text{a}$ or $2\text{d} = 0.01:1:1.5$, 110°C , 6 h, 1 g of IL, inert atmosphere conditions) and extraction (3×5 mL of *n*-heptane at 60°C or 160–180 bar of CO_2 at 40°C , 8 mL/min, 45 min) conditions. The product yields were determined by GC-MS. The extraction yields refer to the mass of products and reactants.

Repetitive batch borylative coupling of **1** with **2d** containing a CO_2 -philic trifluoromethyl group gave a very high product yield (over 90%) up to the seventh cycle for $[\text{BMIm}][\text{OTf}]$ and $[\text{EMPyrr}][\text{NTf}_2]$ (Figure 2c,d), respectively). The last three cycles resulted in a slight decrease in the reaction efficiency,

but it was still at an acceptable level. Nevertheless, high values of cTON were obtained (941–956), showing good system activity.

To investigate the possible cause of the gradual decrease in catalyst activity during the subsequent runs, extracts after the first, second, fifth and eighth runs were analyzed by inductively coupled plasma–mass spectrometry (ICP-MS). The highest ruthenium content was observed for extracts after the first and second runs (7.1–6.6 ppm) if *n*-heptane was applied regardless of the IL used. A pale yellow color was visible in both extracts. Although extracts analyzed after the fifth and eighth cycles were colorless, the ruthenium content was only a bit lower (6.4–4.8 ppm). Clearly better results were observed when scCO₂ was used as an extractant. For all ILs, ruthenium content in the analyzed extracts was comparable and lower than < 1 ppm. It should be pointed out that, despite significantly lower catalyst leaching in scCO₂, the activity of catalytic systems was the same as for processes that used *n*-heptane for extraction. Thus, a gradual decrease in catalyst activity is rather caused by the formation of inactive catalyst species or non-coordinative cyclohexylphosphine oxide than catalyst leaching. Similar observations were made by us during recyclable hydroboration of alkynes in [Ru(CO)Cl(H)(PPh₃)₃]@[EMPyr][NTf₂] or [Ru(CO)Cl(H)(PPh₃)₃]@[EMPyr][OTf]/scCO₂ systems [30].

2.4. Repetitive Batch Borylative Coupling in the Biphasic Solvent System—[Ru(CO)Cl(H)(PCy₃)₂]@ILs/scCO₂

In the final stage of our study we performed a repetitive borylative coupling of **1** with **2a**, **2d** and **2j** in the biphasic catalytic system [Ru(CO)Cl(H)(PCy₃)₂]@[BMIm][OTf]/scCO₂ (Figure 3a–c, respectively). The reactions were performed in 10-mL autoclaves equipped with sapphire windows under optimized reaction and extraction conditions at 180–190 bar of scCO₂ (Figure 3d). Similar to the repetitive trans-borylation of **1** with **2a** in [Ru(CO)Cl(H)(PCy₃)₂]@[BMIm][OTf], very high reaction and extraction yields of **3a** in the biphasic solvent system, were observed. Cumulative TON values were comparable to those obtained for the monophasic system (930 vs. 924).

Figure 3. Repetitive batch borylative coupling of **1** with **2a** (a), **2d** (b) and **2j** (c) in [Ru(CO)Cl(H)(PCy₃)₂]@[BMIm][OTf]/scCO₂ biphasic solvent systems under optimized reaction ([Ru-H]:**1**:**2a**, **2d** or **2j** = 0.01:1:1.5, 110 °C, 6 h, 1 g of [BMIm][OTf], inert atmosphere conditions) and extraction (160–180 bar of CO₂ at 40 °C, 8 mL/min, 45 min) conditions. Visualization of the reaction mixture through the sapphire window of high-pressure autoclave's (d). The product yields were determined by GC-MS. The extraction yields refer to the mass of products and reactants.

For 4-(trifluoromethyl)styrene (**2d**) and vinylcyclohexane (**2j**), very high reaction and extraction yields of products were observed up to the sixth run, whereupon a gradual decrease in reaction yields was noticed. Extraction yields remained at a very high level regardless of the run. Additionally, the negligible amount of metal in all analyzed extracts (0.88–0.54 ppm) clearly suggested that $[\text{Ru}(\text{CO})\text{Cl}(\text{H})(\text{PCy}_3)_2]$ was strongly immobilized in $[\text{BMIm}][\text{OTf}]$ under applied reaction conditions. The satisfactory stability and activity of the $[\text{Ru}(\text{CO})\text{Cl}(\text{H})(\text{PCy}_3)_2]@[\text{BMIm}][\text{OTf}]/\text{scCO}_2$ system creates an opportunity for its application in continuous-flow borylative coupling reactions in the future.

At the end of our investigation on repetitive batch borylative coupling in the biphasic system, we verified the possibility of direct use of extracts in deborylation protocols, i.e., Suzuki coupling and iododeborylation (Scheme 2).

Scheme 2. Transformations of **3a** via Suzuki coupling and iododeborylation reactions.

Suzuki coupling of **3a** with bromobenzene in the presence of $[\text{Pd}(\text{PPh}_3)_4]$ occurred with a complete conversion of **3a** and with a very high isolation yield of (E)-1,2-diphenylethene (**4**) (87%). Similarly, iododeborylation of **3a** with molecular iodine in the presence of sodium hydroxide resulted in a high isolation yield of (E)-(2-iodovinyl)benzene (**5**) (81%). The possibility of applying deborylation protocols with the use of crude extract is an attractive approach from the synthetical point of view because of the lack of necessity of carrying out time- and cost-consuming purification steps, for example, column chromatography or distillation.

3. Materials and Methods

3.1. Materials

Vinylboronic acid pinacol ester (95%, Sigma-Aldrich), styrene (97%, Sigma-Aldrich, Poznań, Poland), 4-bromostyrene (97%, Sigma-Aldrich), 4-fluorostyrene (99%, Sigma-Aldrich), 4-(trifluoromethyl)styrene (98%, Sigma-Aldrich), 3,5-bis(trifluoromethyl)styrene (98%, Alfa Aesar, Kandel, Germany), 4-methylstyrene (96%, Sigma-Aldrich), 2-methylstyrene (95%, Sigma-Aldrich), 4-*t*-butylstyrene (93%, Sigma-Aldrich), 4-methoxystyrene (97%, Sigma-Aldrich), vinylcyclohexane (99%, Sigma-Aldrich) were applied as reagents in borylative coupling reactions. Sodium hydroxide (99%, POCH Basic, Gliwice, Poland), iodine (99.8%, Sigma-Aldrich), diethyl ether (99%, POCH Basic), potassium carbonate (99%, Sigma-Aldrich), bromobenzene (99%, Sigma-Aldrich), tetrakis (triphenylphosphine)palladium (0) (99%, Sigma-Aldrich) were applied as received. 1-Ethyl-1-methylpyrrolidinium trifluoromethanesulfonate (99%, IoLiTec, Heilbronn, Germany), 1-ethyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (98%, Sigma-Aldrich), 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate (95%, Sigma-Aldrich), 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (98%, Sigma-Aldrich), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (98%, Sigma-Aldrich), 1-butyl-3-methylimidazolium trifluoromethanesulfonate (97%, Sigma-Aldrich), 1-butyl-3-methylimidazolium hexafluorophosphate (97%, Sigma-Aldrich), 1-butyl-3-methylimidazolium tetrafluoroborate (98%, Sigma-Aldrich), 1-butyl-3-methylimidazolium chloride (99%, Sigma-Aldrich) were dried in a vacuum before use (70 °C, 18 h). Styrene, 4-methoxystyrene, and 4-*tert*-butylstyrene were purified by the bulb to bulb distillation before use. The carbon dioxide (99.995%, Messer Polska, Chorzów, Poland) was used as a solvent and extractant in the reactions carried out in scCO_2 . The ruthenium catalysts $[\text{Ru}(\text{CO})\text{Cl}(\text{H})(\text{PCy}_3)_2]$ [45] and $[\text{Ru}(\text{CO})\text{Cl}(\text{H})(\text{PPh}_3)_3]$ [46] were prepared according to literature procedures. Deuterium solvents were obtained from Dr. Glaser AG Basel. The *n*-hexane (99%, POCH

Basic), *n*-heptane (99%, Sigma-Aldrich), toluene (99%, POCH Basic), dichloromethane (99%, POCH Basic), tetrahydrofuran (99%, POCH Basic) used in the extractions were distilled and dried prior use.

3.2. General Procedures

All manipulations were performed under an argon atmosphere using standard Schlenk's techniques or in high-pressure autoclaves equipped with sapphire windows for the solubility tests of reagents and catalyst, when scCO₂ was used (For detailed analysis descriptions and NMR spectra of obtained products please see the Supplementary Materials).

3.2.1. Borylative Coupling in the [Ru(CO)Cl(H)(PCy₃)₂]@ILs System under Optimized Reaction/Extraction Conditions with Subsequent *n*-Heptane Extraction

A 50 mL Schlenk's vessel was charged with dried IL (1 g) and [Ru(CO)Cl(H)(PCy₃)₂] (0.01 mmol) in an argon atmosphere. Subsequently, vinylboronic acid pinacol ester (0.5 mmol) and olefin (0.75 mmol) were added. The reaction was carried out for 6 h at 110 °C. The reaction mixture was cooled down and the extractant soluble components were extracted at 60 °C with *n*-heptane (3 × 5 mL). After evaporation, the extracts were weighed and characterized by GC-MS and ¹H NMR analyses. The products (3a–i) were purified on silica by flash chromatography (Biotage IsoleraOne chromatograph) with a UV detector (λ₁ = 255 nm, λ₂ = 280 nm). Purification details: cartridge 10 g, flow rate: 12 mL/min, length: 12 CV (CV = column volume), phase: hexane/ethyl acetate (step 1: hexane 100% by 5 CV, step 2: gradient 10%/CV by 5 CV, step 3: hexane 50% by 2 CV). The non-aromatic 3j was purified on silica using standard column chromatography using *n*-hexane/ethyl acetate (95/5–7/3) as eluents. The products were characterized by GC-MS, ¹H and ¹³C NMR analyses.

3.2.2. Borylative Coupling in the [Ru(CO)Cl(H)(PCy₃)₂]@ILs/scCO₂ System with Subsequent scCO₂ Extraction

A high-pressure stainless steel autoclave reactor (10 mL) equipped with sapphire windows and connected to a Schlenk line, was charged with dried IL (1 g) and [Ru(CO)Cl(H)(PCy₃)₂] (0.01 mmol) in an argon atmosphere. Subsequently, vinylboronic acid pinacol ester (0.5 mmol) and olefin (0.75 mmol) were added and the reactor was pressurized with CO₂ to 55 bar, heated up to 110 °C and pressurized to the required pressure (approx. 170–190 bar). After 6 h, the reactor was cooled to 40 °C and the products were extracted in a CO₂ stream (160–180 bar of CO₂, 8 mL/min, 45 min) into a small amount (10–15 mL) of *n*-heptane (previously cooled down in dry ice/*i*-propanol bath) to avoid product loss during extraction. Then the extracts were evaporated, weighed and characterized by GC-MS and ¹H NMR analyses.

3.2.3. Repetitive Batch Borylative Coupling in [Ru(CO)Cl(H)(PCy₃)₂]@ILs with Subsequent Organic Solvent Extraction

After the extraction process, the Schlenk's vessel was dried under vacuum for 20 min at 60 °C. Then a new portion of substrates was added in an argon atmosphere and subsequent batches, and extractions were carried out according to the procedure described in Section 3.2.1 without the isolation step.

3.2.4. Repetitive Batch Borylative Coupling in [Ru(CO)Cl(H)(PCy₃)₂]@ILs/scCO₂ with Subsequent scCO₂ Extraction

After the extraction process, the autoclave was dried in a vacuum for 20 min at 60 °C. Then a new portion of substrates was added in an argon atmosphere and subsequent batches, and extractions were carried out according to the procedure described in Section 3.2.2.

3.2.5. Suzuki Coupling of **3a** with Bromobenzene

A 100 mL Schlenk vessel equipped with a stirring bar was charged with [Pd(PPh₃)₄] (5 mol%). Subsequently, THF (10 mL), **3a** after scCO₂ extraction (0.5 mmol in 10 mL of *n*-heptane), bromobenzene (0.5 mmol) and 2 M aqueous solution of K₂CO₃ (20 mL) were added. The reaction was carried out for 24 h at 50 °C. Then, the organic phase was separated, and the product was purified on silica by flash chromatography with a UV detector (λ_1 = 255 nm, λ_2 = 280 nm) using the purification conditions described in Section 3.2.1 in 87% yield. The product was characterized by GC-MS, ¹H and ¹³C NMR analyses.

3.2.6. Iododeborylation of **3a** with Molecular Iodine

To a 100 mL, round-bottom flask equipped with a stirring bar **3a** after scCO₂ extraction, 10 mL of *n*-heptane and 5 mL of diethyl ether were added. Then 2 mL of the aqueous solution of NaOH (3 M) was dosed dropwise at 0 °C. Afterward, I₂ (0.85 mmol) in diethyl ether (5 mL) was slowly added. The reaction mixture was stirred for 2 h and then the excess of iodine was quenched with a saturated solution of sodium thiosulfate. The organic solution was separated, and the aqueous solution was washed with diethyl ether. The volatile organic fractions were evaporated, and the crude product was purified on silica by flash chromatography with a UV detector (λ_1 = 255 nm, λ_2 = 280 nm) using the purification conditions described in Section 3.2.1 in 81% yield. The product was characterized by GC-MS, ¹H and ¹³C NMR analyses.

3.3. Product Characterization

(*E*)-4,4,5,5-Tetramethyl-2-styryl-1,3,2-dioxaborolane (**3a**), ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 7.49–7.10 (m, 6H, Ph, =CH(Ph)), 6.09 (d, $J_{\text{H-H}}$ = 18.4 Hz, 1H, =CH(Bpin)), 1.22 (s, 12H, CCH₃) ppm. ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ = 149.6, 137.5, 129.0, 128.6, 127.1, 83.4 (CCH₃), 24.9 (CCH₃) ppm. C $_{\alpha}$ to boron atom was not observed. MS (EI) [m/z (%): 230(M⁺, 29), 215(21), 187(11), 173(8), 157(14), 144(83), 129(100), 118(14), 105(33), 77(19). Isolated yield: 81%. NMR and GC-MS data are in agreement with the literature [29].

(*E*)-2-(4'-Bromostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3b**), ¹H NMR (300 MHz, acetone-*d*₆, 25 °C): δ = 7.66–7.45 (m, 4H, Ph), 7.31 (d, $J_{\text{H-H}}$ = 18.4 Hz, 1H, =CH(Ph)), 6.19 (d, $J_{\text{H-H}}$ = 18.4 Hz, 1H, =CH(Bpin)), 1.28 (s, 12H, CCH₃) ppm. ¹³C NMR (75 MHz, acetone-*d*₆, 25 °C): δ = 148.8, 137.7, 132.8, 129.9, 123.5, 84.2 (CCH₃), 25.3 (CCH₃) ppm. C $_{\alpha}$ to boron atom was not observed. MS (EI) [m/z (%): 310((M + 2)⁺, 21), 308(M⁺, 19), 293(17), 222(6), 209(44), 208(41), 143(100), 129(81), 77(59). Isolated yield: 77%. NMR and GC-MS data are in agreement with the literature [29].

(*E*)-2-(4'-Fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3c**), ¹H NMR (300 MHz, acetone-*d*₆, 25 °C): δ = 7.71–7.55 (m, 2H, Ph), 7.33 (d, $J_{\text{H-H}}$ = 18.4 Hz, 1H, =CH(Ph)), 7.213–7.09 (m, 2H, Ph), 6.10 (d, $J_{\text{H-H}}$ = 18.4 Hz, 1H, =CH(Bpin)), 1.27 (s, 12H, CCH₃) ppm. ¹³C NMR (75 MHz, acetone-*d*₆, 25 °C): δ = 165.7, 162.5, 148.8, 135.0, 130.0, 129.9, 116.5, 116.3, 84.0 (CCH₃), 25.2 (CCH₃) ppm. C $_{\alpha}$ to boron atom was not observed. MS (EI) [m/z (%): 248(M⁺, 23), 233(19), 191(9), 175(11), 162(73), 148(100), 136(21), 123(23), 102(13), 85(19), 57(14). Isolated yield: 78%. NMR and GC-MS data are in agreement with the literature [29].

(*E*)-2-(4'-(Trifluoromethyl)styryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3d**), ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 7.67–7.49 (m, 4H, Ph), 7.41 (d, $J_{\text{H-H}}$ = 18.4 Hz, 1H, =CH(Ph)), 6.26 (d, $J_{\text{H-H}}$ = 18.4 Hz, 1H, =CH(Bpin)), 1.32 (s, 12H, CCH₃) ppm. ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ = 147.8, 140.9, 130.8, 130.4, 127.3, 125.8, 125.7, 83.7 (CCH₃), 25.0 (CCH₃) ppm. C $_{\alpha}$ to boron atom was not observed. MS (EI) [m/z (%): 298(M⁺, (33), 283(27), 241(19), 212(100), 197(77), 179(93), 151(34), 143(50), 85(41), 77(11), 57(30). Isolated yield: 83%. NMR and GC-MS data are in agreement with the literature [29].

(*E*)-2-(3',5'-Bis(trifluoromethyl)styryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3e**), ^1H NMR (300 MHz, CDCl_3 , 25 °C): δ = 7.88 (s, 2H, Ph), 7.78 (s, 1H, Ph), 7.41 (d, $J_{\text{H-H}}$ = 18.4 Hz, 1H, =CH(Ph)), 6.31 (d, $J_{\text{H-H}}$ = 18.4 Hz, 1H, =CH(Bpin)), 1.32 (s, 12H, CCH_3) ppm. ^{13}C NMR (75 MHz, CDCl_3 , 25 °C): δ = 146.0, 139.6, 132.2 (q, $J_{\text{C-F}}$ = 22.3 Hz, $-\text{CF}_3$), 126.9, 124.8, 122.2, 122.0, 83.9 (CCH_3), 25.0 (CCH_3) ppm. C_α to boron atom was not observed. MS (EI) [m/z (%): 366(M^+ , 44), 351(39), 347(22), 309(27), 280(100), 267(31), 247(77), 211(51), 169(19), 151(25), 97(24), 85(70), 59(77). Isolated yield: 81%. NMR and GC-MS data are in agreement with the literature [29].

(*E*)-4,4,5,5-Tetramethyl-2-(4'-methylstyryl)-1,3,2-dioxaborolane (**3f**), ^1H NMR (300 MHz, acetone- d_6 , 25 °C): δ = 7.46 (d, $J_{\text{H-H}}$ = 8.1 Hz, 2H, Ph), 7.33 (d, $J_{\text{H-H}}$ = 18.4 Hz, 1H, =CH(Ph)), 7.18 (d, $J_{\text{H-H}}$ = 8.0 Hz, 2H, Ph), 6.09 (d, $J_{\text{H-H}}$ = 18.4 Hz, 1H, =CH(Bpin)), 2.32 (s, 3H, 4- CH_3 Ph), 1.27 (s, 12H, CCH_3) ppm. ^{13}C NMR (75 MHz, CDCl_3 , 25 °C): δ = 149.6, 139.0, 134.8, 129.4, 127.1, 83.3 (CCH_3), 24.9 (CCH_3), 21.5 (Ph CH_3) ppm. C_α to boron atom was not observed. MS (EI) [m/z (%): 244(M^+ , 27), 229(9), 171(7), 158(51), 143(100), 128(41), 117(51), 105(12), 91(19), 77(8), 57(7). Isolated yield: 79%. NMR and GC-MS data are in agreement with the literature [29].

(*E*)-4,4,5,5-Tetramethyl-2-(2'-methylstyryl)-1,3,2-dioxaborolane (**3g**), ^1H NMR (300 MHz, acetone- d_6 , 25 °C): δ = 7.44–7.09 (m, 5H, Ph, =CH(Ph)), 6.14 (d, $J_{\text{H-H}}$ = 18.4 Hz, 1H, =CH(Bpin)), 2.34 (s, 3H, 2- CH_3 Ph), 1.28 (s, 12H, CCH_3) ppm. ^{13}C NMR (75 MHz, CDCl_3 , 25 °C): δ = 149.8, 138.2, 137.5, 129.9, 128.5, 127.9, 124.3, 83.4 (CCH_3), 24.9 (CCH_3), 21.5 (Ph CH_3) ppm. C_α to boron atom was not observed. MS (EI) [m/z (%): 244(M^+ , 32), 229(12), 171(13), 158(45), 143(100), 128(31), 117(49), 105(11), 91(112), 77(8), 57(10). Isolated yield: 69%. NMR and GC-MS data are in agreement with the literature [29].

(*E*)-2-(4'-(*Tert*-butyl)styryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3h**), ^1H NMR (300 MHz, acetone- d_6 , 25 °C): δ = 7.49 (d, $J_{\text{H-H}}$ = 8.4 Hz, 2H, Ph), 7.41 (d, $J_{\text{H-H}}$ = 8.5 Hz, 2H, Ph), 7.34 (d, $J_{\text{H-H}}$ = 18.4 Hz, 1H, =CH(Ph)), 6.11 (d, $J_{\text{H-H}}$ = 18.4 Hz, 1H, =CH(Bpin)), 1.31 (s, 9H, 4-*t*-BuPh), 1.28 (s, 12H, CCH_3) ppm. ^{13}C NMR (75 MHz, acetone- d_6 , 25 °C): δ = 153.1, 150.2, 135.8, 127.8, 126.5, 83.9 (CCH_3), 35.4, 31.6, 25.3 (CCH_3) ppm. C_α to boron atom was not observed. MS (EI) [m/z (%): 286(M^+ , 219), 271(100), 186(11), 171(19), 155(15), 143(23), 129(9), 83(10), 57(13). Isolated yield: 73%. NMR and GC-MS data are in agreement with the literature [29].

(*E*)-2-(4'-Methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3i**), ^1H NMR (300 MHz, CDCl_3 , 25 °C): δ = 7.44 (d, $J_{\text{H-H}}$ = 8.7 Hz, 2H, Ph), 7.35 (d, $J_{\text{H-H}}$ = 18.4 Hz, 1H, =CH(Ph)), 6.86 (d, $J_{\text{H-H}}$ = 8.7 Hz, 2H, Ph), 6.01 (d, $J_{\text{H-H}}$ = 18.4 Hz, 1H, =CH(Bpin)), 3.81 (s, 3H, 4- OCH_3 Ph), 1.31 (s, 12H, CCH_3) ppm. ^{13}C NMR (75 MHz, CDCl_3 , 25 °C): δ = 160.4, 149.2, 130.5, 128.6, 114.1, 83.3 (CCH_3), 55.4, 25.0 (CCH_3) ppm. C_α to boron atom was not observed. MS (EI) [m/z (%): 260(M^+ , 39), 245(10), 187(9), 174(25), 160(64), 144(100), 129(17), 117(31), 91(19), 77(31), 57(16). Isolated yield: 71%. NMR and GC-MS data are in agreement with the literature [29].

(*E*)-2-(2-Cyclohexylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3j**), ^1H NMR (300 MHz, CDCl_3 , 25 °C): δ = 6.57 (dd, $J_{\text{H-H}}$ = 18.2, 6.2 Hz, 1H, =CH(c-hexyl)), 5.37 (d, $J_{\text{H-H}}$ = 18.2 Hz, 1H, =CH(Bpin)), 1.83–1.55 (m, 7H), 1.26 (s, 12H, CCH_3), 1.22–1.00 (m, 4H) ppm. ^{13}C NMR (75 MHz, CDCl_3 , 25 °C): δ = 160.1, 83.1 (CCH_3), 43.4, 32.0, 26.3, 26.1, 24.9 (CCH_3) ppm. C_α to boron atom was not observed. MS (EI) [m/z (%): 236(M^+ , 4), 221(7), 178(9), 153(15), 135(21), 123(24), 108(58), 84(100), 69(16), 55(14). Isolated yield: 87%. NMR and GC-MS data are in agreement with the literature [29].

(*E*)-1,2-Diphenylethene (**4**), ^1H NMR (300 MHz, CDCl_3 , 25 °C): δ = 7.57 (d, $J_{\text{H-H}}$ = 8.0 Hz, 4H), 7.47–7.27 (m, 6H), 7.17 (s, 2H, =CHPh) ppm. ^{13}C NMR (75 MHz, CDCl_3 , 25 °C): δ = 137.5 (=CHPh), 128.8, 127.8, 126.6 ppm. MS (EI) [m/z (%): 180(M^+ , 100), 165(22), 152(12), 102(11), 89(15), 77(11). Isolated yield: 87%. NMR and GC-MS data are in agreement with the literature [32].

(*E*)-(2-Iodovinyl)benzene (**5**), ^1H NMR (300 MHz, CDCl_3 , 25 °C) δ = 7.42 (d, $J_{\text{H-H}}$ = 14.9 Hz, 1H, =CH), 7.28–7.08 (m, 5H), 6.77 (d, $J_{\text{H-H}}$ = 14.9 Hz, 1H, =CH). ^{13}C NMR (75 MHz, CDCl_3 , 25 °C) δ 144.95, 138.48, 135.15, 129.51, 126.02, 75.49. MS (EI) [m/z (%): 230(M^+ , 100), 127(13), 103(85), 77(53). Isolated yield: 81%. NMR and GC-MS data are in agreement with the literature [34].

4. Conclusions

The new, effective and highly regio- and stereoselective catalytic systems based on the immobilization of $[\text{Ru}(\text{CO})\text{Cl}(\text{H})(\text{PCy}_3)_2]$ in ionic liquids for the borylative coupling of vinylboronic pinacol ester with olefins was presented for the first time within these studies. The best results, characterized by excellent product yields, were obtained when $[\text{BMIm}][\text{OTf}]$ and $[\text{EMPyr}][\text{NTf}_2]$ were used as solvents and catalyst immobilization media. The system permitted a transformation of various vinyl-substituted olefins (styrene (**2a**), functionalized styrenes (**2b–i**) and vinylcyclohexane (**2j**)) into useful borylsubstituted unsaturated products, which can be used in deborylation or Suzuki coupling reactions. The application of ILs permitted catalyst reuse and the carrying out of repetitive batch borylative coupling in monophasic $[\text{Ru}(\text{CO})\text{Cl}(\text{H})(\text{PCy}_3)_2]@[\text{ILs}]$ or biphasic $[\text{Ru}(\text{CO})\text{Cl}(\text{H})(\text{PCy}_3)_2]@[\text{BMIm}][\text{OTf}]/\text{scCO}_2$ systems with product extraction with non-polar *n*-heptane or scCO_2 . These new protocols, under optimized reaction ($[\text{Ru-H}]:1:2 = 0.01:1:1.5$, 110 °C, 6 h, 1 g IL, inert atmosphere conditions) and extraction (3×5 mL of the *n*-heptane at 60 °C or 160–180 bar of CO_2 at 40 °C, 8 mL/min, 45 min) conditions, allowed of the catalyst to be reused 5–7 times without any significant loss of activity or stability. The application of scCO_2 as an extractant in monophasic or biphasic solvent systems significantly reduced catalyst leaching during the separation process (<1 ppm in each batch), compared to the extraction with *n*-heptane. Moreover, the good solubility of the reagents and products in scCO_2 and the high catalyst stability creates future possibilities for carrying out this process under a continuous flow method. In addition, it was found that the application of ILs as reaction media has a positive impact on the reaction rate, shortening the process from 24 h to 6 h. Such an approach based on multiple catalyst use enabled an intensification of the cumulative TON values (up to 956) in comparison to the single batch (~50–100), showing the potential of the system reported within this research, which was developed according to the sustainable development rules. The catalyst reuse, simplification of the separation process, increased process productivity and possibilities to carry out the reaction in repetitive batch borylative coupling of olefins are in agreement with green chemistry paradigms.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/10/7/762/s1>, Procedure description of GC-MS, NMR and ICP-MS analyses, NMR spectra for all isolated products (**3a–j**, **4**, **5**).

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