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A recyclable Ru(CO)Cl(H)(PPh₃)₃/PEG catalytic system for regio- and stereoselective hydroboration of terminal and internal alkynes

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Abstract. This paper reports on the first repetitive batch selective hydroboration of terminal and internal alkynes in a series of poly(ethylene glycols) (PEGs), used as solvents and media for the immobilization of a Ru(CO)Cl(H)(PPh₃)₃ catalyst. The system based on 2 mol% of Ru-H complex and poly(ethylene glycol) with α -methyl/ ω -trimethylsilyl ending groups (Mw = 2000) was found to be the most efficient, and was able to carry out over 19 complete runs with the Z-addition of pinacolborane to the phenylacetylene.

With the use of one portion of the developed catalytic system, the hydroboration of five different alkynes was performed consecutively, and led to five different products being obtained with high yields and purities. The developed strategy was characterized by high TON values and it was found to be the best recyclable protocol, leading to alkenyl boronates in all reported cases.

Keywords: Hydroboration; alkynes; poly(ethylene glycols); catalyst recycling; immobilization; ruthenium

Introduction

Transition-metal (TM) catalyzed hydroboration of alkynes provides a straightforward, 100% atom economical, and simple method for the synthesis of unsaturated organoboron compounds which are one of the most versatile intermediates currently available in organic chemistry transformations (coupling reactions, deborylation processes).^[1-5] In this context, their efficient and selective syntheses are of great importance.

There are several catalytic and non-catalytic methods leading to alkenyl boronates (e.g. the addition of diboron compounds to alkynes,^[6] codimerization of vinyl boronates with alkynes,^[7] metathesis^[5b, 8] or borylative coupling^[9]) but hydroboration is the most versatile and frequently used. It occurs in a radical and non-catalytic manner, but, to obtain a specific isomeric product, the application of a molecular catalyst is often required.^[10]

The hydroboration of alkynes in the presence of TM-complexes is a well-established process.^[11] In most cases the process occurs under homogeneous conditions, which provides high selectivity. However, a large amount of volatile organic solvents (VOS) is required to ensure appropriate solubility of the reagents and catalysts. The contamination of the

products by TM species and problems with the recovery and reuse of the catalyst are the biggest drawbacks to this approach. Additionally, multi-step and time-consuming product isolation protocols are involved which is often not favourable from an economic and environmental point of view, especially in a gram or multi-gram scale synthesis.^[12]

For these reasons, effective methods for catalyst immobilization, which will build long-lasting and efficient catalytic systems, are still a challenge. The new synthetic strategies that utilize alkyne hydroboration and more environmentally friendly conditions, through recycling of catalysts (e.g. nanoparticles) in organic solvents, have already been studied.^[13]

In recent years, the application of green solvents (e.g. water,^[14] fluorous media,^[15] ionic liquids $(ILs)^{[16]}$ or the supercritical CO₂ (scCO₂) which has previously been described by us^[17]) in the synthesis of alkenyl boronates in repetitive batches has attracted increasing interest (Scheme 1).

The repetitive batch hydroboration of alkynes in water or perfluorinated methylcyclohexane occurred with low TON (46 and 474) within 5 and 2 cycles. A discussion on the process selectivity in appropriate cycles is not provided.



Scheme 1. Alkyne hydroboration in green solvents. under repetitive batch mode.

On the other hand, the application of ILs in repetitive hydroboration has been studied in only one paper by Vaultier *et al.*^[16] They tested RhCl(PPh₃)₃ (0.8 mol%) immobilized in [BMIM][Cl][ZnCl₂] in the hydroboration of *n*-hexyne, which was recycled six times. The activity of this system decreased by the 2^{nd} cycle, indicating low efficiency.

Recently, we have applied $scCO_2$ as a solvent and extractant in the hydroboration of alkynes in the presence of a self-dosing Ru(CO)Cl(H)(PPh₃)₃ catalyst. The 2 mol% loading of the catalyst permitted us to carry out 19 runs, with excellent yields up to the 16th cycle. This resulted in a system with TON 886, which was the highest among all reported.^[17]

These results encouraged us to use other green solvents such as poly(ethylene glycols) (PEGs) for the hydroboration of alkynes.

PEGs, due to their unique physicochemical properties (low melting points, negligible vapour pressure, high stability in both acidic and basic media, miscibility with polar and non-polar organic, organometallic or even inorganic compounds, lack of toxicity and low price[18]), are commonly used in many branches of science and industry.^[19] Recently, several examples of their applications as solvents for TM-catalyzed reactions, such as hydrogenation,^[19c, 20] C-C formations,^[21] bond **Buchwald-Hartwig** amination,^[22] and polymerization^[23] have been described. The moderate polarity of PEGs allows the immobilization of polar, organometallic and molecular catalysts and their effective recycling and reuse.^[24] Therefore, in contrast to perfluorinated solvents, scCO₂ or water, modification of the catalyst structure is not needed to increase its affinity to a solvent. Therefore, PEGs are an excellent alternative to toxic volatile organic solvents. Moreover. PEGs ethylene oxide preparation of via polymerization is more environmentally benign, than that of ILs.[25]

The hydroboration of the carbon-carbon triple bonds (C=C) in PEGs has never been explored.

To date, only two reports on the hydroboration of carbon-carbon double bond (C=C) in PEGs have been published. One is related to the hydroboration of internal olefins in the presence of PEG ($M_w = 400$) by diborane generated *in situ* and the subsequent isomerization of alkylboranes, followed by their oxidation to alcohols.^[26] In the second, the catalytic cartridge system based on a Rh(acac)(CO)₂ complex, with PEG-modified phosphine ligand and scCO₂ in sequential hydroboration/ hydroformylation/ hydrogenation, and, again the hydroboration reaction/ extraction method was used.^[27]

Taking into account the solvent properties of PEGs, the lack of reports on the hydroboration of alkynes in these media and our experience in the synthesis and application of unsaturated organoboron or silicon compounds,^[5a, 7b, 9b, 17, 28] in this work, we decided to develop an efficient, and environmentally friendly protocol for the hydroboration of alkynes in PEGs in repetitive batches.

Our goal was to build a new strategy leading to a regio- and stereoselective synthesis of alkenyl boronates in which i) homogeneity of the process was maintained, ii) pure products were isolated from the catalyst in a one-step separation protocol, iii) a molecular catalyst and polymeric solvent were reused iv) a gram-scale synthesis was performed and v) the scope and limitations of proposed procedure were determined.

Results and Discussion

In the first stage of our research, various poly(ethylene glycols) with different molecular weights were tested, in a model hydroboration reaction of phenylacetylene (2 a) with pinacolborane (pinBH, 1) in the presence of $Ru(CO)Cl(H)(PPh_3)_3$

(1 mol%) to determine process feasibility and its optimal conditions (Table 1).

Screening of the PEGs showed that the length of their chains, as well as the type of end-groups, had a crucial influence on the reaction yields.

The reaction with the uses of **PEG 1-5**, which possess terminal hydroxyl groups did not lead to product formation regardless of the molecular weight of the PEGs, the reaction temperature and time (Table 1, entries 1-6).

It can be explained by the competitive reaction of pinacolborane with OH-ending groups in PEGs and the simultaneous formation of aloxypinacolborane and evolution of hydrogen, proved by the reaction of ethylene glycol with pinacolborane in a sealed NMR tube. This simple experiment proved that hydroxylated PEGs are not suitable for hydroboration reactions, as pinacolborane reacted rapidly with the solvent.^[29] The reaction performed in PEG 6-11 (containing OH groups blocked with SiMe₃ or Me groups) led smoothly to product 3 a with very high yields at 100 °C for 3 hours, which was determined by the GC-MS and ¹H NMR analyses (Table 1, entries 7-8, 10, 12, 17, 22). The absence of the reactive hydroxyl groups in the PEG 6-11 chain was essential for the desired course of the reaction. Almost exclusive formation of β -(*E*)-alkenyl boronate was observed.

Our further studies were focused on determining the effect of temperature on product yields and selectivities. In a standard hydroboration procedure in $scCO_2$, 100 °C was used to obtain the total conversion of reagents.^[17] Lowering the reaction temperature from 100 to 60 °C had a negative influence on substrate conversion when the reaction was carried out in **PEG 6-9** and **PEG 11**. Hydroboration of **2 a** with **1** in **PEG 10** at 60 °C for 3 hours resulted in almost complete substrate conversion, as found at 100 °C. The selectivity of the process was comparable at both temperatures for all solvents. Reduction of the process time resulted in a deterioration of product yields (Table 1, entries 18-20).

Encouraged by these promising results for the hydroboration of **2 a** with **1** at 100 °C in **PEG 6-11** as well, as in **PEG 10** at 60 °C, and their limited miscibility with organic, nonpolar solvents we decided to examine the recyclability of the developed catalytic system (Figure 1).

To determine the reaction yield after each catalytic cycle, products were extracted quantitatively with *n*-hexane (3x5 mL). If the lower PEG phase-bearing catalyst solidified, the upper hexane phase with extracted products was easily decanted. Subsequently, traces of the organic solvent were removed under vacuum from the immobilized molecular complex and the reactor was refilled with the next substrate load.

It should be noted that the replacement of polar hydroxyl groups with non-polar TMS groups at the ends of appropriate PEGs significantly changed their physicochemical properties. In all PEGs, with Table 1. Optimization of ruthenium-catalyzedhydroboration of phenylacetylene (2a) withpinacolborane (1) in different types of PEGs.

D BH + P pinBH, 1	h-== 1 mo 2 a	I% [Ru(CO PE time, tem)CI(H)(PPh :G perature	3)3]Br Ph3 a	bin + Ph _ Bpin _ Bpin + ← + ← Ph 4 a 5 a
Mw = 600 R = H PEG 1	1000 H PEG 2	1500 H PEG 3	2000 H PEG 4	2000 Me PEG 5	R _O , O
Mw = 600 R = TMS R' = TMS PEG 6	1000 TMS TMS PEG 7	1500 TMS TMS PEG 8	2000 TMS TMS PEG 9	2000 Me TMS PEG 10	2000 Me ^R O { O }

entry	solvent	temp. [°C]	time [h]	conv. of 2a ^{a)} [%]	yield of 3a^{b)} [%]	+
1	PEG 1	100	24	0	0	
2	PEG 2	100	24	0	0	5
3	PEG 3	100	24	0	0	(
4	PEG 4	100	24	0	0	
5	PEG 5	100	24	0	0	
6	PEG 5	130	48	0	0	
7	PEG 6	100	3	91	90	1
8	PEG 7	100	3	98	97	
9	PEG 7	60	3	89	88	
10	PEG 8	100	3	98	97	
11	PEG 8	60	3	88	87	7
12	PEG 9	100	3	99	98	
13	PEG 9	60	3	80	79	1
14	PEG 10	100	0.5	71	68	7
15	PEG 10	100	1	96	95	
16	PEG 10	100	2	97	95	
17	PEG 10	100	3	99	98	
18	PEG 10	60	0.5	48	45	
19	PEG 10	60	1	82	80	<
20	PEG 10	60	2	94	91	
21	PEG 10	60	3	98	97	
22	PEG 11	100	3	100	99	
23	PEG 11	60	3	94	93	

Reaction conditions: [catalyst]:[2a]:[1]: = [0.01]:[1]:[1.2], 0.55 g of PEG (approx. 0.5 M), argon. ^{a)} Determined by GC-MS analysis. ^{b)} Determined by ¹H NMR and GC-MS analyses.



Figure 1. Hydroboration of **2 a** with **1** in the presence of $Ru(CO)Cl(H)(PPh_3)_3$ (1 mol%) under repetitive batch mode at 100 °C (**PEG 6-10**) and at 60 °C (**PEG 10***).

trimethylsilyl ending groups (PEG 6-10), lower melting points, as well as better miscibility with nonpolar solvents, e.g. n-hexane, were observed.^[30] These phenomena were especially visible for PEGs with lower molecular weights. PEG 6 was fully miscible with *n*-hexane, *n*-heptane or *n*-octane, thus isolation of the products without solvent and catalyst leaching was not possible, even at low temperatures $(-20 - 4 \,^{\circ}\text{C})$. Therefore, only one catalytic cycle was performed. Significantly better phase separation was observed for PEG 7, although partial mutual solubility of PEG 7 and *n*-hexane during product extraction was also observed. Thus, a reduction of the reaction yield was noticed in the 3rd run. For PEG 9 and PEG 10, with much higher average molecular weights, excellent conversions and selectivities were observed for 8 and 10 cycles. The reaction in PEG 11 with methyl ending groups, enabled us to obtain very high yields of **3 a** for 10 cycles. However, after the 5th run, a decrease in alkyne conversion was noticed. The high molecular weight prevented the PEGs from mixing with *n*-hexane, which was used for product extraction. The hydroboration of 2a with 1 in **PEG 10** was also very effective for up to 10 catalytic cycles at 60 °C.

For all PEGs, yellow/orange homogeneous reaction mixtures were observed throughout the entire process. The extracts were analysed by ICP-MS to determine catalyst leaching and the quality of the TM-complex immobilization. In all these experiments, the Ru content in the extracts was at almost undetectable level (approximately 0.1 - 0.5 ppm). It proved that PEGs can be effectively used for catalyst immobilization. The extraction method did not affect metal leaching.^[30]

Thus, the optimum reaction conditions involved the use of $Ru(CO)Cl(H)(PPh_3)_3$ (1 mol%) in **PEG 10** at 60 °C for 3 h in an argon atmosphere, in repetitive cycles.



Scheme 2. Scope of alkynes used in hydroboration with 1 under optimized reaction conditions in **PEG 10**

Table	2.	Hydro	bora	ation	of	ter	minal	(2	a-g)	and
internal	al	lkynes	(2	h-j)	un	der	optim	ized	read	ction

entry	alkyne	conv. of selectivity ^{b)} alkyne alkyne ^{a)} 3/4/5 or 3/4		isolated yield of 3 [%]
1	2a	100	99/1/0	91
2	2b	100	98/1/1	89
3	2c	100	97/2/1	83
4	2d	77 (93) ^{c)}	90/5/5 (94/3/3) ^{c)}	78 ^{c)}
5	2e	57 (90) ^{c)}	83/7/10 (84/5/11) ^{c)}	66 ^{c)}
6	2f	100	65/22/13	55
7	2g	99	95/2/3	89
8	2h	46 (49) ^{c)} (80) ^{d)} (82) ^{e)}	93/7 (94/6) ^{c), d), e)}	71 ^{e)}
9	2i	72 (74) ^{c)} (87) ^{d)} (88) ^{e)}	83/17 (82/18) ^{c)} (80/20) ^{d), e)}	60 ^{e)}
10	2j	72 (73) ^{c)} (89) ^{d)} (91) ^{e)}	96/4 (96/4) ^{c)} (95/5) ^{d), e)}	79 ^{e)}

Reaction conditions: [catalyst]:[2]:[1]: = [0.01]:[1]:[1.2], 60 °C, 3 h, 0.55 g of**PEG 10**(approx. 0.5 M), argon. ^{a)} Determined by GC-MS analysis. ^{b)} Determined by ¹H NMR and GC-MS analyzes. ^{c)} After 24 h. ^{d)} After 3 h at 100 °C. ^{e)} After 6 h at 100 °C.

For the optimized conditions, the hydroboration of a wide scope of terminal (2 a-g) and internal alkynes 1 (2 h-j)with was examined (Scheme 2) Phenylacetylene and its derivatives (2 a-c) proceeded almost quantitatively to β -(*E*)-alkenyl boronates (3 ac). Conversion and selectivity in hydroboration of silvlsubstituted alkynes (2 d-e) were lower in comparison to phenylacetylenes but still at a relatively high level. Extending the reaction time to 24 hours resulted in a significant improvement in conversion without losing selectivity. Hydroboration of 2f and 2g proceeded with full conversions. However, poor selectivity was obtained if 2 f was used as a reagent. Similar results were observed for hydroboration of aliphatic alkynes performed in

 $scCO_2$.^[17] Additionally, the product **3** g was obtained with a high selectivity due to steric hindrance of alkyne **2** g (Table 2).

The hydroboration of internal alkynes (2 h-j) with 1 was also carried out, under optimized reaction conditions (Table 2, entries 8-10). In all cases, time and temperature, previously determined for terminal alkynes, was not sufficient to obtain a complete conversion of the reagents. The reason for this is the lower reactivity of internal alkynes and more shielded triple C=C bonds. Extension of the reaction time to 24 hours did not significantly improve conversion for all alkynes. The process temperature had a greater influence. Increasing the temperature from 60 °C to 100 °C resulted in better alkyne conversion in the reaction carried out for 3 h. Doubling the reaction time (to 6 h) had a weak influence on alkyne conversions. Selectivities were comparable at both temperatures. Conducting the process at a higher temperature also had a positive effect on reaction homogeneity.

If the hydroboration of 2 h and 2 i with 1 at 100 °C was performed, dissolution of all the components was observed, whereas at 60 °C the system was not fully homogeneous.

In order to show the reusability, versatility and utility of our catalytic system based on 1 mol% of Ru(CO)Cl(H)(PPh₃)₃ in **PEG 10**, we carried out subsequent hydroboration reactions of different terminal alkynes within the same catalyst load (Scheme 3). Hydroboration/extraction sequences of **2 a**, **2 d**, **2 f**, **2 b**, **2 c** and again **2 a** were performed with excellent conversions and very good



Scheme 3. Reusability of the catalytic system (Ru(CO)Cl(H)(PPh₃)₃/**PEG 10** in hydroboration of terminal alkynes.



Figure 2. Hydroboration/extraction sequences performed in 1 mol% Ru(CO)Cl(H)(PPh₃)₃/**PEG 10** catalytic system for series of terminal alkynes.

selectivities. All products were easily and quantitatively extracted with *n*-hexane before the next run (Figure 2).

The products obtained from each cycle were free from reagents and products from the previous cycle, showing the excellent efficiency of the developed catalytic system.

Besides high activity, the applied synthetic protocol is characterized by high tolerance to various chemical functionalities presented in the alkyne structures. Therefore, it can be considered as one of the most efficient, universal and environmentally benign tools for the hydroboration of alkynes. Moreover, the high stability of the system based on **PEG 10**, the absence of catalyst leaching, as well as the simple and easy separation protocols, (extraction/solvent evaporation) clearly affect the process sustainability.

It is worth emphasizing that the obtained products due to the presence of reactive moieties (boryl, silyl, bromo groups) and unsaturated double carbon-carbon bonds (C=C), are valuable building blocks in organic synthesis. and can be applied further in transformations, e.g. Suzuki, Hiyama and Heck couplings, deborylation or desilylation reactions. To demonstrate this capability, we used crude *n*-hexane extract, containing **3 a**, in a Suzuki coupling with bromobenzene (Scheme 4) (detailed procedure can be found in the supporting information). The reaction resulted in the complete conversion of **3 a** and 94 % isolation yield of (*E*)-1,2-diphenylethene.



Scheme 4. Suzuki coupling of 3 a (crude extract) with bromobenzene.

Finally, we investigated whether increasing the catalytic load would have an influence on the number of repetitive batches, and if the gram-scale synthesis of alkenyl boronates could be performed with the previously discussed catalytic system.

To check whether the effect of catalyst loading on the process efficiency was detectable for the hydroboration of 2 a, the reaction was performed with 2 mol% of Ru(CO)Cl(H)(PPh₃)₃ in **PEG 10**. Doubling the catalyst content allowed 19 complete





Figure 3. Hydroboration of **2 a** with **1** in **PEG 10** in the presence of a) $1 \mod 8$ and b) $2 \mod 8$ of Ru(CO)Cl(H)(PPh₃)₃ at 60 °C in 3 hours.

catalytic runs to be carried out, after which a gradual decrease in 3 a yield was observed. Accumulative TON values were comparable for both catalyst loads (1109 and 1123, respectively) (Figure 3).

To the best of our knowledge, the method developed by us is the most efficient system for the recyclable hydroboration of alkynes (according to the protocols previously described in literature).

To check the possibility of carrying out gram-scale synthesis, 2 a (10 mmol, 1.02 g) was reacted with 1 optimized reaction (12 mmol, 1.54 g) under conditions to give **3** a, with 88 % yield. Despite the fact that substrate concentrations were 40-times higher compared to the milligram-scale level, we did not observe a significant decrease in reaction selectivity (96/2/2 vs 99/1/0; 3 a/4 a/5 a). However, a very low catalyst load (0.025 mol%) was not sufficient for the complete conversion of 2a (conv. 92 %). It should be emphasized that a very high TON (3520) was obtained. It should also be pointed out that during the extraction process, partial mutual miscibility of the catalyst-bearing PEG and the product-rich *n*-hexane phase was evident, so simple filtration through a syringe filter was needed. Additionally, after some time, the precipitation of a white solid (PEG 10 and catalyst) in the first and second extract was observed. This phenomenon can be explained through the partial dissolution of the catalytic system in the relatively large product volumes in the *n*-hexane phase, which affects its solvent properties. In general, 16 % mass loss of the catalytic system during extraction was observed. Nevertheless, the applied methodology resulted in an excellent TON value. Our actual research concerns the possibility of utilizing the immobilization of Rucatalyst in PEG 10 in a continuous flow system. This strategy will use the potential of the catalytic system to eliminate mistakes derived from the reaction during subsequent runs and to enable us to intensify TON values using lower concentrations of reagents, controlled by their flow rate and residence time in the reactor.

Conclusion

A system using a Ru(CO)Cl(H)(PPh₃)₃ catalyst in PEGs with α -, ω -methyl or silvl ending groups, for regio- and stereoselective hydroboration of a wide range of alkynes in repetitive batches, was developed. The system was found to be the most productive, compared to previously described recyclable hydroboration methods. PEG 10 with 2 mol% of Ru catalyst gave the best results terms of efficiency and recyclability in the reaction of pinacolborane (1) with phenylacetylene (2a). It allowed the completion of 19 runs with the accumulative TON 1123, which clearly indicates high system efficiency. Moreover, it was possible to reduce the temperature of the process from 100 °C to 60 °C in comparison to the previously described reaction performed in scCO₂. Almost undetectable levels of leaching of the catalyst, monitored by the ICP-MS, confirmed its good immobilization in PEGs. The same catalyst load was applied for the synthesis of a series of different alkenyl boronates, one after another, in the subsequent catalytic cycles. The effective reaction/extraction procedure enabled pure products to be obtained without contamination of the postreaction mixture with compounds from the previous cycle. For terminal alkynes (E)-isomers were formed in a significant amount at 60 °C in 3 h, while internal alkynes yield (Z)-isomers in more extreme conditions (100 °C, 6-24 h)

Finally, the gram-scale synthesis of (E)-4,4,5,5tetramethyl-2-styryl-1,3,2-dioxaborolane (3 a) was carried out with a very high TON (3520). The partial miscibility of the catalytic system and the reagents used in gram amounts caused leaching of the catalyst during the extraction. The proper concentration of reagents, which could be achieved by the application of continuous flow instead of repetitive batches, would allow steady state reaction conditions to be maintained. Nevertheless, the hydroboration system based on PEGs fulfils the green chemistry requirements, while the catalyst recyclability and easy, low-cost reaction/separation method enables the sustainability of the process.

Experimental Section

All manipulations were carried out in an argon atmosphere using standard Schlenk's line techniques.

Preparation of PEG 10

To a dry three-neck round bottom flask equipped with stirring bar and reflux condenser, 10 mmol of **PEG 5** was added and dried under vacuum at 65 °C for over 16 hours. Subsequently, 25 mmol of hexamethyldisilazane (HMDS) at 65 °C was slowly added. The reaction was allowed to continue until no further evidence of ammonia was observed. Excess of HMDS was easily removed under vacuum at 65 °C within 2 hours. After cooling to room temperature, **PEG 10** was solidified at 97 % yield and characterized by FTIR and ¹H, ¹³C NMR analyses, as well as melting point measurement.

PEG 6-9 were prepared in the above-described procedure.

Hydroboration of alkynes in PEG 10

The **PEG 10** (0.55 g) was placed into a Schlenk's vessel equipped with a stirring bar and dried under vacuum at 40 °C, for 16 hours. Subsequently, a catalyst (0.0025 mmol) was added to the reactor, evacuated for 1 hour and refiled with argon. Next, alkyne (0.25 mmol) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.3 mmol) were added and the reactions were performed at 60 °C for 3 hours for terminal alkynes and at 100 °C for 6 hours for internal alkynes. The molar concentration of the reagents was approximately 0.5M. When the reactions were complete, the products were extracted with dry *n*-hexane (3x5 mL). The combined extracts were filtered (if necessary) and isolated on silica gel using flash chromatography and hexane/ethyl acetate (9:1) as the eluent. The purity of the product was confirmed by ¹H, ¹³C NMR and GC-MS analysis.

Hydroboration of alkynes in PEG 10 in repetitive batches

PEG 10 (0.55 g) was placed into a Schlenk's vessel equipped with a stirring bar and dried under vacuum at 40 °C, for over 16 hours. Subsequently, a catalyst (0.0025 mmol) was added and evacuated for 1 hour and refiled with argon. Next, the alkyne (0.25 mmol) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.3 mmol) were added and the reactions were carried out at 60 °C. The molar concentration of reagents was approximately 0.5M. After 3 hours the products were extracted with dry *n*-hexane (3x5 mL). The combined extracts were filtered (if necessary) and analyzed by GC-MS and ¹H analyses. Subsequently, the traces of *n*-hexane were removed under vacuum. A new substrate load was added, and the process was repeated in the above-described conditions.

Gram-scale hydroboration in PEG 10

A catalytic system (**PEG10**/catalyst) was prepared in same manner as described for hydroboration of alkynes in **PEG 10**. Subsequently, the alkyne (10 mmol, 1.02 g) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (12 mmol, 1.54 g) were added and the reactions were carried out at 60 °C for 3 hours. When reaction was complete, the products were extracted quantitatively with the *n*-hexane (7x5 mL). Previously filtered extracts were combined, evaporated under vacuum and isolated on silica gel using flash chromatography and hexane/ethyl acetate (9: 1) as the eluent to give 2.01 g of **3 a** (88%).

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- [30] See supporting inforamtion.

FULL PAPER

A recyclable Ru(CO)Cl(H)(PPh₃)₃/PEG catalytic system for regio- and stereoselective hydroboration of terminal and internal alkynes

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