Suzuki reactions in aqueous multi-phase systems promoted by supported detergents

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Abstract

The coupling reaction of p-iodoanisole with phenyl boronic acid occurs in high yield in a water–toluene biphasic system catalyzed by palladium complexes with water-soluble phosphine ligands. Silica supports amphiphilized by different types of detergents were prepared and used as phase-transfer reagents. A novel approach to the amphiphilization of the supports was applied to modify phase-transfer stages and to embed the catalytic system in this bipolar surface layer. The reaction was accelerated using these immobilized amphiphiles and the conversion was increased in comparison to the detergent-free homogeneous systems.
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1. Introduction

Carbon–carbon bond formation is of general importance in transition metal catalyzed organic synthesis [1]. In this regard the reaction of organoboron compounds with aryl, alkenyl and alkynyl halides catalyzed by palladium complexes is a modern and successful coupling process (Suzuki reaction) [2]. Most of the syntheses have been realized in organic solvents because of the solubility of typical reaction components like aryl, allyl or benzyl halogenides and boronic acids as well as their coupling products.

Only a few papers deal with the reaction in aqueous two-phase systems [3–7] with water-soluble palladium complexes as catalysts allowing easy separation of the water phase which contains the palladium catalyst and a strong base to bind the formed hydrogen halide.

Here and in our previous studies, we used p-iodoanisole (**1**) or alternatively p-bromoanisole and phenyl boronic acid (**2**) as coupling compounds (Scheme 1). To improve the solubilization of the reactants, the Suzuki-type coupling was performed in an aqueous micellar medium. However, precipitation of the diaryl products could not be

avoided. Therefore, a two-phase system consisting of water and toluene was used [8]. Several suitable phase-transfer reagents were added to promote the transport of the water-soluble palladium catalyst to the interface of the reactant-containing toluene phase. An accelerating effect on the reaction was found in dependence on the structure of the added amphiphiles [9].

However, the phase separation after the reaction was difficult in the presence of surfactants, because of the formation of an emulsion. Certain improvements could be achieved by the use of a new type of triphase catalyst [10–12] which contains an amphiphilic layer in a heterogenized form.

In a recent work, we used two different types of mesoporous supports synthesized by a template method consisting mainly of silica and alumina. The functionalized (sulfonated) MCM 41 was loaded with a palladium (II) complex and used in a aqueous two-phase Suzuki-type C–C coupling reaction [13,14] but the small particles were sensitive against the strong base (Na_2CO_3), mechanically labile against stirring and finally not to recycle by filtration.

In the present work, we investigated reactions in a thin layer of amphiphiles on a commercially available silica gel. The system is comparable with immobilized micelles or "triphase" (phase-transfer) catalysts [10]. Here, the catalytic active palladium complex is embedded in the amphiphilic layer.

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X = Br or I
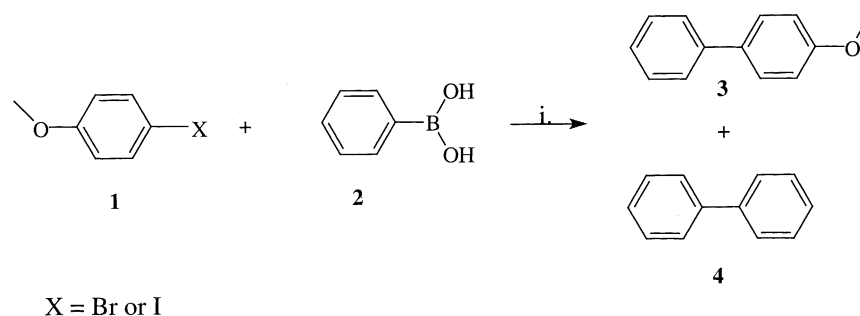
Scheme 1. Standard Suzuki system: i = 15 mmol PhB(OH)$_2$; 13.5 mmol *p*-iodoanisole; toluene/ethanol/water (15/15/15 [ml]), 0.01 mmol PdCl$_2$[Ph$_2$P(CH$_2$)$_4$SO$_3$K]$_2$; substrate/catalyst = 1350; 1.00 g immobilized amphiphile (**5–8**); 45 mmol Na$_2$CO$_3$ × 10 H$_2$O; up to 24 h at 78 °C.

2. Results and discussion

Recently, we worked in a liquid–liquid two phase system and observed high catalytic activity of water-soluble palladium phosphine complexes, we also observed an accelerating effect in the presence of colloidal dispersed surfactants [8,9]. Usually, PdCl$_2$[Ph$_2$P(CH$_2$)$_4$SO$_3$K]$_2$ or the in situ formed complex derived from (NH$_4$)$_2$PdCl$_4$ and 2Ph$_2$P(CH$_2$)$_4$SO$_3$K were used. The desired product is the substituted biaryl **3** and was formed with a selectivity of more than 95%.
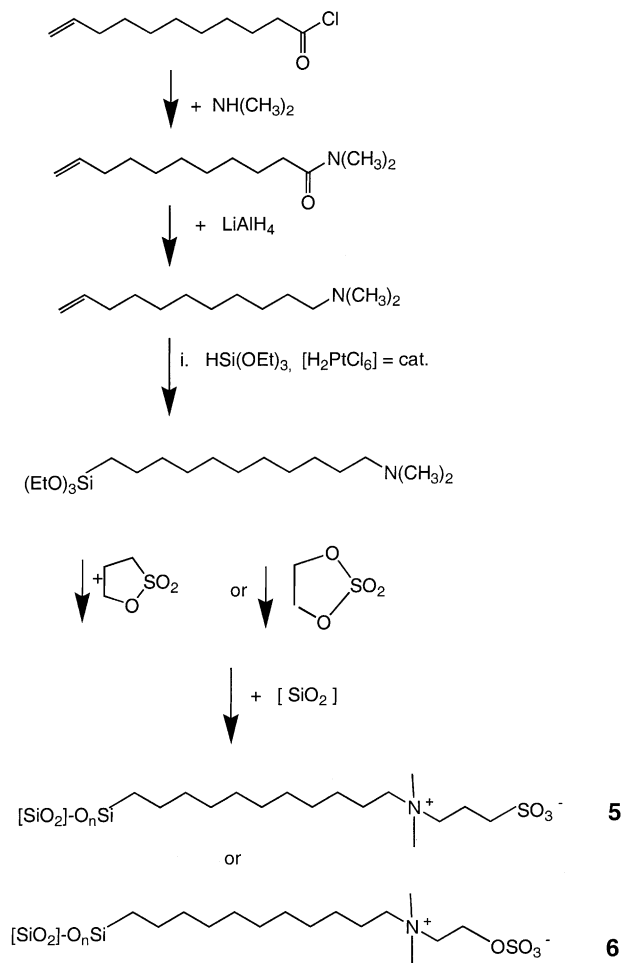
Addition of a surfactant as phase-transfer reagent, e.g. cetyltrimethylammonium bromide (CTAB), accelerated the reaction and enhanced the conversion. Moreover, the selectivity was increased and the yield of the by-product **4** was <0.5%. This can be attributed to a phase-transfer effect but we found a dependence on the structure of the surfactant and observed the best results with micelle forming amphiphiles [9]. The amount of phosphine plays an important role in the effectivity of the in situ formed catalyst. More than two moles of the phosphine per mole of palladium inhibit the reaction. Although the catalytic reaction was successful, we could not realize recycling of the catalyst because of the soap effect of the surfactant within the phase separation.

Table 1 summarizes the immobilized surfactants used in this work. In all examples commercially available silica gel (Merck, silica gel 60, 0.043–0.060 mm) was applied after dehydration at 200 °C in vacuum for 12 h. The sequence of synthesis for the zwitterionic amphiphiles **5** and **6** is presented in Scheme 2.

Dimethylamine was acylated with 10-undecenoyl chloride and the resulting dimethylamide was reduced with lithium aluminium hydride. After hydrosilylation with triethoxysilane the resulting amine was reacted alternatively with propanesultone to give **5** or with ethylene sulfate to give **6**. In the last step the surfactant was fixed on the silica gel. The anchored amount is given in Table 1. It is worth noting that compound **7** consists of two different preparations of the same supported amphiphile (loading see in parentheses). The synthesis is shown in Scheme 3.
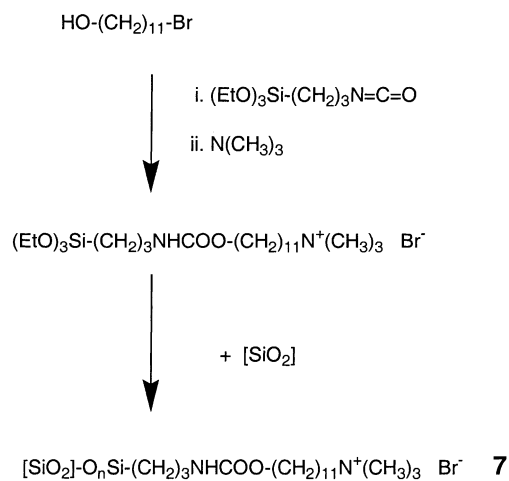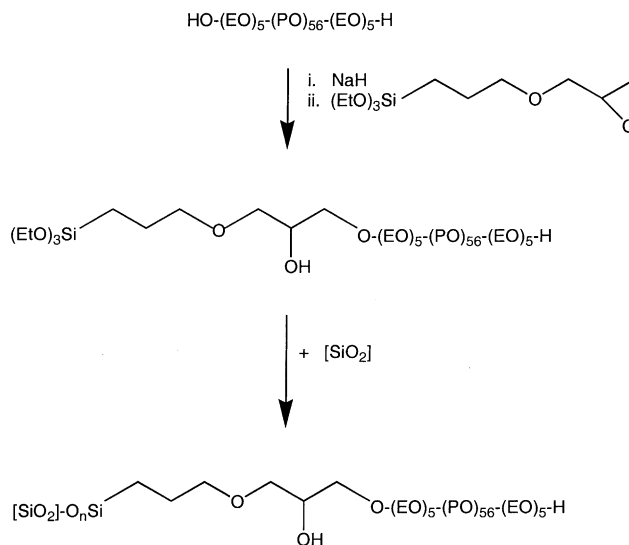
Here, ω-bromoundecanol was reacted with commercially available 3-triethoxysilylpropyl-isocyanate to the

Table 1
Different heterogeneous detergents of support (mmol/g)

Heterogeneous detergent	Anchored amount
[SiO$_2$]-O$_n$Si-(CH$_2$)$_{11}$N$^+$(CH$_3$)$_2$(CH$_2$)$_3$SO$_3^-$ (**5**)	0.26
[SiO$_2$]-O$_n$Si-(CH$_2$)$_{11}$N$^+$(CH$_3$)$_2$(CH$_2$)$_3$OSO$_3^-$ (**6**)	0.73
[SiO$_2$]-O$_n$Si-(CH$_2$)$_3$NHCOO-(CH$_2$)$_{11}$N$^+$(CH$_3$)$_3$ Br$^-$ (**7**)	0.42, 0.41
[SiO$_2$]-O$_n$Si-(CH$_2$)$_3$OCH$_2$CH(OH)-(EO)$_5$-(PO)$_{56}$-(EO)$_5$ (**8**)	0.027, 0.024

Scheme 2. Synthesis of the immobilized amphiphiles **5** and **6**.

HO-(CH$_2$)$_{11}$-Br

i. (EtO)$_3$Si-(CH$_2$)$_3$N=C=O

ii. N(CH$_3$)$_3$

(EtO)$_3$Si-(CH$_2$)$_3$NHCOO-(CH$_2$)$_{11}$N$^+$(CH$_3$)$_3$ Br$^-$

+ [SiO$_2$]

[SiO$_2$]-O$_n$Si-(CH$_2$)$_3$NHCOO-(CH$_2$)$_{11}$N$^+$(CH$_3$)$_3$ Br$^-$ **7**

Scheme 3. Synthesis of the immobilized amphiphile **7**.

HO-(EO)$_5$-(PO)$_{56}$-(EO)$_5$-H

i. NaH
ii. (EtO)$_3$Si

(EtO)$_3$Si ... O ... O-(EO)$_5$-(PO)$_{56}$-(EO)$_5$-H
OH

+ [SiO$_2$]

[SiO$_2$]-O$_n$Si ... O ... O-(EO)$_5$-(PO)$_{56}$-(EO)$_5$-H
OH

8

EO = -CH$_2$CH$_2$O- , PO = -CH$_2$-CH(CH$_3$)-O-

Scheme 4. Synthesis of the immobilized amphiphile **8**.

corresponding carbamate and this was converted with trimethylamine to ω-(3-triethoxysilyl-propylcarbamato)un-decyl-trimethylammonium bromide which was fixed on silica gel in the common procedure.

The last type of immobilized surfactants (**8**) is a nonionic block co-polymer with a hydrophobic poly(oxypropylene) chain as center and two hydrophilic poly(oxyethylene) chains as wings (Scheme 4). These Synperonics or Pluronics are commercially available surfactants. We chose the Synperonic L 101 for our experiments and reacted this with two equivalents of NaH and subsequently with 3-glycidoxypropyltrimethoxysilane.

After fixation on silica gel the coating seems to be low but of the catalytic test reactions higher loading would inhibit the separation by filtration. The influence of the immobilized

surfactants on the conversion of the catalytic test reactions is shown in Fig. 1.

As expected, there is a clear improvement in comparison to the system without surfactant: after about 30 min the activity (TOF) is higher for all experiments with surfactants. The lower productivity of the surfactant-free system (only 70% conversion after 6 h) is an indication of a lower stability of the catalyst under these conditions (lower TON).

Best results gave surfactants of types **7** and **8** in accordance with the related monomeric amphiphiles, which
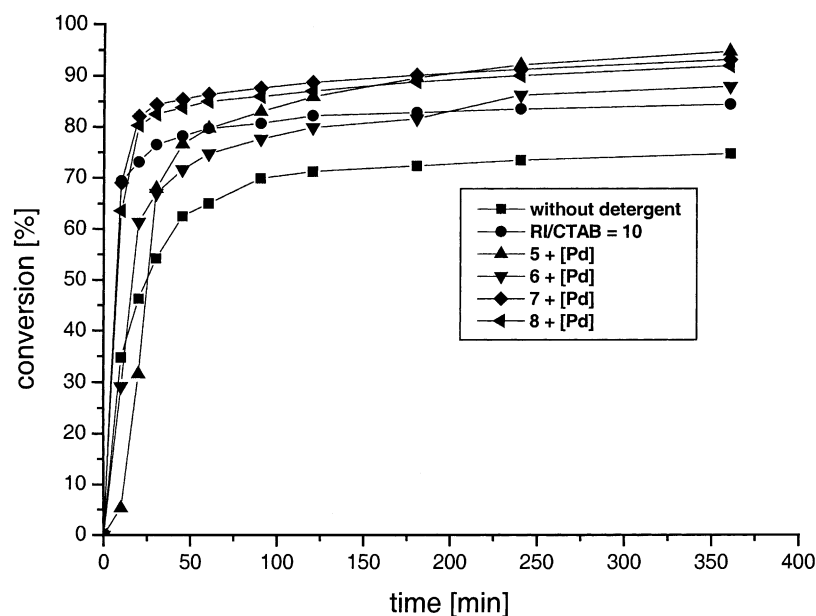

Fig. 1. Use of different immobilized amphiphiles (**5–8**) as phase-transfer reagent in the Suzuki reaction (see Scheme 1) in comparison to monomeric CTAB (RI/CTAB = aryl iodide/surfactant). [Pd] = PdCl$_2$[Ph$_2$P(CH$_2$)$_4$SO$_3$K]$_2$.
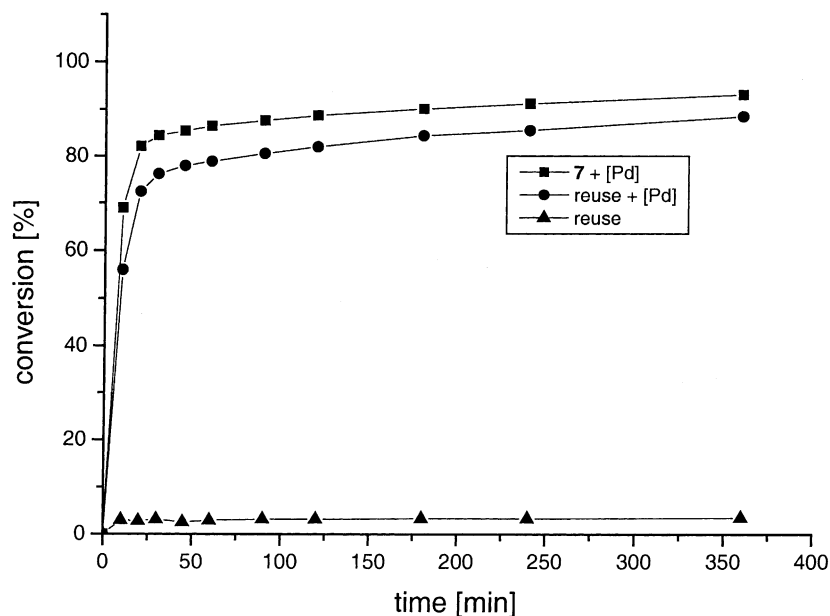
Fig. 2. Recycle experiments with the immobilized amphiphile **7** (see Scheme 1) $[Pd] = PdCl_2[Ph_2P(CH_2)_4SO_3K]_2$.

provided outstanding effects with cationic surfactants (e.g. CTAB).

Surprisingly, the immobilized polyoxyalkylene block co-polymers showed an optimal promoting effect. The non-ionic system can successfully compete with the cationic one. Especially in recycling experiments there are some advantages.

Fig. 2 contains recycling experiments with the immobilized cationic surfactant **7**.

After the reaction, support **7** was filtered, washed and reused in a new experiment, but without any effect. Obviously, the catalyst remained in the aqueous phase (as to be seen by the brown color) after the first experiment the coated silica was inactive. Addition of the original amount of palladium complex resulted in a catalytic system with acceptable activity. One should note here that the supported amphiphiles have only the function of phase-transfer reagents.
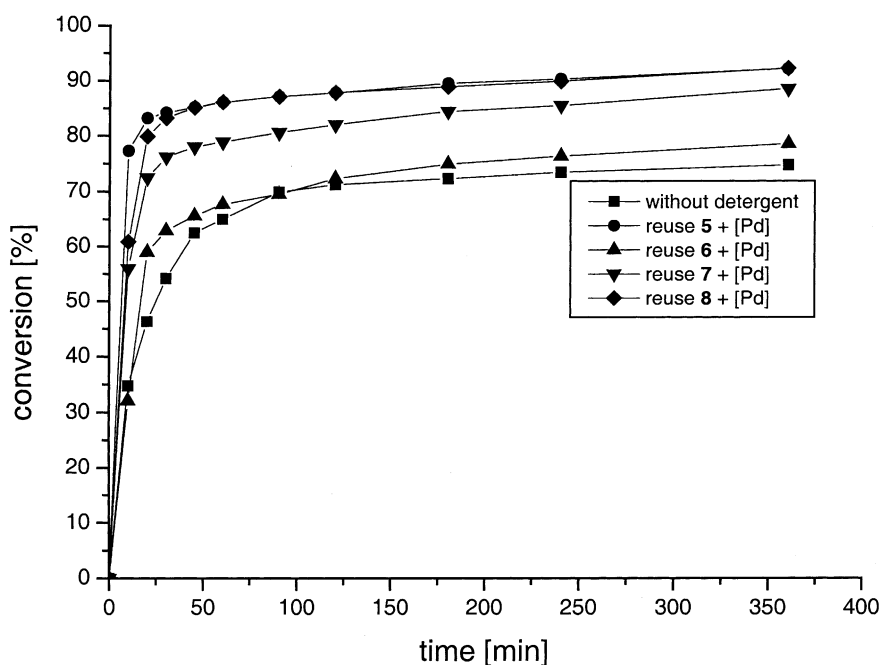

Fig. 3. First reuse experiments with the immobilized amphiphiles **5–8**. New addition of the catalytic palladium complex $[Pd] = PdCl_2[Ph_2P(CH_2)_4SO_3K]_2$.

The recycling experiments of all supported amphiphiles are summarized in Fig. 3.

System **6** lost its accelerating effect (perhaps because of a saponification of the sulfate ester group). In accordance with Fig. 2, system **7** was also less active than in the original experiment. Systems **5** and **8** gave about the same effects as in the first use.

The recovery of these reagents ("triphase" catalysts) is very convenient but the catalytically active palladium complex is not reusable by this method. We cannot use the aqueous phase a second time because of the high concentration of base and potassium iodide. The advantage of our procedure is the enhancement of the reaction rate by the immobilized amphiphile and a convenient phase separation after recovery of the phase-transfer reagent by filtration.

In future experiments, the amphiphilic layer should contain phosphine as an anchor group for the palladium complex.

3. Experimental

The chemicals were purchased from Aldrich, Fluka, Merck or Lancaster, except the water-soluble phosphine $Ph_2P(CH_2)_4SO_3K$ which was prepared in our laboratory by reaction of potassium diphenylphosphide with 1,4-butanesultone [15].

All catalytic reactions were performed in oxygen-free solvents under argon atmosphere.

The ^1H and ^{13}C NMR spectra were recorded on an ARX 400 Bruker spectrometer using $CDCl_3$, DMSO-d_6 and D_2O as solvents. The mass spectrometry was performed on an GC–MS instrument HP 6890.

3.1. Synthesis of 5 and 6

3.1.1. 10-Undecenoyl dimethylamide

10-Undecenoyl dimethylamide was prepared according to [16]. Purification by distillation (100–120 °C/1.2–1.9 mbar) yielding 23.6 g (55%) of the product.

^1H NMR (400 MHz, $CDCl_3$): δ 1.2–1.4 (m, 10H, 5 CH_2), 1.6 (m, 2H, CH_2), 2.0 (m, 2H, CH_2), 2.3 (t, 2H, CH_2CO), 3.8–4.0 (m, 2H, CH_2=), 5.0 (d, 6H, CH_3), 5.8 (m, 1H, CH=).

^{13}C NMR (100 MHz, $CDCl_3$): δ 23.9, 27.6, 27.8, 28.0, 28.2, 32.1, 32.5, 34.0 (CH_2), 36.0 (CH_3), 112.8 0 (CH_2=), 137.8, CH=), 171.9 (C=O).

GC–MS: $m/z = 211(M^+)$.

Analytically calculated for $C_{13}H_{25}NO$ (211.34): C 73.9, H 11.9, N 6.6. Found: C 73.9, H 11.9, N 6.4%.

3.1.2. ω-Dimethylamino-undec-1-ene

ω-Dimethylamino-undec-1-ene was prepared in accordance to [17]. The product was distilled in vacuum (60–62 °C/0.5 mbar) yielding 21.6 g (98%) as a colorless oil.

^1H NMR (400 MHz, $CDCl_3$): δ 1.1–1.3 (m, 10H, 5CH_2), 1.3 (m, 2H, CH_2), 1.4 (m, 2H, CH_2), 1.9 (m, 2H, CH_2), 2.1 (s, 6H, 2CH_3), 2.2 (m, 2H, CH_2N), 3.8–4.0 (m, 2H, CH_2=), 5.7 (m, 1H, CH=).

^{13}C NMR (100 MHz, $CDCl_3$): δ 27.9, 28.2, 29.3, 29.5, 29.8, 29.9, 30.0, 34.2 (CH_2), 45.9 (CH_3), 60.4 (CH_2N), 114.5 (CH_2=), 139.6 (CH=)

GC–MS: $m/z = 197(M^+)$.

Analytically calculated for $C_{13}H_{27}N$ (197.36): C 79.1, H 13.8, N 7.1. Found: C 79.1, H 13.7, N 7.0%.

3.1.3. ω-Triethoxysilylundecyldimethylamine

ω-Triethoxysilylundecyldimethylamine was prepared in accordance to [16]. The product was distilled in vacuum (135–140 °C, 0.7–1 mbar) yielding 12.0 g (66%).

^1H NMR (400 MHz, $CDCl_3$): δ 0.5 (2H, CH_2Si), 1.1–1.3 (m, 27H, 9CH_2, 3CH_3), 2.0–2.1 (m, 8H, 2NCH_3, CH_2N), 3.8–4.0 (m, 6H, 3OCH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ 10.7 (CH_2Si), 18.6 (3 CH_3), 23.2 (Si$CH_2\underline{CH_2}$), 27.9, 28.1, 29.6, 29.9 (CH_2), 33.6 (CH_2N), 45.8 (CH_3N), 58.6 (CH_2O), 60.3 (CH_2N).

GC–MS: $m/z = 361(M^+)$.

Analytically calculated for $C_{19}H_{43}NO_3Si$ (361.64): C 63.1, H 12.0, N 3.9. Found: C 79.1, H 13.7, N 7.0%.

3.1.4. 3-(ω-Triethoxysilylundecyldimethylammonio)-propane sulfonate

3-(ω-Triethoxysilylundecyldimethylammonio)-propane sulfonate was prepared according to [18]. The product was filtered, washed with cyclohexane and dried in vacuum (yield 3.8 g, 81%), mp 220 °C.

^1H NMR (400 MHz, DMSO-d_6): δ 0.5 (t, 2H, SiCH_2), 1.1 (t, 9H, 3CH_3), 1.3–1.4 (16H, 8CH_2), 1.6 (m, 2H, CH_2), 1.9 (m, 2H, CH_2), 2.4 (t, 2H, CH_2SO_3), 2.95 (s, 6H, 2CH_3N), 3.3–3.5 (m, 4H, 2CH_2N). 3.72 (q, 6H, 3CH_2O).

^{13}C NMR (100 MHz, DMSO-d_6): δ 10.2 (CH_2Si), 18.6 (3CH_3), 19.3, 22.0, 22.7, 25.8, 26.2, 28.9, 29.0, 29.2, 29.3, 32.7, 48.0, (11CH_2), 50.3 (2CH_3N), 58.0 (3CH_2O), 62.5 , 63.2 (2CH_2N).

Analytically calculated for $C_{22}H_{49}NO_6SSi$ (483.77): C 54.6, H 10.2, N 2.9, S 6.6. Found: C 53.3, H 10.5, N 2.8, S 6.4%.

3.1.5. 2-(ω-Triethoxysilylundecyldimethylammonio)ethyl sulfate

2-(ω-Triethoxysilylundecyldimethylammonio)ethyl sulfate was prepared according to [19]. The precipitated product was filtered off at 0 °C (yield: 2.2 g, 66%).^1H NMR (400 MHz, DMSO-d_6): δ 0.4 (t, 2H, CH_2Si), 1.0 (t, 9H, 3CH_3) 1.1–1.3 (m, 16H, 8CH_2), 1.6 (m, 2H, CH_2), 2.4 (t, 2H, CH_2OS), 2.9 (s, 6H, 2CH_3), 3.2 (m, 2H, CH_2N), 3.4 (m, 2H, CH_2N), 3.7 (q, 6H, 3$CH_3\underline{CH_2}$).

^{13}C NMR (100 MHz, DMSO-d_6): δ 14.3 (CH_2Si), 18.9 (3CH_3), 22.1 (Si$CH_2\underline{CH_2}$), 23.3, 26.1, 28.9, 29.2, 29.3, 33.2 (CH_2), 42.5, 51.1, 55.3, 56.4 (CH_3N), 60.0, 61.6 (CH_2N), 62.1(3CH_2O), 64.5 (CH_2N), 64.9 (CH_2SO_4).

Analytically calculated for $C_{21}H_{47}NO_7SSi$ (485.76): C 51.9, H 9.8, N 2.9, S 6.6. Found: C 48.8, H 9.2, N 2.9, S 7.0%.

3.1.6. Supporting of 3-(ω-Triethoxysilylundecyldimethylammonio)-propane sulfonate on SiO_2 (5)

To 5.5 g of silica gel (Merck 60, 0.040–0.063 mm, dried in vacuum <1 mbar at 200 °C for 12 h), 3.1 g (6.4 mmol) of 3-(ω-triethoxysilylundecyldimethylammonio)-propane sulfonate dissolved in 20 ml of toluene was added under argon. The mixture was shaken overnight and then refluxed for 2 h. The half of solvent amount was distilled off. Ten milliliter of toluene was added and 10 ml was distilled off again. The mixture was filtered and washed with 30 ml of hot toluene, 50 ml of hot ethanol and twice with 50 ml of ether. The support was dried overnight in vacuum (analytically found: C 5.9, H 1.44, N 0.40, S 0.74%. 218 mg organic substance/g (5), see Table 1).

3.1.7. Supporting of 2-(ω-Triethoxysilylundecyldimethylammonio)ethyl sulfate on SiO_2 (6)

To 5 g of silica gel (Merck 60, 0.040–0.063 mm, dried in vacuum <1 mbar at 200 °C for 12 h), 2.2 g (4.54 mmol) of 2-(ω-triethoxysilylundecyldimethylammonio)ethyl sulfate dissolved in 15 ml of toluene was added under argon. The mixture was shaken overnight and then refluxed for 3 h. The half of solvent amount was distilled off. Ten milliliter of toluene was added and 10 ml was distilled off again. The mixture was filtered and washed with 30 ml of hot toluene, 50 ml of hot ethanol and two times with 50 ml of ether. The support was dried overnight in vacuum (analytically found: C 14.2, H 2.85, N 1.05, S 2.30%. 354 mg organic substance/g (6), see Table 1).

3.2. Synthesis of 7

3.2.1. 3-(ω-Bromoundecylcarbamato)propyltriethoxysilane

The 2.51 g (10 mmol) of ω-bromoundecan-1-ol and 3.0 ml (12 mmol) of 3-(triethoxysilyl)propyl isocyanate were heated at 80 °C in a sealed tube for 14 h. The reaction was controlled by TLC ($CHCl_3$/EtOAc = 10/1). The product was isolated by column chromatography (crude product: 4.5 ml, purified product: 3.1 ml, 68%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.5 (t, 2H, $SiCH_2$), 1.1 (t, 9H, $3CH_3$), 1.15–1.3 (m, 16H, $8CH_2$), 1.5 (m, 4H, $2CH_2$), 1.7 (q, 2H, CH_2) 3.0 (m, 2H, CH_2O), 3.3 (t, 2H, CH_2Br), 3.7 (q, 6H, $3CH_3\underline{CH_2}$), 5.0 (bs, 1H, NH).

^{13}C NMR (100 MHz, $CDCl_3$): δ 7.8, ($SiCH_2$), 18.5 ($3CH_3$), 23.6 ($SiCH_2\underline{CH_2}$), 25.5, 26.0, 29.0, 29.4, 29.6, 29.7, 30.0, 32.8, 33.1, 34.1, 43.7, 45.7, 53.1, 57.2 (CH_2), 60.7 (CH_2O), 63.1 (CH_2Br), 65.0 ($3CH_2O$).

Analytically calculated for $C_{21}H_{44}BrNO_5Si$ (498.57): C 50.6, H 8.9, Br 16.0, N 2.8. Found: C 50.0, H 8.4, Br 17.6.

3.2.2. Quaternization of 3-(ω-bromoundecylcarbamato)propyltriethoxysilane [20]

The 3.0 ml (6.67 mmol) of 3-(ω-bromoundecylcarbamato)propyltriethoxysilane and 20 ml of a solution of trimethylamine in ethanol were heated at 80 °C for 14 h. The resulting mixture was concentrated by using a vacuum rotary evaporator and dried in vacuum (5 mbar, 50 °C) overnight to give a colorless waxy product (yield: 3.2 g; 81%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.5 (t, 2H, $SiCH_2$), 1.05 (t, 9H, $3\underline{CH_3}CH_2$), 1.1–1.3 (m, 18H, $9CH_2$), 1.5 (m, 4H, $2CH_2$), 1.7 (m, 2H, CH_2), 3.0 (m, 2H, CH_2OCO), 3.3 (s, 9H, $3NCH_3$), 3.7 (q, 6H, $3\underline{CH_2}CH_3$), 4.9 (bs, 1H, NH).

^{13}C NMR (100 MHz, $CDCl_3$): δ 7.9 ($SiCH_2$), 18.6 ($3\underline{CH_3}CH_2$), 23.6, 26.0, 26.5, 27.2, 29.2, 29.4, 29,5, 29.7, 32.9 ($9CH_2$), 45.2 (Me_3N), 53.7 (CH_2), 58.8 ($3\underline{CH_2}CH_3$), 60.9 (CH_2N), 65.1 (CH_2N), 67.2 (CH_2OCO), 157.1 (C=O).

Analytically calculated for $C_{27}H_{53}BrN_2O_5Si$ (593.72): C 54.6, H 9.0, Br 13.5, N 4.7. Found: C 53.9, H 9.2, Br 14.2, N 4.9%.

3.2.3. Supporting of ω-(3-triethoxysilylpropylcarbamato)undecyl-trimethylammonium bromide on SiO_2 (7)

To 10 g of silica gel (Merck 60, 0.040–0.063 mm), dried in vacuum (<1 mbar) at 200 °C for 12 h, 3.2 g (5.76 mmol) of ω-(3-triethoxysilylpropylcarbamato)undecyl-trimethylammonium bromide dissolved in 15 ml of toluene was added under argon. The mixture was shaken overnight and then refluxed for additional 3 h. The half of solvent amount was distilled off. Ten milliliter of toluene was added and 10 ml was distilled off. The mixture was filtered and washed with 30 ml of hot toluene, 50 ml of hot ethanol and twice with 50 ml of ether. The support was dried overnight in vacuum (found: C 5.47, H 1.52, N 0.56, Br 1.35%. 233 mg organic substance/g (7), see Table 1).

3.3. Synthesis of 8

3.3.1. Silylation of Synperonic L 101

7.4 g (2 mmol) Synperonic L 101 (HO-$(EO)_5$-$(PO)_{56}$-$(EO)_5$-H) and 50 mg (2.1 mmol) of NaH were stirred in 10 ml of absolute THF at room temperature for 3 h. One milliliter (4 mmol) of (3-glycidoxypropyl)trimethoxysilane was added and the mixture refluxed for 48 h. After the solvent was removed the product was dried at 120 °C in vacuum for 1 day (yield: quan.). ^{1}H NMR ($CDCl_3$): 1–1.1 (CH_3), 3.2–3.6 (CH_xO).

Analytically calculated for $C_{196}H_{404}O_{73}Si$ (3957.26): C 59.5, H 10.3. Found: C 56.9, H 10.5.

3.3.2. Supporting of silylated Synperonic L 101 on SiO_2

To 20 g of silica gel (Merck, 60, 0.043–0.060 mm), dried in vacuum (<1 mbar) at 200 °C for 12 h, was added 8.0 g (2 mmol) of the trialkoxysilane compound dissolved in 40 ml of toluene under argon. The mixture was shaken overnight and then refluxed for additional 2 h. The half of solvent

amount was distilled off. Forty milliliter of toluene was added and 20 ml were distilled off. The mixture was filtered and washed with 40 ml of hot toluene, 60 ml of hot ethanol and twice with 20 ml of ether. The support was dried overnight in vacuum. (Found: C 9.96, H 2.2%. 270 mg organic substance/g (**8**), see Table 1).

3.3.3. Catalytic reactions and analysis [8,9]

All preparations were performed in argon atmosphere. *p*-Iodoanisole (3.20 g, 13.5 mmol) was dissolved in 15 ml toluene and phenyl boronic acid (1.83 g, 15 mmol) was dissolved in 15 ml ethanol using two separate Schlenk tubes. Sodium carbonate decahydrate (11.6 g, 45 mmol) and 1.00 g supported amphiphile **5** (or alternatively **6**, **7**, **8**, see Table 1) (instead of cetyltrimethylammonium bromide, 1.27 g, 3.38 mmol, as homogeneous amphiphile) were placed in a 100 ml water-thermostated flask and dispersed in 15 ml water. The solutions of *p*-iodoanisole and phenyl boronic acid were added and the first sample was taken. Then the reaction mixture was heated to $78\,^\circ$C and the complex $PdCl_2[Ph_2P(CH_2)_4SO_3K]_2$ (9 mg, 0.01 mmol) was added under vigorous stirring (>1000 rpm). Samples of 0.2 ml were taken after 10, 20, 30, 45, 60, 90, 120, 180, . . . min, diluted with 0.8 ml toluene, dried with sodium sulfate, and finally analyzed by GLC (capillary HP1; program: 2 min at $50\,^\circ$C then $10\,^\circ$C/min up to $260\,^\circ$C). After the completion of the reaction, the mixture was extracted with 20 ml toluene, the organic phase was dried with sodium sulfate, the solvent evaporated and the residue was dissolved in 10 ml hexane. The product was purified by column chromatography (silica gel, eluant: *n*-heptane/ethyl acetate = 7/1) and analytically characterized by ^{1}H NMR, ^{13}C NMR and GLC–MS.

For the recycling of the heterogenized amphiphile, the support was isolated by filtration and washed three times with water, ethanol, toluene and ether and dried in vacuum. For a second run, the dried amphiphile was added to a solution of 9 mg (0.01 mmol) $PdCl_2[Ph_2P(CH_2)_4SO_3K]_2$ and 11.6 g (45 mmol) of $Na_2CO_3 \times 10\,H_2O$ in 15 ml water and after mixing with a fresh toluene and ethanol phase (see above) the reaction was repeated.

4. Conclusions

Four different types of amphiphilic supports were synthesized and characterized. It was achieved, that the activity of the catalysts in the Suzuki reaction was increased by acceleration with heterogenized detergents, which could be recycled simply by filtration. The selectivity with respect to compound **3** was in all cases better than 99%.

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