

Three Phase Microemulsion/Sol–Gel System for Aqueous C–C Coupling of Hydrophobic Substrates

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Keywords: C–C coupling / Green chemistry / Sustainable chemistry / Microemulsion / Palladium / Sol–gel processes

Heck, Stille, Suzuki and three-component coupling reactions with hydrophobic substrates have been carried out in water. The substrates are initially transformed by a general procedure into a microemulsion, which consists of nearly 90 % water with the aid of sodium dodecyl sulfate and either *PrOH* or *BuOH*. The surfactant carries the molecules of the substrates to $\text{Pd}(\text{OAc})_2$ entrapped within a hydrophobicitized silica sol–gel matrix where the coupling between the substrates is assumed to take place. The products are then returned by

the surfactant into the microemulsion from which it can be released. The immobilized palladium catalyst is leach proof and recyclable. It can be used in various coupling processes at least six times without loss of activity. Experiments with D_2O have revealed that the water does not take part in the coupling process, but it has an effect on the pore size of the sol–gel matrix, which hosts the palladium catalyst. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2008)

Introduction

The public concern over the massive use of organic solvents in industrial processes^[1] leads to much effort to replace the harmful media by water, which is both the cheapest and the least risky solvent.^[2] The main problem with the application of water in organic synthesis is the insolubility of many reagents and catalysts in this medium. In specific cases, this shortcoming can be overcome by modification of the reaction components (substrates and/or catalysts) with hydrophilic auxiliaries.^[2,3] Other noteworthy strategies that enable the formation of certain reactions of hydrophobic reagents in water are the application of the “on water” process,^[2,4] the application of hydrophilic cosolvents,^[2,5] the use of phase-transfer catalysis,^[6] pH regulation of the reaction mixture,^[2,7] the use of super-heated water^[8] or the application of ultrasound or microwave irradiation.^[1,8b] Sometimes it is sufficient to employ a suitable surfactant or a micelle-producing agent to “solubilized” the reactants as emulsions.^[3f,9] However, the recovery of the catalysts from such systems is usually difficult. In order to solve this problem we have found it useful to combine two domains, the emulsifications and the sol–gel technology.^[10] For example, when an emulsion of hydrophobic substrates is subjected to an organometallic catalyst that has been entrapped within a hydrophobicitized silica sol–gel, the surfactant molecules that carry the reactants absorb/desorb reversibly on the sur-

face of the sol–gel matrix and may spill the load of substrates into the porous medium that contains the catalyst. Consequently, a catalytic reaction takes place within the sol–gel material to form the products. The latter are then extracted by the desorbing surfactant, which carries them back, in their emulsified form, into the aqueous medium from where the free products can be separated.^[11] This catalytic system, which relies on a three-phase emulsion/sol–gel transport model (EST), proved already applicable to various hydrogenations of hydrophobic substrates.^[11] The EST system could be further developed and improved by replacement of the traditional emulsions by microemulsions.^[12] This change in medium enables further selective hydrogenations, as well as catalytic hydroformylations, to be carried out in aqueous media.^[13] The use of microemulsion (which are formed by titration of regular emulsions to clarity with an alcoholic cosurfactant) face, however, a major drawback associated with the fact that the component of the microemulsions are usually different in nature and quantity for each substrate and for each catalytic reaction. Thus, we found it imperative to seek in the framework of this work a general formula for the composition of stable microemulsions, suitable for the various hydrophobic substrates. Positive results led us to further investigation of the ability to utilize the microemulsion/sol–gel system to additional catalytic processes, apart from the aforementioned hydrogenations and hydroformylations. In this paper, we describe the use of this catalyst system in the Heck, Stille and Suzuki reactions, including the three-component coupling of phenylboronic acid with a diarylalkyne and an iodoarene. In all these processes the catalyst could be recovered at the end of the reactions and recycled.

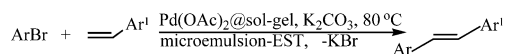
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Results and Discussion

Reinvestigation of our previous work in which we hydrogenated olefinic and aromatic carbon–carbon bonds under EST conditions^[13a] revealed that by lowering the concentration of the hydrophobic substrate, highly stable microemulsions are formed. These microemulsions could be employed to all unsaturated substrates studied so far. A typical composition of such a microemulsion is 89.3 wt.-% of water, 3.3 wt.-% of the surfactant sodium dodecyl sulfate (SDS), 6.6 wt.-% of the cosurfactant (usually *n*BuOH or *n*PrOH) and 0.8 wt.-% of the hydrophobic substrates. Microemulsions having this composition proved suitable not only for hydrogen-transfer processes but also for a variety of palladium-catalyzed C–C coupling processes.

A series of Heck coupling reactions of aryl bromides with styrene derivatives are shown in Scheme 1, and they were carried out under comparable EST conditions. The results are presented in Table 1. The catalyst in these reactions, as well as in those described below, was phosphane-free Pd(OAc)₂ entrapped within a silica sol–gel matrix hydrophobized with *n*-octyltri(ethoxy)silane (OTEOS). The optimal molar ratio of the palladium compound and the substrates is 1:100. Smaller ratios can be used but much lower ones cause a decrease in the reaction rate. For example, a ratio of 1:200 in the experiment described in Entry 1 affords only 84% of (*E*)-stilbene under the conditions of Table 1. Attempts to use Pd(OAc)₂ entrapped within regular, nonhydrophobized sol–gel resulted in exceedingly low yields. The coupling reactions of chlorine-free substrates (Table 1, Entries 1–4) afforded the corresponding stereochemically pure (*E*)-stilbene derivatives. Chlorine-containing substrates (either bromides or styrenes) gave, however, small amounts of the (*Z*) products (Table 1, Entries 5–8), and the reaction of 4-ClC₆H₄Br with 4-CH₃C₆H₄CH=CH₂ yielded, in addition to the (*E*)- and (*Z*)-stilbenes, trace amounts of 1-chloro-4-[1-(4'-methylphenyl)ethenyl]benzene. We recall that the formation of these isomers of (*E*)-stilbenes are common in the Heck coupling under conventional homogeneous and heterogeneous conditions.^[14,15] When the reactions listed in Table 1 were con-

ducted for short time periods it became clear that under EST conditions the coupling is affected by both electronic and steric effects. Electron-attracting substituents (located either on the styrene or on the bromide) enhance the coupling and vice versa for electron-releasing groups. When one of the components of the Heck reaction (either the styrene or the bromide) is electron rich and the other one is electron poor, the effect of the electron releasing substituents prevails and causes the process to slow down (Table 1, Entries 7 and 8). This observation suggests that neither the oxidative addition nor the final reductive elimination step are rate limiting. Bulky substituents have a strong inhibiting effect on the reaction. Thus, 1-bromonaphthalene, as well as 2-bromotoluene, that couple in homogeneous systems, hardly react under our standard conditions. It is also notable that nonsubstituted bromobenzene and styrene react as fast as the chlorinated reagents probably owing to their smaller size, which allows the substrate to penetrate more easily into the small pores of the sol–gel matrix (vide infra).^[16]



Scheme 1.

In all reactions listed in Table 1, the catalyst proved to be perfectly recyclable. For example, the reaction listed as Entry 1 in Table 1 (coupling of bromobenzene with styrene) gave a quantitative yield of pure (*E*)-stilbene in all six runs studied. In order to examine whether the water takes part in the coupling under EST conditions, we carried out a series of experiments in D₂O instead in H₂O. In none of these experiments did we observe any incorporation of deuterium in the products (or in the recovered starting materials).

In analogy to the Heck reaction, we performed Suzuki cross-coupling experiments with hydrophobic bromoarenes in water (Scheme 2). Several representative examples are summarized in Table 2. The table indicates that under the EST conditions the coupling is highly selective. Except for Entry 1 (where the formation of biphenyl was expected), no

Table 1. Heck coupling of styrene derivatives and bromoarenes by sol–gel encaged Pd(OAc)₂ under comparable microemulsion–EST conditions.^[a]

Entry	Ar in the bromide	Ar ¹ in the alkene	Major product	% Yield after 4 h in the 1st run ^[b]
1	C ₆ H ₅	C ₆ H ₅	<i>E</i> -C ₆ H ₅ CH=CHC ₆ H ₅	>99
2	4-C ₆ H ₄ CH ₃	C ₆ H ₅	<i>E</i> -C ₆ H ₅ CH=CH-4-C ₆ H ₄ CH ₃	33 ^[c]
3	C ₆ H ₅	4-C ₆ H ₄ CH ₃	<i>E</i> -C ₆ H ₅ CH=CH-4-C ₆ H ₄ CH ₃	47
4	C ₆ H ₅	4-C ₆ H ₄ F	<i>E</i> -C ₆ H ₅ CH=CH-4-C ₆ H ₄ F	82
5	4-C ₆ H ₄ Cl	C ₆ H ₅	<i>E</i> -C ₆ H ₅ CH=CH-4-C ₆ H ₄ Cl	>99 ^[d]
6	C ₆ H ₅	4-C ₆ H ₄ Cl	<i>E</i> -C ₆ H ₅ CH=CH-4-C ₆ H ₄ Cl	>99 ^[d]
7	4-C ₆ H ₄ Cl	4-C ₆ H ₄ CH ₃	<i>E</i> -4-ClC ₆ H ₄ CH=CH-4-C ₆ H ₄ CH ₃	20 ^[e]
8	4-C ₆ H ₄ CH ₃	4-C ₆ H ₄ Cl	<i>E</i> -4-ClC ₆ H ₄ CH=CH-4-C ₆ H ₄ CH ₃	21 ^[f]

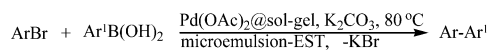
[a] Reaction conditions: Pd(OAc)₂ (3 mg, 0.0134 mmol) entrapped within a hydrophobized sol–gel matrix prepared from *n*-octyltri(ethoxy)silane and tetramethoxysilane (TMOS) as described in the Experimental Section; composition of the microemulsion 0.8 wt.-% of the substrates (1.34 mmol of each of them), 3.3 wt.-% of sodium dodecyl sulfate (SDS), 6.6 wt.-% of *n*BuOH and 89.3 wt.-% H₂O; K₂CO₃ (2 mmol); 80 °C. [b] The yields were determined by both GC and ¹H NMR spectroscopic analysis and are the average of at least two experiments that did not differ by more than ±3%. [c] A quantitative yield was obtained only after 48 h. [d] Contains 4% of the (*Z*) isomer. [e] Contaminated with 3% of the (*Z*) isomer and 1% of 1-chloro-4-[1-(4'-methylphenyl)ethenyl]benzene. [f] Contains 3% of the (*Z*) isomer.

Table 2. Suzuki coupling of bromoarenes with arylboronic acids under microemulsion–EST conditions catalyzed by sol–gel entrapped $\text{Pd}(\text{OAc})_2$.^[a]

Entry	Ar in the bromide	Ar ¹ in the boronic acid	Product	% Yield after 7 h in the 1 st run ^[b]
1	phenyl	phenyl	biphenyl	> 99
2	4-methylphenyl	phenyl	4-methylbiphenyl	87
3	4-methylphenyl	mesityl	4-methylbiphenyl	33 ^[c]
4	4-methoxyphenyl	phenyl	4-methoxybiphenyl	64
5	4-chlorophenyl	phenyl	4-chlorobiphenyl	96
6	1-naphthyl	phenyl	1-phenylnaphthalene	92
7	anthracen-9-yl ^[d]	phenyl	9-phenylanthracene	80 ^[e]

[a] Reaction conditions: $\text{Pd}(\text{OAc})_2$ (0.0134 mmol) entrapped within hydrophobized sol–gel as described in the Experimental Section; microemulsion of the bromoarene (1.34 mmol) and the boronic acid (1.34 mmol). The composition of the microemulsion was identical with that described in Table 1 except that it contained phenylboronic acid instead of styrene; K_2CO_3 (2 mmol); 80 °C. [b] The yields are the average of at least two experiments that did not differ by more than $\pm 3\%$ and were determined both by GC and ^1H NMR spectroscopic analysis. [c] Yield after 15 h. [d] Dissolved in CH_2Cl_2 (3 mL). [e] When the octyltri(ethoxy)silane in the hydrophobized matrix was replaced by trimethyl(methoxy)silane the yield rose to 99%.

formation of biphenyl was observed. Thus, unlike the situation in many cases of the Suzuki coupling under conventional conditions,^[17] no homocoupling takes place.



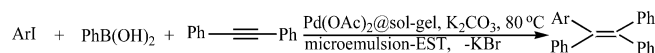
Scheme 2.

Owing to the hydrophilic nature of boronic acids it is not uncommon that Suzuki couplings of partially water-soluble halides can be performed also in water (see, for example, the reactions reported by Byun and Lee^[18]). When, however, the halide is highly hydrophobic, as for example 9-bromoanthracene, no coupling takes place in this medium. Table 2 indicates that by application of the EST technique even such water-insoluble substrates undergo smooth coupling in high yields.

Except for Entry 3, the coupling of the halides listed in Table 2 with phenylboronic acid give within 20 h nearly a quantitative yield of the expected biaryls. Only when the unsubstituted acid was replaced by the sterically hindered mesitylboronic acid was the yield substantially reduced. Experiments conducted for shorter reaction periods (e.g., 4 h) revealed the existence of a clear electronic effect similar to that observed in the Heck reaction. The Suzuki cross-coupling reaction under the EST conditions resembles the Heck reaction also with respect to the recyclability of the immobilized catalyst. In a typical series of six runs in which 4-bromotoluene was coupled with phenylboronic acid at 80 °C for 20 h the yields of 4-phenyltoluene were nearly quantitative. In contrast to many other catalysts by sol–gel entrapped metallic compounds,^[10,16] the heterogenized catalyst seems not to suffer from clogging of the pores by the substrate and product molecules. BET/BJH (Brunner, Emmet, Teller/Barett, Joyner, Halenda) measurements indicated that within the aqueous medium, the average pore diameters of the matrix do not decrease with time. On the contrary, owing to some Si–O bond cleavage by water, they even increase in size after each run. For example, in the coupling of bromobenzene and phenylboronic acid, the BJH- N_2 adsorption average pore diameter (4V/A) of the immobilized catalyst increased after the second run from 31.5 to 34.4 Å and after six further runs it became as large

as 40 Å. A similar increase in the pore size was observed in the catalyst used for the Heck coupling of bromobenzene with styrene. One significant difference between the Heck and Suzuki coupling under the EST condition is, however, remarkable. Although bulky bromoarenes couple either very slowly or not at all with styrene, they react quite smoothly with phenylboronic acid.

The palladium-catalyzed three-component coupling of iodoarenes, internal alkynes and arylboronic acid shown in Scheme 3 may be regarded as a modification of the Suzuki reaction.^[19] Thus, we were able to couple phenylboronic acid with diphenylacetylene and several substituted iodo-benzenes (Scheme 3). Representative results are summarized in Table 3. We noticed that the reaction proceeds faster under the EST conditions than that in a homogeneous system with the same [palladium]/[substrate] ratio. This rate acceleration may be associated with the promotion of the three-component coupling reaction by water.^[20] In the EST system, the three-component coupling seems to follow a different mechanism than that under the homogeneous conditions. In the presence of the non-entrapped palladium catalyst, electron-donating substituents enhance the process and electron attracting groups cause it to slow down (the nitro group stalls the reaction completely^[19]). In our reaction system, the opposite trend was observed. Whereas Entries 1, 3 and 4 (Table 3) were complete within less than 2 h to form >97% of analytically pure tetraarylethylenes, the reaction of 1-iodo-4-methylbenzene, diphenylacetylene and phenylboronic acid (Entry 2) was complete only after 10 h. Recycling of the heterogenized catalyst in the reactions listed in Table 3 did not decrease the activity at all for at least six runs.



Scheme 3.

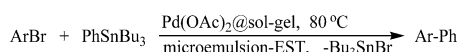
Another cross-coupling of hydrophobic reagents that proved to take place in an aqueous medium is the Stille reaction (Scheme 4).^[21] Some representative results are listed in Table 4. At 80 °C, the reaction seems not to depend on the electronic nature of the substrate, as in the other

Table 3. Three component coupling of iodoarenes, diphenylacetylene and phenylboronic acid.^[a]

Entry	Iodoarene	Time [h]	Product	% Yield ^[b]
1	C ₆ H ₅ I	2	(C ₆ H ₅) ₂ C=C(C ₆ H ₅) ₂	98
2	4-IC ₆ H ₄ CH ₃	10	(4-C ₆ H ₄ CH ₃)(C ₆ H ₅)-C=C(C ₆ H ₅) ₂	97
3	4-IC ₆ H ₄ Br	2	(4-C ₆ H ₄ Br)(C ₆ H ₅)-C=C(C ₆ H ₅) ₂	98
4	4-IC ₆ H ₄ NO ₂	2	(4-C ₆ H ₄ NO ₂)(C ₆ H ₅)-C=C(C ₆ H ₅) ₂	98

[a] Reaction conditions: catalyst and composition of the microemulsion as described in the Experimental Section. The amounts of the iodoarene, the diphenylacetylene and the phenylboronic acid were 1.34 mol each; K₂CO₃ (2 mmol); 80 °C. [b] Yield of isolated product.

coupling processes. The catalyst proved completely recyclable in further runs without any loss in catalytic activity for at least six runs. For example, the reaction of bromobenzene and phenyltributylstannane under the conditions of Table 4 gave quantitatively pure biphenyl in each run, and the coupling of 4-bromotoluene formed 70–75% of 4-methyl-1,1'-biphenyl in each of the first six cycles.



Scheme 4.

Table 4. Stille cross-coupling of some bromoarenes with tributylphenylstannane under microemulsion-EST conditions by sol-gel entrapped Pd(OAc)₂.^[a]

Entry	Bromoarene	Product	% Yield ^[b]
1	C ₆ H ₅ Br	biphenyl	98
2	4-BrC ₆ H ₄ CH ₃	4-methyl-1,1'-biphenyl	73
3	4-BrC ₆ H ₄ OCH ₃	4-methoxy-1,1'-biphenyl	81
4	4-BrC ₆ H ₄ CHO	1,1'-biphenyl-4-carboxaldehyde	86

[a] Reaction conditions: immobilized catalyst containing 0.0134 mmol Pd(OAc)₂ as described in the Experimental Section; bromoarene (1.34 mmol) and PhBu₃Sn (1.34 mmol); the microemulsion as described in the Experimental Section; 80 °C, 7 h. [b] The yields are the average of isolated products obtained at least in two experiments that did not differ by more than ±3%.

Because the Heck and other C–C coupling reactions by supported palladium compounds have sometimes been attributed to the action of soluble nanoclusters derived from the original precatalyst (see for example, refs.^[15,22,23]), we assume that in our system, palladium nanoparticles may also be involved. Pd⁰ can result from the Pd^{II} acetate by transfer hydrogenation from the carbinols released during the preparation of the sol-gel matrix, as well as from the alcoholic cosurfactant. In any event, if such nanoparticles were formed they must be entrapped with the sol-gel matrix rather than dispersed in the solution. Inductivity coupled plasma (ICP) analysis indicated that the concentration of palladium in the reaction solution after removal of the sol-gel material by filtration is less than 1 ppm. In addition, we found that the filtrate has absolutely no catalytic activity (even after concentration). Further support of the assumption that the coupling process takes place within the matrix was found in a set of experiments in which the Pd(OAc)₂ had been entrapped in differently hydrophobized sol-gel. The

yield of the coupling product of bromobenzene and styrene extended from 0 to 100% depending on the nature of the hydrophobic part of the sol-gel (these experiments will be announced in a separate publication). It was already mentioned that Pd(OAc)₂ encaged within a nonhydrophobized matrix is catalytically inactive. If the reactions were promoted by leached palladium, the yields (obtained under identical conditions) should not have been dependent on the nature of the sol-gel.

Conclusions

Although conventional conditions for the catalytic Heck, Stille, Suzuki and three-component coupling reactions usually involve organic solvents, by using a three-phase microemulsion/sol-gel transport system it is possible to perform these processes under “greener” conditions, in aqueous solutions, even with water-insoluble hydrophobic substrates. All the reactants are solubilized by the formation of microemulsions of the same general composition that contain almost 90% water. The catalyst in these reactions is phosphane-free palladium acetate entrapped within a hydrophobized silica sol-gel matrix. This enables facile recovery and recycling of the used palladium compound. Palladium acetate that is encaged in regular hydrophilic sol-gel material fails to react with the emulsified substrates and consequently hardly any coupling reactions take place in such a system.

Experimental Section

General: ¹H and ¹³C NMR spectra were recorded with either a Bruker AMX-300 or a Bruker AMX-400 instrument in CDCl₃. Infrared spectra were taken with a Bruker Vector 22-FRIT spectrometer. Mass-spectral measurements were performed with a Hewlett-Packard model 4989 A mass spectrometer equipped with an HP gas chromatograph. ICP analyses were performed with the aid of a Perkin-Elmer model Optima 3000 instrument. A Micrometrics ASAP 2020 instrument was used for BET-N₂ and BJH-N₂ surface area and pore diameter measurements of the sol-gel matrices. The following starting materials and reference compounds were obtained from commercial sources: tetramethoxysilane, octyltriethoxysilane, trimethylmethoxysilane, palladium acetate, sodium dodecyl sulfate, bromobenzene, iodobenzene, 1-bromo-4-methylbenzene, 1-bromo-4-chlorobenzene, 4-bromobenzaldehyde, 1-bromo-4-methoxybenzene, 1-bromo-4-iodobenzene, 1-iodo-4-methylbenzene, 1-iodo-4-nitrobenzene, 1-bromonaphthalene, 9-bromoanthracene, ethenylbenzene, 1-ethenyl-4-methylbenzene, 1-chloro-4-ethenylbenzene, 1-ethenyl-4-fluorobenzene, B-phenylboronic acid, B-(2,4,6-trimethylphenyl)boronic acid, tributylphenylstannane, 1,1'-(1,2-ethynediyl)bis(benzene), 1,1'-(1Z)- and 1,1'-(1E)-(1,2-ethenediyl)-bis(benzene), 1-methyl-4-[(1E)-2-phenylethenyl]benzene, 1-methoxy-4-[(1E)-2-phenylethenyl]benzene, 1-chloro-4-[(1E)-2-phenylethenyl]benzene, 1-fluoro-4-[(1E)-2-phenylethenyl]benzene, 9-[(1E)-phenylethenyl]anthracene, biphenyl, 4-methyl-1,1'-biphenyl, 4-methoxy-1,1'-biphenyl, [1,1'-biphenyl]-4-carboxaldehyde and 1,1',1'',1'''-(1,2-ethenediylidene)tetrakisbenzene. The following chemicals were prepared according to literature procedures: 1-chloro-4-[(1E)-2-(methylphenylethenyl)]benzene,^[24] 1-methyl-4-(1,2,2-triphenylethenyl)benzene,^[25] 1-bromo-4-(1,2,2-triphenylethenyl)benzene^[26] and 1-nitro-4-(1,2,2-triphenylethenyl)benzene.^[19] The structures of 1-chloro-4-[(1Z)-2-phenylethenyl]ben-

zene^[27] and 1-chloro-4-[1-(4'-methylphenyl)ethenyl]benzene,^[28] which were obtained in this study in minute amounts as mixtures, were deduced from the ¹H NMR and MS spectra of the mixture of products.

Entrapment of Palladium Acetate within a Hydrophobicitized Sol–gel Matrix: Typically, *n*-octyl(triethoxy)silane (OTEOS, 2.1 mL, 6.68 mmol) was stirred magnetically at 20 °C for 24 h with a mixture of EtOH (5.6 mL, 729 mmol) and triply distilled water (TDW, 0.4 mL, 22.2 mmol). Separately, tetramethoxysilane (TMOS, 3.6 mL, 24.2 mmol) was stirred for 10 min at 20 °C with MeOH (2.4 mL, 59.3 mmol) and TDW (2.0 mL, 111 mmol). The two solutions were mixed and stirred for an additional 10 min and added to a stirred solution of Pd(OAc)₂ (30 mg, 0.134 mmol) in CH₂Cl₂ (4 mL). Gelation was achieved within 10–12 h. The gel was dried at 80 °C/0.1 Torr for 24 h then washed with CH₂Cl₂ (3 × 10 mL) and redried under the same conditions to yield the immobilized palladium compound (3.0 g). Analysis of the combined washing revealed that they rarely contained more than 1 ppm of palladium. The resulting sol–gel material was then divided into ten equal portions for the catalytic processes.

For comparison, nonhydrophobicitized sol–gel entrapped Pd(OAc)₂ was prepared, which did not include the OTEOS.

Preparation of the Microemulsions: Typically, the microemulsions were prepared by mixing the hydrophobic substrates (1.34 mmol of each) with TDW (89.3 wt.-%), sodium dodecyl sulfate (SDS, 3.3 wt.-%) and the cosurfactant (6.6 wt.-% of either *n*-propanol or *n*-butanol) at room temperature (20–25 °C) for 20 min. It was seldom necessary to add a few additional drops of the carbinol to prevent trace amounts or foam or turbidity. Solid substrates were initially dissolved in CH₂Cl₂ (3 mL for 1.34 mmol of substrate).

General Procedures for the Various Coupling Reactions: The immobilized catalyst [usually containing 3 mg, 0.0134 mmol Pd(OAc)₂] was added to a freshly prepared microemulsion of the substrates (0.67–1.34 mmol of each) and, except for the Stille reaction, K₂CO₃ (280 mg, 2 mmol) was also added. The reaction mixture was then heated with stirring at the desired temperature for the required length of time. After cooling to room temperature, NaCl (2 g) was added to the reaction mixture. This caused the emulsion to separate into two phases. (In the Stille coupling 10 mL of a saturated KF solution was also added). The organic layer was diluted with diethyl ether (50 mL), dried with MgSO₄ and concentrated. The ceramic catalyst was extracted with ether (usually 3 × 50 mL), dried and concentrated under reduced pressure. The residue was then analyzed for leached palladium by ICP. The products can be either separated by column chromatography or analyzed by GC, GC–MS and NMR spectroscopy. The physical data of the products were compared with those of authentic samples. All the products obtained in this study are known compounds and their physical data, except the ¹H and ¹³C NMR spectra of 1-bromo-4-(1,2,2-triphenylethenyl)benzene,^[26] have already been published in the literature. The NMR spectra of this bromo compound are as follows: ¹H NMR (400 MHz, CDCl₃): δ = 7.26–7.36 (m, 5 H), 7.46–7.49 (m, 6 H), 7.57–7.60 (m, 8 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 121.5, 122.2, 123.3, 127.0, 128.2, 128.4, 128.8, 128.9, 131.6, 131.9, 133.5, 139.1, 140.0, 140.2 ppm. The filtered sol–gel-entrapped used catalyst was washed with water (3 × 40 mL) to remove remains of the surfactant, sonicated for 10 min with CH₂Cl₂ (3 × 30 mL) and dried at 80 °C/0.1 Torr for 12 h. The washings were combined and again analyzed for the presence of palladium. The dried catalyst was ready for use in the next run.

Acknowledgments

We gratefully acknowledge the support of this study by the Israel Science Foundation (ISF) through grant no. 269/06.

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Received: January 10, 2008

Published Online: March 27, 2008