

C–C Coupling Reaction of Triphenylbismuth(V) Derivatives and Olefins in the Presence of Palladium Nanoparticles Immobilized in Spherical Polyelectrolyte Brushes

Yulia B. Malysheva,^[a,b] Alexey V. Gushchin,^[b] Yu Mei,^[c] Yan Lu,^[c] Matthias Ballauff,^[c] Sebastian Proch,^[a] and Rhett Kempe^{*[a]}

Keywords: Bismuth / Cross-coupling / Heck-type products / Nanoparticles / Palladium / Polyelectrolytes

Carbon–carbon coupling reactions were carried out by using the triphenylbismuth(V) derivatives Ph_3BiX_2 ($\text{X} = \text{O}_2\text{CH}$, O_2CMe , O_2CEt , O_2CnPr , O_2CnBu , O_2CtBu , O_2CPh , $\text{O}_2\text{CCH}_2\text{Cl}$, O_2CCCl_3 , O_2CCF_3) and a variety of olefins in the presence of palladium nanoparticles immobilized in spherical polyelectrolyte brushes (Pd@SPB) under mild conditions (50 °C). The effects of the organobismuth derivatives and the unsaturated compounds and the influence of the ratio of solvents (THF and water) on the yield of cross-coupled products were studied. The most active organobismuth compound studied was triphenylbismuth bis(trifluoroacetate), Ph_3Bi –

$(\text{O}_2\text{CCF}_3)_2$. This system, which is based on the use of organobismuth compounds, allows the formation of Heck-type products without the addition of base. Time-dependent product and side-product formation is indicative of a variety of fast (relative to product formation) organobismuth decomposition pathways that lower the overall yield of the coupling reactions. In comparison to homogeneous catalyst systems used for this type of C–C coupling reaction, we only used a very low Pd loading.

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Introduction

Heck-type chemistry is a powerful tool for carbon–carbon bond-forming processes. It is broadly defined as a Pd-catalyzed C-arylation reaction of unsaturated compounds. Normally, aryl halides are used as arylating agents in these transformations,^[1] but other arylating agents have also been tested for the formation of Heck-type products.^[2,3] This research is directed towards finding more reactive substrates and milder procedures that would allow for a base-free arylation. It was shown that different organometallic derivatives such as boronic acids,^[4–8] arylsilanols,^[9] arylstannanes,^[10] aryltellurides,^[11–13] organolead,^[14] organoantimony,^[15–19] and organobismuth^[20] derivatives can be used to form Heck-type products.

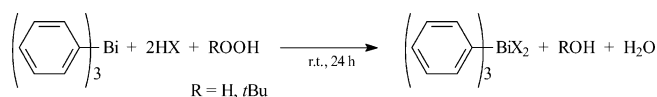
Recent developments of “ligand-free” heterogeneous Pd catalysts have provided interesting and practically important alternatives to common ligand-assisted methodologies.^[21] Metal nanoparticles exhibit different properties than their bulk materials and their isolated atoms. Because of their high surface area per volume, metal nanoparticles are ideal candidates for catalysis as well.^[22,23] Within the

last decade, a variety of reports have focused on the use of palladium nanoparticles as catalyst in classic Heck coupling reactions.^[24] At temperatures above 100 °C, molecular species are highly relevant and the palladium bulk material may act as a Pd reservoir.^[25] Classic Heck coupling reactions were performed, for instance, with Pd particles on inorganic supports,^[26] on chemically rather inert polymer supports,^[27] or stabilized in ionic liquids.^[28]

Recently, we showed that well-defined gold, platinum, and palladium nanoparticles could be generated in a spherical polyelectrolyte brush and used as a catalyst.^[29–31] We report here on the use of well-defined Pd particles supported on spherical polyelectrolyte brushes (Pd@SPB) as a catalyst for the organobismuth/olefin C–C coupling reaction under mild conditions.

Results and Discussion

Triphenylbismuth dicarboxylates Ph_3BiX_2 ($\text{X} = \text{O}_2\text{CH}$, O_2CMe , O_2CEt , O_2CnPr , O_2CnBu , O_2CtBu , O_2CPh , $\text{O}_2\text{CCH}_2\text{Cl}$, O_2CCCl_3 , O_2CCF_3 ; Scheme 1) were obtained

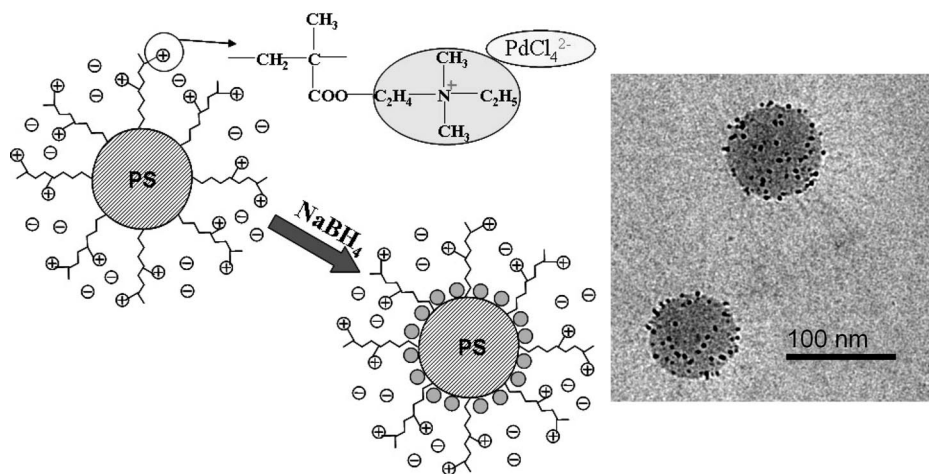


Scheme 1. Synthesis of triphenylbismuth dicarboxylates ($\text{X} = \text{O}_2\text{CH}$, O_2CMe , O_2CEt , O_2CnPr , O_2CnBu , O_2CtBu , O_2CPh , $\text{O}_2\text{CCH}_2\text{Cl}$, O_2CCCl_3 , O_2CCF_3).

[a] Lehrstuhl für Anorganische Chemie II, Universität Bayreuth, 95440 Bayreuth, Germany
E-mail: kempe@uni-bayreuth.de

[b] Department of Organic Chemistry, Nizhny Novgorod State University,
23 Gagarin Avenue, 603950 Nizhny Novgorod, Russia

[c] Lehrstuhl für Physikalische Chemie I, Universität Bayreuth, 95440 Bayreuth, Germany



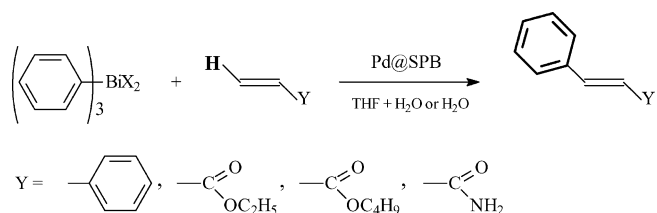
Scheme 2. Synthesis of the spherical polyelectrolyte (left) and CryoTEM of Pd@SPB (right). Long chains of poly[(2-methylpropenyloxy-ethyl)trimethylammonium chloride] were grafted onto polystyrene cores of ca. 100 nm diameter. PdCl_4^{2-} ions were introduced as counterions and reduction by NaBH_4 in aqueous solution led to Pd nanoparticles with diameters of 2.6 ± 0.5 nm that are immobilized on the surface of the carrier particles.

by the one-step reaction of triphenylbismuth with the appropriate carboxylic acid in the presence of equimolar amounts of peroxide.^[20,32]

Scheme 2 shows the structure of the spherical polyelectrolyte brushes (SPB) in a schematic manner: Long polyelectrolyte chains with quaternized amino groups were chemically grafted onto the colloidal polymer particles with diameters of ca. 100 nm.

The layer of polyelectrolyte chains attached to the surface of the carrier particles is very dense, that is, the contour length L_c of the chains is much higher than their average distance on the surface of the carrier particle. In this way, a polyelectrolyte “brush” results in a system of strongly interacting polymer chains inserted densely to a curved surface. The counterions neutralizing the charge of the polyelectrolyte chains are nearly fully confined in the brush layer. Metal ions, for example, PdCl_4^{2-} , can be immobilized in this way and reduced to well-defined metal nanoparticles.^[30] Pd@SPB were synthesized by using a literature procedure developed by us.^[29–31] It should be noted that the metal nanoparticles generated in this way are not stabilized by any surface group or other stabilizing agents (besides water). Colloidal stability is brought about only by the carrier particles. In this way, “naked” Pd nanoparticles are generated, and their reactivity is not impeded by any group bound chemically to the surface.

The synthesized organobismuth compounds Ph_3BiX_2 were employed in C–C coupling reactions with different unsaturated compounds (styrene, ethyl acrylate, butyl acrylate, acryl amide) in the presence of palladium nanoparticles immobilized in spherical polyelectrolyte brushes (Scheme 3). The reactions were carried out in water or in a mixture of water and THF. The C-phenylation product (Heck-type product) and biphenyl (homocoupled byproduct) were found as the organic products in all cases, and benzene was found as a byproduct in some cases in trace amounts.



Scheme 3. Organobismuth Heck-type cross-coupling reaction ($\text{X} = \text{O}_2\text{CH}$, O_2CMe , O_2CEt , O_2CnPr , O_2CnBu , O_2CtBu , O_2CPh , $\text{O}_2\text{CCH}_2\text{Cl}$, O_2CCl_3 , O_2CCF_3).

We started with styrene as the coupling partner of the organobismuth compounds in the presence of Pd@SPB (0.09 mol-%, on the basis of the corresponding organobismuth compound) and tetrabutylammonium bromide (TBAB) as a phase-transfer reagent in THF/ H_2O (5:1) at 50 °C for 20 h (Table 1). Because classic Heck-type reactions usually require the presence of a base, we tested its influence in the reaction. As previously observed for homogeneous catalyst systems in organobismuth C–C coupling reactions,^[20] the addition of a base into the reaction mixture decreases the reactivity of the substrate. When *t*BuOK was omitted from the reaction mixture, the yield of *trans*-stilbene increased from 3 to 7% and the yield of biphenyl increased from 49 to 68% (Table 1, Entries 1, 2). Triphenylbismuth bis(trifluoroacetate), $\text{Ph}_3\text{Bi}(\text{O}_2\text{CCF}_3)_2$, was the most selective organobismuth compound towards the formation of the olefin C-phenylation product. *trans*-Stilbene and biphenyl were obtained in 15 and 35% yield, respectively (Table 1, Entry 11). The selectivity is probably caused by the presence of the most polar carboxylic group in this organobismuth derivative among the studied compounds. The yield of *trans*-stilbene increased to 18% and the yield of biphenyl decreased to 15% when triphenylbismuth bis(trifluoroacetate) was treated with styrene in the absence of a phase-transfer reagent (Table 1, Entry 12).

Benzene was found in all reactions in trace amounts only. In conclusion, the introduced catalyst system does not need a base or a phase-transfer reagent.

Table 1. Palladium-catalyzed reaction of Ph_3BiX_2 with styrene and the influence of the nature of the substituent X.^[a]

Entry	Ph_3BiX_2	Yield ^[b] [%]	
		<i>trans</i> -Stilbene	Biphenyl
1 ^[c]	$\text{Ph}_3\text{Bi}(\text{O}_2\text{CH})_2$	3	49
2	$\text{Ph}_3\text{Bi}(\text{O}_2\text{CH})_2$	7	68
3	$\text{Ph}_3\text{Bi}(\text{O}_2\text{CMe})_2$	4	73
4	$\text{Ph}_3\text{Bi}(\text{O}_2\text{CEt})_2$	2	36
5	$\text{Ph}_3\text{Bi}(\text{O}_2\text{CnPr})_2$	6	79
6	$\text{Ph}_3\text{Bi}(\text{O}_2\text{CnBu})_2$	4	65
7	$\text{Ph}_3\text{Bi}(\text{O}_2\text{CtBu})_2$	6	63
8	$\text{Ph}_3\text{Bi}(\text{O}_2\text{CPh})_2$	5	63
9	$\text{Ph}_3\text{Bi}(\text{O}_2\text{CCH}_2\text{Cl})_2$	6	56
10	$\text{Ph}_3\text{Bi}(\text{O}_2\text{CCCl}_3)_2$	6	45
11	$\text{Ph}_3\text{Bi}(\text{O}_2\text{CCF}_3)_2$	15	35
12 ^[d]	$\text{Ph}_3\text{Bi}(\text{O}_2\text{CCF}_3)_2$	18	15

[a] Reaction conditions: Ph_3BiX_2 (0.1 mmol), styrene (0.3 mmol), TBAB (0.1 mmol), Pd@SPB (0.09 mol-% Pd) in THF/ H_2O (5:1) at 50 °C for 20 h in air. [b] Yields were determined by GC: 0.3 mmol of *trans*-stilbene corresponds to 100%; 0.15 mmol of Ph_2 corresponds to 100%; 0.3 mmol of benzene corresponds to 100%. [c] In the presence of *t*BuOK (0.1 mmol). [d] In the absence of TBAB.

It was shown in the reaction of $\text{Ph}_3\text{Bi}(\text{O}_2\text{CCF}_3)_2$ with styrene in the presence of Pd@SPB and without TBAB (THF/ H_2O , 5:1; 50 °C; 20 h) that changes in the concentration of the palladium catalyst in the range from 0.04 to 0.3 mol-% Pd [on the basis of triphenylbismuth bis(trifluoroacetate)] did not significantly affect the yield of the C-phenylation product. Thus, in the following experiments the concentration of catalyst was decreased from 0.09 to 0.04 mol-% Pd.

The reaction of $\text{Ph}_3\text{Bi}(\text{O}_2\text{CCF}_3)_2$ with styrene in the presence of Pd@SPB (0.04 mol-% Pd) at 50 °C for 24 h was carried out in THF/ H_2O with varying ratios of these solvents. The results are presented in the Table 2. It was found that this system can be used with similar results in THF, water, and mixture of THF and water. Addition of THF to the reaction mixture decreases the yields of biphenyl by-products to some extent. Benzene was found in some reactions in trace amounts.

Table 2. Palladium-catalyzed reaction of $\text{Ph}_3\text{Bi}(\text{O}_2\text{CCF}_3)_2$ with styrene, and the influence of the ratio of solvents.^[a]

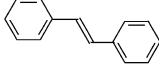
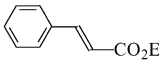
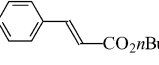
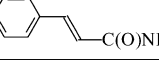
Entry	Solvent	THF/ H_2O ratio	Yield ^[b] [%]	
			<i>trans</i> -Stilbene	Biphenyl
1	THF	–	19	8
2	THF + H_2O	5:1	19	15
3	THF + H_2O	2:1	17	15
4	THF + H_2O	1:1	16	18
5	H_2O	–	20	35

[a] Reaction conditions: $\text{Ph}_3\text{Bi}(\text{O}_2\text{CCF}_3)_2$ (0.1 mmol), styrene (0.3 mmol), Pd@SPB (0.04 mol-% Pd) in THF/ H_2O (5:1) at 50 °C for 24 h in air. [b] Yields were determined by GC: 0.3 mmol *trans*-stilbene corresponds to 100%; 0.15 mmol Ph_2 corresponds to 100%; 0.3 mmol benzene corresponds to 100%.

In the reaction of $\text{Ph}_3\text{Bi}(\text{O}_2\text{CCF}_3)_2$, which showed the highest conversion, with different unsaturated compounds,

the yields of cross-coupled products were almost the same independent of the nature of substrates (Table 3). The cross-coupled products were obtained in 37–52% yield. The yields of biphenyl were 7–16%. Again, benzene was found in nearly all reaction mixtures in trace amounts.

Table 3. Palladium-catalyzed reaction of $\text{Ph}_3\text{Bi}(\text{O}_2\text{CCF}_3)_2$ with different unsaturated compounds, and the influence of the nature of the substrates.^[a]

Entry	Unsaturated compound	Cross-coupled product	Yield ^[b] [%]		
			Cross-coupled product	Ph_2	PhH
1			42	16	trace
2			43	13	trace
3			52	15	trace
4			37	7	6

[a] Reaction conditions: $\text{Ph}_3\text{Bi}(\text{O}_2\text{CCF}_3)_2$ (0.1 mmol), unsaturated compound (0.1 mmol), Pd@SPB (0.04 mol-% Pd) in THF/ H_2O (5:1) at 50 °C for 24 h in air. [b] Yields were determined by GC: 0.1 mmol of cross-coupling product corresponds to 100%; 0.15 mmol of Ph_2 corresponds to 100%; 0.3 mmol of benzene corresponds to 100%.

Attempts to investigate possible reaction pathways in the particle-catalyzed version of the organobismuth C–C coupling reaction were made by following one of the reactions by ^1H NMR spectroscopy. Possible reaction pathways of this reaction by using molecular palladium catalysts were recently described.^[20] The C-arylation reaction of ethyl acrylate with tris(*para*-tolyl)bismuth bis(trifluoroacetate), *p*-Tol₃Bi(O_2CCF_3)₂ (ratio 3:1), in the presence of Pd@SPB (0.04 mol-% Pd) at 50 °C was carried out in a mixture of [D_8]THF/ D_2O (5:1). The time-dependent formation of the olefin product and the biaryl byproduct is shown in Figure 1.

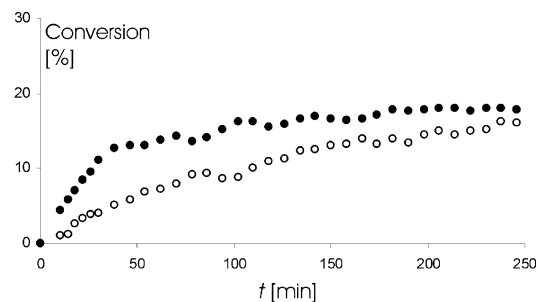


Figure 1. Formation of the organic products in the C-arylation reaction of ethyl acrylate with *p*-Tol₃Bi(O_2CCF_3)₂ in the presence of Pd@SPB followed by ^1H NMR spectroscopy (● *p*-TolCH=CH-CO₂Et; ○ *p*-Tol₂; *p*-Tol = *para*-tolyl).

The formation of the Heck-type products (Figure 1) proceeds with an initial rate of 8.9 mmol l^{−1} h^{−1} and the forma-

tion of the bitoluylyl byproduct with an initial rate of around $2.7 \text{ mmol l}^{-1} \text{ h}^{-1}$. This means that the initial formation of the Heck-type product is around three times faster than biaryl formation. Conversion reaches around 15% for product and byproduct formation, and the mass balance is indicative that a variety of other aryl compounds (most likely organobismuth derivatives) must have been formed. Analysis of the involved bismuth compounds (Figure 2) revealed that the organobismuth(V) compound (starting material) is nearly completely consumed after 150 min. The following organobismuth(III) compounds could be identified as byproducts by NMR spectroscopy: $p\text{Tol}_2\text{Bi}(\text{O}_2\text{CCF}_3)_3$, $p\text{TolBi}(\text{O}_2\text{CCF}_3)_2$, and $p\text{Tol}_3\text{Bi}$. Because organobismuth(III) compounds are inactive for olefin arylation chemistry, only a minor amount of aryl functions are available for olefin functionalization. As a consequence, lower olefin loading increases the yield calculated in relation to the olefin starting material, as the starting olefin remains untouched to a large amount if equimolar addition [related to the organobismuth(V) derivative] took place.

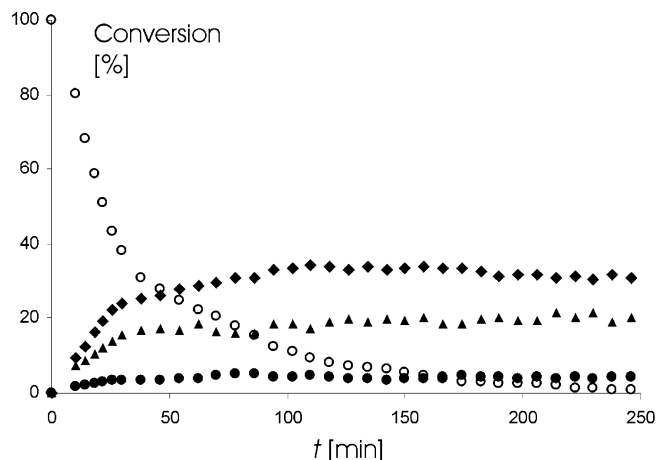


Figure 2. Conversion of the starting organobismuth(V) compound followed by ^1H NMR spectroscopy and yield of the organobismuth(III) compounds in the C-arylation reaction of ethyl acrylate with $p\text{Tol}_3\text{Bi}(\text{O}_2\text{CCF}_3)_2$ in the presence of Pd@SPB [○ $p\text{Tol}_3\text{Bi}(\text{O}_2\text{CCF}_3)_2$, ◆ $p\text{Tol}_2\text{Bi}(\text{O}_2\text{CCF}_3)_3$, ▲ $p\text{TolBi}(\text{O}_2\text{CCF}_3)_2$, ● $p\text{Tol}_3\text{Bi}$].

It was shown that various palladium salts introduced as homogeneous catalysts (coordination compound) catalyze C–C coupling reactions by using triphenylbismuth dicarboxylates.^[20] Comparison of this catalyst system with Pd@SPB reveals a high degree of similarity in terms of the product selectivity. To solidify these similarities, we used $[\text{Pd}(\text{cod})\text{Cl}_2]$ as a catalyst and a catalyst loading similar to those used for other homogeneous systems, and the substrates were coupled with the Pd@SPB catalyst system. Similar selectivity results were observed for both the $[\text{Pd}(\text{cod})\text{Cl}_2]$ and Pd@SPB catalyst systems (Tables 3 and 4). Because these homogeneous catalyst systems^[20] produce similar product selectivities, it is likely that particle precipitation is involved in these reactions as well. Indicative of such a similarity is also the fact that phosphane ligands poison the “homogeneous” catalyst systems.^[20]

Table 4. $[\text{Pd}(\text{cod})\text{Cl}_2]$ -catalyzed (cod = 1,5-cyclooctadiene) reaction of $\text{Ph}_3\text{Bi}(\text{O}_2\text{CCF}_3)_2$ with different unsaturated compounds: selectivity data.^[a]

Entry	Unsaturated compound	Cross-coupled product	Yield ^[b] [%]		
			Cross-coupled product	Ph_2	PhH
1			43	12	19
2			33	21	8
3			38	21	9
4			45	trace	30
5 ^[c]			55	trace	38

[a] Reaction conditions: $\text{Ph}_3\text{Bi}(\text{O}_2\text{CCF}_3)_2$ (0.5 mmol), unsaturated compound (1.5 mmol), $\text{Pd}(\text{cod})\text{Cl}_2$ (4 mol-%) in CH_3CN at room temperature for 24 h in air. [b] Yields were determined by GC: 1.5 mmol of cross-coupling product corresponds to 100%; 0.75 mmol of Ph_2 corresponds to 100%; 1.5 mmol of benzene corresponds to 100%. [c] The reaction was run for 48 h.

Conclusions

$\text{Ph}_3\text{Bi}(\text{O}_2\text{CCF}_3)_2$ can be used as a phenylating agent in organobismuth C–C coupling reactions with various unsaturated compounds in the presence of palladium nanoparticles immobilized in spherical polyelectrolyte brushes, and the reactions can be performed in water or in a mixture of water and THF. The reaction proceeds under mild conditions. Only a small amount of the arylbismuth functionalities are available for C-arylation, as rather fast formation of catalytically inactive bismuth(III) compounds is observed. In contrast to classic Heck-type reactions, these catalyst systems do not need a base to obtain the olefin arylation products. The efficiency of the organobismuth C–C coupling reaction in comparison to the classical Heck reaction is low.^[32] It is also interesting to note that Pd@SPB works with a much lower catalyst loading in the organobismuth C–C coupling reaction in comparison to homogeneous catalyst systems described so far. Also noteworthy is that Pd@SPB is an efficient catalyst for classical Heck reactions under mild conditions.^[33]

Experimental Section

General Methods: Gas chromatographic analysis was carried out with an Agilent 6890N with FID equipped with an Agilent 19091J-413, HP-5 column. ^1H NMR spectra were measured with a Varian Inova Unity 400 spectrometer for solutions in $[\text{D}_8]\text{THF}/\text{D}_2\text{O}$ (5:1). Styrene, ethyl acrylate, butyl acrylate, acryl amide, and tetrabutylammonium bromide are commercially available. Organobismuth compounds Ph_3BiX_2 were prepared by the reported methods.^[20,34,35] Synthesis and characterization of the spherical polyelectrolyte brush and immobilization of palladium nanoparticles can be found elsewhere.^[29–31] All catalytic experiments were carried out in pressure tubes resealable with a Teflon stopper.

Representative Procedure for Heck-Type Reactions: To a pressure tube containing $\text{Ph}_3\text{Bi}(\text{O}_2\text{CCF}_3)_2$ (67 mg) in THF (10 mL) and H_2O (2 mL) was added styrene (0.034 mL). A solution of the Pd catalyst (solid content 0.4%, 1% Pd@SPB, 0.1 mL) was then added, and TBAB (32 mg) was used as the phase transfer reagent. The tube was sealed, and the reaction mixture was kept at 50 °C for 24 h. The organic products were extracted with ether (3 mL). The conversion was determined by GC with dodecane (0.023 mL) as an internal standard.

Procedure for ^1H NMR Spectroscopic Study: A mixture of $p\text{Tol}_3\text{Bi}(\text{O}_2\text{CF}_3)_2$ (35 mg), ethyl acrylate (0.017 mL), and the Pd catalyst solution in D_2O (solid content 0.4%, 0.5% Pd@SPB, 0.1 mL) in $[\text{D}_8]\text{THF}$ (1 mL) and D_2O (0.1 mL) was placed in an NMR tube. The tube was sealed. The reaction was monitored by ^1H NMR spectroscopy every 4 min at 50 °C.

Acknowledgments

Financial support by the Deutsch Akademische Austausch Dienst, grant for Y. B. M., and the Deutsche Forschungsgemeinschaft, Sonderforschungsbereich 481, Bayreuth, is gratefully acknowledged. This work was supported by NanoCat, an International Graduate Program within the Elitenetzwerk Bayern.

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Received: August 6, 2007

Published Online: November 8, 2007