A Polymer-Supported β-Ketoesterate Complex of Palladium as an Efficient, Phosphane-Free, Air-Stable, Recyclable Catalyst for the Heck Reaction

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The coupling between aryl iodides and bromides with olefins (Heck reaction) has been studied with a polymer-supported palladium catalyst in the presence of sodium or potassium acetate. The reactions can be performed in air without any activating phosphorus ligands and with non dried solvents. Under suitable conditions the catalyst, which exhibits high activity and selectivity, is recyclable several times with negligible leaching of metal.

Introduction

The Heck reaction[1] remains one of the most useful and versatile C−C bond forming reaction known. Although this vinylation of aryl halides has been widely studied in academia, there are not many industrial examples of its exploitation. The reasons for this are economic. Heck reactions are mostly catalysed by palladium complexes in homogeneous solution in the presence of phosphorus ligands, which are toxic and unrecoverable. In addition, these expensive catalysts give problems due to their instability at high reaction temperatures, and their separation and recovery after use. These problems can be overcome, however, by the use of heterogeneous systems,[2] made up of supported palladium complexes, which, moreover, are generally phosphane-free. Palladium metal colloids, in some cases stabilised by the presence of the support, appear to be the active species[3] for phosphane-free catalytic systems.

Polymer-supported palladium complexes have been used for the activation of aryl iodides by several research groups. An early report on a palladium catalyst based on triphenylphosphane-bonded polystyrene resin[4] describes the arylation of olefins by iodoarenes, although no studies on the activity of the recycled resin are reported. In a more recent paper, polymer-supported 1,2-bis(diisopropylphosphanyl)benzene has been used for preparing a palladium catalyst for the reaction of iodobenzene with methyl acrylate.[5]

The reaction between Pd^{II} salts and a polypyrrole containing a phosphane-borane moiety resulted in another type of solid-supported palladium catalyst[6] that was moderately active in the coupling of iodobenzene with acrylic esters. The support could be recycled, though it needed to be recharged with $Pd(dba)_2$ in each subsequent run.

A palladium complex prepared from a triphenylphosphane amphiphilic resin and a palladium π-allyl chloride dimer has been used as an active catalyst for Suzuki cross-coupling and for the arylation of allylic acetates.[7]

All the heterogenised catalysts in which the support is a polymer with pendant phosphanes suffer from the same problem when used in Heck-type reactions: the irreversible loss of metal from the matrix due both to degradation of the phosphane moieties[2] and to the reaction mechanism itself.[8a] As an example, metal leaching was observed when palladium supported on glass beads was used as catalyst for Heck reactions, owing to the oxidation of phosphanes that bound the metal atoms onto the matrix.[9]

Various examples can be found in the literature concerning non-phosphinated organic polymers as supports for palladium-based catalysts. Among them, Pd^{II} coordinated to a pincer-type κ^3-S,C,S ligand attached to soluble organic polymers has been described as an active and recyclable catalyst for the olefination of iodoarenes at 95−110 °C under homogeneous[10] or liquid/liquid biphasic conditions.[11]

Polymer-supported carbene complexes of palladium have been used as recyclable catalysts for the Heck reaction of aryl bromides at 150 °C, although with significant loss of metal ($60\%_{wt}$) during the first run.[12]

Recently, a bis(pyrimidine)-based palladium polymer-supported catalyst for Heck-type reactions has been synthesised,[13] but no data on the activity of the recovered catalyst has been reported.

Another class of supports onto which catalytically active palladium is dispersed is represented by inorganic matrices. Pd on charcoal and Pd on different metal oxides have been found to be active catalysts for the Heck reaction of aryl

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iodides.[2] Arai et al.[14] have studied the coupling between iodobenzene and methyl acrylate at 160 °C in the presence of 0.28−1.4 mol % of Pd supported on carbon or silica. Unfortunately, these conventional supported palladium catalysts are unselective when the substrates are bromoarenes, with dehalogenation being the dominant reaction. Pd particles supported on mesoporous silica have also been employed for the coupling of aryl bromides,[15] although satisfactory yields were obtained only with activated substrates such as *p*-bromonitrobenzene.

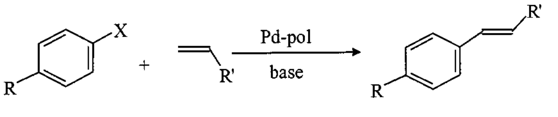
Very recently, Djakovitch et al. have described Pd-modified zeolites that are very active and recyclable catalysts for the Heck reaction of aryl bromides with olefins.[16]

Herein we report our studies on Heck reactions using a β-ketoesterato polymeric palladium complex (referred to as Pd-pol) as catalyst that exhibits satisfactory activities towards activated and nonactivated iodo- and bromoarene substrates. The supported complex (1.98%$_w$ Pd) was obtained by co-polymerisation of Pd(AAEMA)$_2$ [AAEMA$^-$ is the deprotonated form of 2-(acetoacetoxy)ethylmethacrylate] with ethyl methacrylate and ethylene glycol dimethacrylate.[17]

In this work we have considered the influence of solvent, base, temperature and additives on the performance and the recyclability of the catalyst.

Results and Discussion

Scheme 1 illustrates the scope of the investigated Heck reactions catalysed by Pd-pol. The molar ratio between the limiting substrate (aryl halide) and palladium was optimised at 1000 for reactions with aryl iodide and 500 for reactions with aryl bromides. A general feature of all the Pd-pol catalysed reactions is the simplicity of the set-up and work-up. All manipulations could be performed in an air atmosphere and with non-dried solvents because of the oxygen and moisture stability of the supported catalyst.

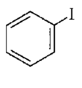
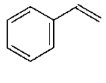
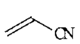
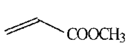
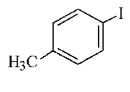
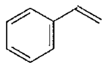
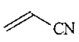
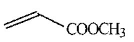
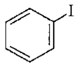
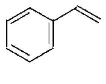
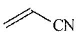
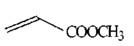


X = I, Br
R = H, CH$_3$, NO$_2$, COCH$_3$
R' = COOCH$_3$, CN, C$_6$H$_5$

Scheme 1

The effect of the base was examined first. In preliminary experiments triethylamine (the typical base for many homogeneous and heterogeneous catalytic Heck reactions[1,2]) was used, but this organic base caused significant metal leaching. This is probably due to the higher coordination ability of trialkylamines towards palladium[18] than inorganic bases such as alkaline acetates or carbonates. For this reason, all subsequent tests were performed using inorganic bases such as potassium or sodium acetate. As for the choice of solvent, among those tested [toluene, *N*-methylpyrrolidine, dioxane, dimethyl sulfoxide, *N*,*N*-dimethylformamide (DMF), diethylene glycol (DEG)] the best results in terms of catalyst activity were obtained using DMF (with aryl iodides) and DEG (with aryl bromides).

Table 1. Heck coupling reactions of aryl iodides catalysed by Pd-pol; reaction conditions: a molar ratio of 1:1.2:2.4 was used for the aryl iodide (5 mmol):alkene:base (AcOK) in 6 mL DMF; T = 90 °C; molar ratio Pd/ArI = 1:1000; for all reactions the conversion of the aryl iodide was quantitative

Entry	Aryl iodide	Alkene	Additive	*t* (h)	Yield (%)[a]	
					trans	*cis*
1			–	6	93	7
2	"		–	6	51	48
3	"		–	2	90	10
4			–	4	89	11
5	"		–	6	61	29
6	"		–	4	90	10
7			DMG [b]	5	90	10
8	"		DMG [b]	3	58	40
9	"		PPh$_3$ [c]	2	95	5

[a] GLC yields. [b] Molar ratio Pd:DMG = 1:20. [c] Molar ratio Pd:PPh$_3$ = 1:5.

Table 1 summarises the results obtained in the reactions between activated and nonactivated aryl halides with different vinylic substrates. In all cases the conversions were quantitative.

The coupling between iodobenzene and styrene at 90 °C in the presence of 0.10 mol % of supported palladium gave, after 6 h, a 100% yield of stilbene (93% *trans*, 7% *cis*, entry 1). Under the same reaction conditions acrylonitrile afforded 99% cinnamonitrile with no selectivity between the *cis* and *trans* isomers (entry 2). The reaction between iodobenzene and methyl acrylate was faster, giving, at 90 °C, a 90% yield of *trans*-methyl cinnamate after 2 h (entry 3).

Reacting *p*-iodotoluene with styrene (entry 4), acrylonitrile (entry 5) or methyl acrylate (entry 6) resulted in quantitative yields of the desired coupling products.

The same reactions reported in entries 1, 2 and 3 of Table 1 were also carried out at 140 °C, in order to study the influence of the temperature. The reactions at 140 °C were slightly faster than those carried out at 90 °C. In particular, the reaction between iodobenzene and styrene was complete after 5 h, giving a 93% yield of *trans*-stilbene. The reaction between iodobenzene and methyl acrylate gave a quantitative conversion of the limiting substrate after 1 h with a 98% yield of *trans*-methyl cinnamate. The coupling between iodobenzene and acrylonitrile was complete after 3 h giving a 76% yield of *trans*-cinnamonitrile and a 24% yield of *cis*-cinnamonitrile. In the two latter cases the selectivity was shifted towards the thermodynamically favoured *trans* adduct.

In order to study the influence of additives on the catalyst performance, the reactions of entries 1 and 2 were carried out in the presence of *N*,*N*-dimethylglycine (DMG), which is known to improve the activity and selectivity in the homogeneous phosphane-free Heck coupling of aryl bromides.[19] A slight improvement in the activity was observed. In fact, the TOFs for the reactions without DMG were 167 h^{-1} (entries 1, 2), whereas the TOFs for reactions carried out in the presence of a 20:1 DMG/Pd (mol/mol) ratio were 200 h^{-1} (styrene, entry 7) or 333 h^{-1} (acrylonitrile, entry 8).

The influence of a phosphorus additive, such as triphenylphosphane, was also investigated. The coupling between iodobenzene and methyl acrylate carried out in the presence of triphenylphosphane (5:1 P/Pd mol/mol) gave, after 2 h, a quantitative yield of methyl cinnamate (95% *trans* and 5% *cis*, entry 9), a result similar to that obtained in the phosphane-free reaction (entry 3). However, the presence of triphenylphosphane caused severe metal leaching from the supported catalyst.

In the case of the reaction of entry 9, the recovered catalyst became inactive after three cycles in the presence of PPh_3. On the contrary, the catalyst of the phosphane-free reaction described in entry 1 (Table 1) remained active for at least six cycles (Figure 1).

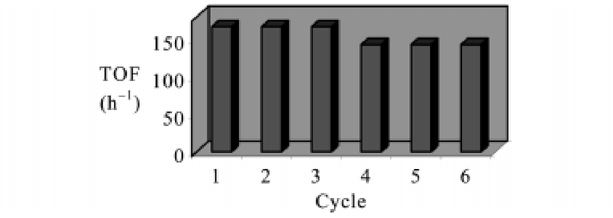


Figure 1. Recyclability of Pd-pol in Heck reactions between iodobenzene and styrene at 90 °C; in each reaction the conversion of iodobenzene was quantitative; TOF = [moles of coupling product (both isomers)]/[(moles of Pd) × (reaction time in hours)]

This behaviour was found to be general: the catalyst of all the phosphane-free reactions described in this work (including those in the presence of DMG) could be recycled at least three times with no loss of activity or selectivity.

The catalyst recycling was performed by filtration, washing with acetone and diethyl ether and with water (for removal of the excess base, its conjugate acid and the formed alkaline halides). This latter treatment did not affect the activity of the catalyst, as occurs in the case of palladium supported on zeolites and metal oxides.[20]

In addition, the mother liquor of all the described phosphane-free reactions (including those in the presence of DMG) showed negligible catalytic activity. On the other hand, the mother liquor of the reaction carried out in the presence of PPh_3 (entry 9) showed a moderate activity, giving a 50% conversion of fresh iodobenzene after 20 h reaction.

It is possible to explain the observed metal leaching in solutions containing PPh_3 as additive by referring to the commonly accepted mechanism.[1] Triphenylphosphane reduces palladium(II) to palladium(0) giving Ph_3PO and the coordinatively unsaturated $Pd(PPh_3)_2$, which can start the catalytic cycle through the oxidative addition of the aryl halide. Hence, the Pd^{II} centre must lose its counteranion (chloride, acetate, etc.) in order to enter the reaction cycle. Loss of the polymer-$AAEMA^-$ ligands, however, forms under-ligated palladium(0), which leaches irreversibly into solution.

Another mechanism, recently proposed by Amatore,[21] claims the intermediacy of anionic palladium complexes. In this case, the pre-activation step gives an anionic palladium(0) complex, which is able to start the catalytic cycle. This cycle is reported in Scheme 2 for the reaction promoted by Pd-pol in the presence of an *n*-fold excess PPh_3.

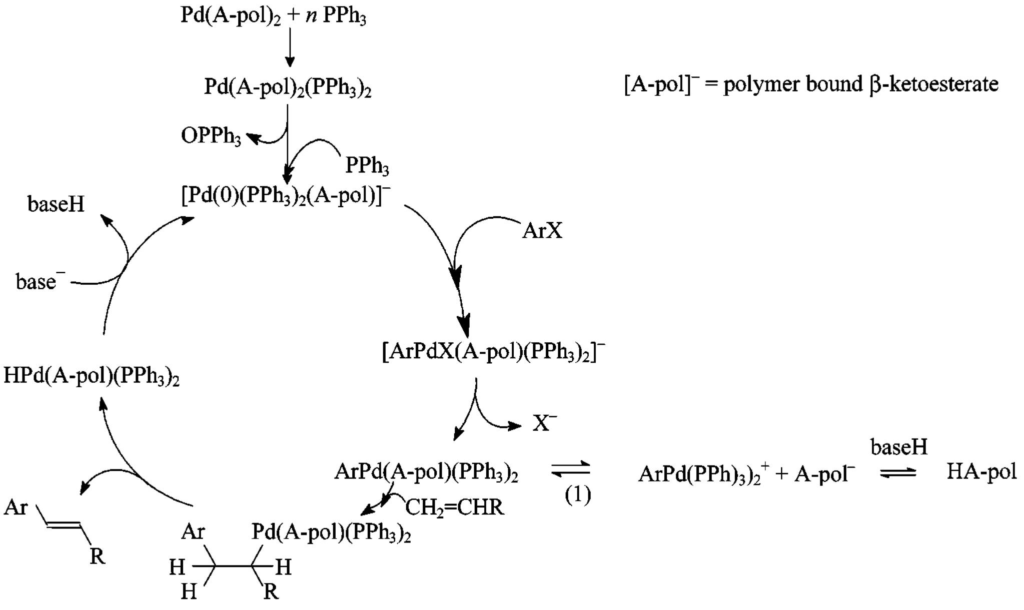
The anionic complex in our context should be $[Pd^0(PPh_3)_2(A\text{-pol})]^-$ ($[A\text{-pol}]^-$ = polymer-bound β-ketoesterate). Following this type of mechanism the leaching should occur at the stage of the equilibrium (1) of Scheme 2.

In order to study the influence of equilibrium (1) on the metal leaching, one and two equivalents of base (respect to the olefin) were used in two parallel phosphane-assisted reactions. The reaction between iodobenzene and methyl acrylate carried out at 140 °C in the presence of one equivalent of base, 0.50 mol % of PPh_3 and 0.10 mol % of supported Pd, gave a 90% conversion and a 94% yield of *trans*-methyl cinnamate after 5 h. The same reaction carried out in the presence of two equivalents of base gave a quantitative conversion and a 98% yield of *trans*-methyl cinnamate after 1 h. In addition, the recovered resin of the former reaction (1 equiv. of base) was inactive for a second run, while the Pd-pol recovered after the second experiment (2 equiv. of base) was still active even after five further catalytic runs. However, contrary to what happens in phosphane-free reactions, the leaching is not completely inhibited even in the presence of 2 equiv. of base, since the mother liquor of the solution after each cycle revealed a high activity (80% of fresh iodobenzene converted after 3 h reaction).

The lower catalyst activity shown in the reaction carried out with 1 equiv. of base compared with that with 2 equiv. of base (the relevant TOF's are 200 h^{-1} and 1000 h^{-1}, respectively) can be ascribed to the formation of the less active[21a] cationic Pd complex $[ArPd(PPh_3)_2]^+$ generated through the equilibrium (1) of Scheme 2.

Although deeper mechanistic studies are required, these results seem to indicate that the reaction pathway proposed by Amatore is operative in our system.

The effect of the amount of base on metal leaching and on catalyst activity was observed by us also in the phosphane-free reactions. For example, the reaction between iodobenzene and styrene proceeded with TOFs of 83 h^{-1} or 167 h^{-1} when the molar ratio of olefin/base was 1 or 2, respectively. Furthermore, in the former case the copolymer leached out all its palladium loading after three cycles, whereas in the second case the metal content passed from

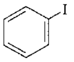
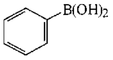
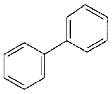
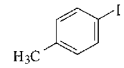
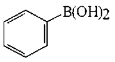
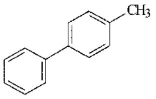
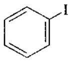
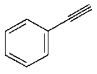
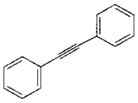
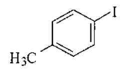
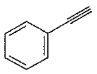
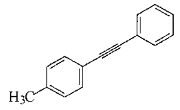


Scheme 2. Catalytic cycle via anionic palladium(0) complexes

1.98% before reaction to 1.67% after six cycles. It is possible to assume that the double amount of base inhibits the protonation of the polymer-supported β-ketoesterate ligand (AAEMA$^-$). Only if it remains anionic, in fact, is the polymeric ligand able to bind the palladium(II) and palladium(0) species involved in the different stages of the reaction cycle. The leaching of the metal could therefore be due to the protonation of the polymeric ligand by the acetic acid formed during the reaction.

In order to verify the influence of the presence of an acid in the reaction medium on metal leaching, the Suzuki reaction between aryl iodides and phenylboronic acid was carried out (Table 2). Quantitative yields of the corresponding coupling products were obtained starting from iodobenzene (entry 1) or *p*-iodotoluene (entry 2) with TOFs of 67 h^{-1} (iodobenzene) and 83 h^{-1} (*p*-iodotoluene). However, as expected, the initially yellow catalyst leached out all its palladium loading into solution and was inactive in subsequent runs.

Table 2. Suzuki and Sonogashira coupling reactions of aryl iodides catalysed by Pd-pol; typical reaction conditions: a molar ratio of 1:1.2:2.4 was used for ArI (5 mmol):phenyl boronic acid or phenylacetylene:base (AcOK) in 6 mL DMF; T = 90 °C; molar ratio Pd/aryl iodide = 1:1000; for all reactions the conversion of the aryl iodide was quantitative

Entry	Aryl iodide	Alkyl boron or Alkyne	Time (h)	Product	Yield(%) [a]
1			15		quantitative
2			9		quantitative
3			6		55
4			7		34

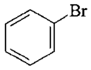
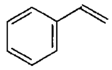
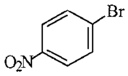
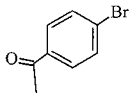
[a] GLC yields.

Although in the case of the polymeric β-ketoesterato support the presence of a double amount of acetate results in increasing activity and recyclability of the supported catalyst, this effect is not generalizable.

The results reported in the literature seem to indicate that the amount of base and its nature can influence the metal leaching, *in function of the support used*. In fact, it has been recently claimed[22] that when Pd/alumina, Pd/C or sulfonated polystyrene-supported palladium are used to promote Heck reactions, the metal loss is enhanced by the presence of acetate ions (and of the aryl halide), presumably due to the formation of soluble ArPdBr(OAc)$_n$ or ArPd(OAc)$_n$ species.[8] Moreover, Arai et al.[14] reported that the Pd species leached out into the solvent during Heck reactions promoted by Pd/C or Pd/SiO$_2$ redeposited onto the surface of the supports at the end of the reaction only when 1 equiv. of Na_2CO_3 and 1 equiv. triethylamine were used at the same time.

The possibility of activating economically more interesting aryl bromides was also examined (Table 3). Pd-pol was used as catalyst for the Heck reaction of bromobenzene with styrene at 160 °C using a 1:500 Pd/substrate molar ratio, in the presence of DMG. Under these reaction conditions the conversion of the substrate was quantitative after 12 h affording a 95% yield of *trans*-stilbene (entry 1). In the absence of DMG the conversion was quantitative after 24 h and the yield of *trans*-stilbene was 91% (entry 2). After the initial catalytic run, the resin used in the reaction of entry 1 was recovered, washed and recycled five times with negligible loss of activity (Figure 2).

Table 3. Heck coupling reactions of aryl bromides catalysed by Pd-pol; typical reaction conditions: a molar ratio of 1:1.2:2.4 was used for ArBr (5 mmol):alkene:base (NaOAc) in 6 mL DEG; T = 160 °C; molar ratio Pd/ArBr = 1:500

Entry	Aryl bromide	Alkene	Additive	*t* (h)	Yield(%)[a]	
					trans	*cis*
1			DMG [b]	12	95	5
2	"	"	–	24	91	9
3		"	DMG [b]	10	90	10
4		"	DMG [b]	10	92	8
			DMG [b]	12	95	5

[a] GLC yields. [b] Molar ratio Pd:DMG = 1:20.

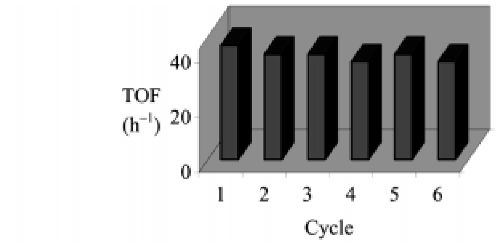


Figure 2. Recyclability of Pd-pol in Heck reactions between bromobenzene and styrene at 160 °C, in the presence of DMG; in each reaction the conversion of bromobenzene was quantitative; TOF = [moles of coupling product (both isomers)]/[(moles of Pd) × (reaction time in hours)]

The reactions of 4-bromonitrobenzene and 4-bromoacetophenone with styrene took 10 h to reach completion giving 90% (entry 3) and 92% yield (entry 4) of the *trans*-coupling adduct, respectively.

The possibility to use aryl chlorides as substrates in the Pd-pol catalytic system has also been examined. Unfortunately, the reactions between chlorobenzene and methyl acrylate or between *p*-chloronitrobenzene and styrene at 180 °C in the presence of DMG and Ph_4PCl[19b] were not effective, and only a small degree of dehalogenation occurred.

Finally, Pd-pol was used as catalyst for the coupling of aryl iodides with phenylacetylene at 90 °C (Sonogashira reaction), but the selectivities were poor (Table 2).

Experimental Section

All preparations, manipulations and reactions were carried out under air. All chemicals were purchased from Aldrich and used as received. The supported catalyst (Pd-pol) was prepared according to the procedure reported in ref.[17] The palladium content in the supported catalyst was determined by atomic absorption spectrometry using a Perkin−Elmer 3110 instrument. Chromatographic analyses were carried out on Hewlett Packard 6890 instruments using an HP-PLOT Molecular Sieve 5A (15.0m × 0.53 mm × 25.0 μm) column (injector temperature 280 °C, FID temperature 280 °C, carrier: nitrogen or helium). GCMS data (EI, 70 eV) were acquired on an HP 6890 instrument (injector temperature 280 °C, carrier: helium) using an HP-1 crosslinked methyl siloxane (60.0 m × 0.25 mm × 1.0 μm) capillary column coupled with a mass spectrometer HP 5973. The products were identified by comparison of their GC and GC-MS features with those of authentic samples. Conversions and yields were calculated by gas chromatography using *n*-dodecane as an internal standard calibrated to the corresponding pure compound. In the case of entry 1 of Table 1, the isolated yield was also assessed as described below.

General Procedure for the Heck, Suzuki and Sonogashira Reactions: A 50 mL pressure tube was charged with Pd-pol (1.98$\%_w$ Pd), potassium or sodium acetate (12 mmol), aryl halide (5.0 mmol), olefin, alkyne or arylboronic acid (6.0 mmol), *n*-dodecane as internal standard, the additive (when present) and the solvent (DMF or DEG, 6 mL). The aryl iodide/Pd molar ratio was 1000, whereas the aryl bromide/Pd molar ratio was 500. The mixture was heated whilst stirring at the desired temperature until reaction completion as monitored by GLC and GCMS analyses. After reaction the catalyst was recovered by filtration, washed with acetone, water, acetone and diethyl ether, and dried under vacuum.

Isolation of *trans*-Stilbene: After separation of Pd-pol, the reaction mixture was diluted with CH_2Cl_2 (20 mL) and washed with H_2O (3 × 15 mL). After separation of the organic phase and drying over Na_2SO_4, the solution was concentrated under reduced pressure. Separation of the *cis*/*trans* isomers was carried out by silica gel chromatography with pentane/diethyl ether (1:1) solvent mixtures. The product was obtained in an analytically pure form after recrystallization from diethyl ether at −18 °C (0.808 g, isolated yield = 89.8%).

Catalytic Test for the Determination of the Activity of the Mother Liquor: The clear filtrate obtained from the catalyst was used as solvent for these experiments. This solution was obtained by filtration at 90 °C over celite, in order to remove the fine particles. Fresh reactants (5.0 mmol aryl halide, 6.0 mmol olefin, 12 mmol base) were added to the filtrate and the resulting mixture was heated at the desired temperature whilst stirring for 20 h. The reaction course (if any) was monitored by GLC as described above.

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