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Stille coupling reactions catalysed by a polymer supported palladium complex

Maria Michela Dell'Anna [a], Antonio Lofù [a], Piero Mastrorilli [a],
Vittoria Mucciante [b], Cosimo Francesco Nobile [a],*

[a] *Dipartimento di Ingegneria delle Acque e di Chimica del Politecnico di Bari and CNR centre ICCOM (section of Bari),
Via Orabona, 4 I-70125 Bari, Italy*
[b] *Dipartimento di Chimica e Ingegneria Chimica dell'Università degli Studi dell'Aquila, Località Monteluco di Roio, 67040 L'Aquila, Italy*

Abstract

The coupling between aryl iodides and bromides with organostannanes (Stille reaction) has been investigated in the presence of a polymer supported palladium catalyst. The reaction could be performed in air without any activating ligand and with non-dried solvents. The catalyst, which acts by releasing controlled amounts of soluble active species, could be recycled several times in the coupling between $Sn(CH_3)_4$ or $^nBu_3SnPh$ with iodoarenes or activated bromoarenes.
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1. Introduction

The Stille reaction [1] is an important palladium catalysed cross-coupling reaction, in which one of the coupling partners is a trialkylorganotin compound. This reaction is of widespread use because tin reagents are easily synthesized and purified and tolerate a wide variety of functional groups [2]. Typical alkyl groups on tin are methyls or butyls: trimethyltin derivatives as by-products are easy to remove but toxic, while tributyltin by-products are less toxic but difficult to take off. To avoid this problem, several studies have been carried out on the possibility of attaching the substrate [3] or the organostannane [4] on a solid support.

The Stille reaction is generally promoted by palladium complexes in homogeneous phase, and there are only few examples of heterogeneous catalysts used to carry out the coupling between haloarenes and trialkylorganotin compounds. Among them, the most recent ones are palladium-coated poly(vinylpyridine) nanospheres [5], polyoxometalates [6] or layered double hydroxides [7] supported nanopalladium, dendrimer-encapsulated Pd nanoparticles [8], and a polymeric catalyst prepared by molecular imprinting [9].

An alternative solution for catalyst recycling is the use of room-temperature ionic liquids in which the Stille coupling reactions of aryl iodides and bromides can be performed [10].

Among the typical C–C bond forming reactions promoted by Pd(0)/Pd(II) catalytic route, several efforts have been devoted to the synthesis of supported metal catalysts to be employed in the Heck [11,12] and in the Suzuki [13,14] reactions, such as, for example, palladium supported on zeolites [15], carbon [16], silicates [17] and polymers [18,19]. In most cases it was clearly demonstrated that heterogeneous catalysts were reservoirs for controlled amount of highly active soluble palladium

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species [20]. In this regard it has been recently reported the use of a palladium loaded mercaptopropyl modified mesoporous silica which acted both as active catalyst for Heck and Suzuki reactions, and as a scavenger for Pd(0) and Pd(II) soluble species [21].

During our studies on the activity [22] of a polymer supported palladium complex (Pd-pol, Fig. 1), obtained by co-polymerisation of Pd(AAEMA)$_2$ [AAEMA$^-$ is the deprotonated form of 2-(acetoacetoxy)ethyl methacrylate] with ethyl methacrylate and ethylene glycol dimethacrylate [23], we employed Pd-pol as active and in some cases recyclable catalyst for C–C bond forming reactions, such as Heck [24] and asymmetric allylic alkylation [25] reactions.

Herein, we report on the use of Pd-pol as catalyst for Stille reactions between iodo- or bromoarenes and different organostannanes.

1.1. Results and discussion

Catalytic Activity. In preliminary experiments, the catalytic activity of Pd-pol in the Stille coupling between aryl iodides and different organotin compounds such as Sn(CH$_3$)$_4$, ^{n}Bu$_3$SnPh and ^{n}Bu$_3$SnC≡CPh was investigated (Table 1).

Among the tested solvents for the Pd-pol catalysed reaction between *p*-iodonitrobenzene and Sn(CH$_3$)$_4$, polar aprotic solvents having an ability to additionally stabilize palladium species by weak coordination, such as HMPA (hexamethylphosphoramide) and DMF (*N*, *N*-dimethylformamide) gave satisfactory results, contrary to toluene in which the catalysis did not proceed.
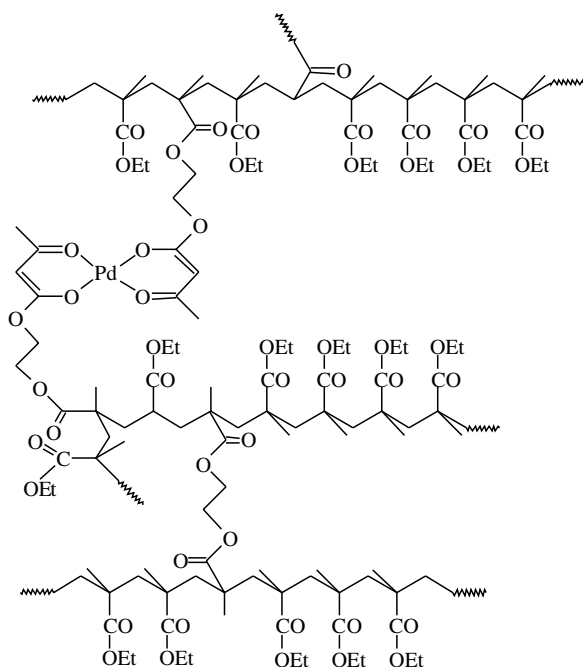

Fig. 1. Pd-pol.

In DMF the reaction led to quantitative conversion of the substrate after 3 h, with selectivity in *p*-nitrotoluene as high as 80% (the remainder being nitrobenzene, the de-halogenated by-product) (entry 1-1). In HMPA the substrate was transformed quantitatively to the coupling product after 1 h reaction both in the first cycle (entry 2-1) and in the recycle (entry 3-1). However from the recyclability point of view the behaviour of DMF was preferable, since the recovering of the supported catalyst from HMPA was hampered by its exceedingly high swelling properties that rendered the polymer mushy.

The recyclability of Pd-pol in the coupling between *p*-iodonitrobenzene and Sn(CH$_3$)$_4$ in DMF is reported in Fig. 2, showing how the same catalyst could be used in six subsequent runs with turnover frequencies ranging from 8.0 to 13.3 h^{-1}.

The activity of Pd-pol in DMF was also tested in the Stille coupling between *p*-iodonitrobenzene and ^{n}Bu$_3$SnPh or ^{n}Bu$_3$SnC≡CPh.

In the reaction with ^{n}Bu$_3$SnPh a quantitative yield in the coupling product was obtained after 1 h (entry 4-1). As expected on the base of the reactivity scale of organostannanes [26] the reaction with ^{n}Bu$_3$SnC≡CPh was faster giving a quantitative yield in the coupling product after only 10 min (entry 5-1). In both cases the catalysts were recovered at the end of the reaction and recycled in subsequent runs (Figs. 3 and 4).

Figs. 3 and 4 show that the recyclability of Pd-pol depends on the organostannane used: when the organostannane was ^{n}Bu$_3$SnPh a significant drop of activity was observed in the third cycle, while using ^{n}Bu$_3$SnC≡CPh the catalyst became nearly inactive after three cycles.

The reaction between iodobenzene and ^{n}Bu$_3$SnPh gave 84% yield (entry 6-1) and 82% yield (entry 7-1) in biphenyl in the first cycle and in the recycle respectively. However in this case the reaction was much slower taking 20 h to reach completion.

The yields in the first cycle and in the recycle of the reaction between ^{n}Bu$_3$SnC≡CPh and iodobenzene were 90% (entry 8-1) and 89% (entry 9-1). The reactions between *p*-iodotoluene and the same organostannane gave yields of 99% (first cycle, entry 10-1) and 87% (recycle, entry 11-1).

The catalytic activity of Pd-pol was investigated also in Stille reactions involving aryl bromides. From Table 2 it is apparent that satisfactory yields in the coupling products and a good recyclability were obtained in the reactions between *p*-bromonitrobenzene and ^{n}Bu$_3$SnPh (entries 1-2 and 2-2) or Sn(CH$_3$)$_4$ (entries 6-2 and 7-2). When the organo-tin compound was ^{n}Bu$_3$SnC≡CPh a significant decrease of the catalytic activity was observed for the recycles (entries 3-2, 4-2 and 5-2).

With the less active substrates *p*-bromoacetophenone and bromobenzene the catalytic system was inactive at temperatures below 100 °C. At 120 °C Pd-pol was

Table 1
Stille reactions of aryl iodides catalysed by Pd-pol[a]
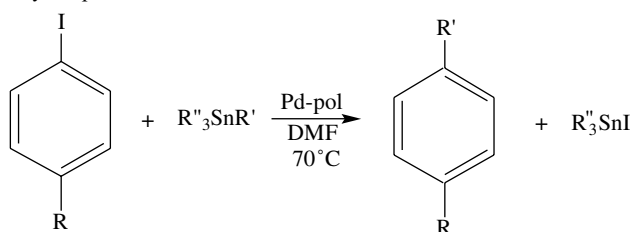
Entry	R	R'	R''	Time (h)	Yield (%)
1-1	$-NO_2$	$-CH_3$	$-CH_3$	3.0	80
2-1[b]	$-NO_2$	$-CH_3$	$-CH_3$	1.0	>99
3-1[b,c]	$-NO_2$	$-CH_3$	$-CH_3$	1.0	>99
4-1	$-NO_2$	$-Ph$	$-^{n}Bu$	1.0	>99
5-1	$-NO_2$	$Ph-C\equiv C-$	$-^{n}Bu$	0.17	>99
6-1	$-H$	$-Ph$	$-^{n}Bu$	20	84
7-1[c]	$-H$	$-Ph$	$-^{n}Bu$	20	82
8-1[c]	$-H$	$Ph-C\equiv C-$	$-^{n}Bu$	13	90[d]
9-1[c]	$-H$	$Ph-C\equiv C-$	$-^{n}Bu$	13	89[d]
10-1	$-CH_3$	$Ph-C\equiv C-$	$-^{n}Bu$	8.0	>99
11-1[c]	$-CH_3$	$Ph-C\equiv C-$	$-^{n}Bu$	22	87

[a] Reaction conditions: 0.50 mmol aryl iodides, 0.55 mmol organotin compound, Pd-pol (0.01 mmol of Pd), 2.0 ml DMF, 70 °C.
[b] In HMPA (2.0 ml).
[c] Recycle of the previous run.
[d] Isolated yield.

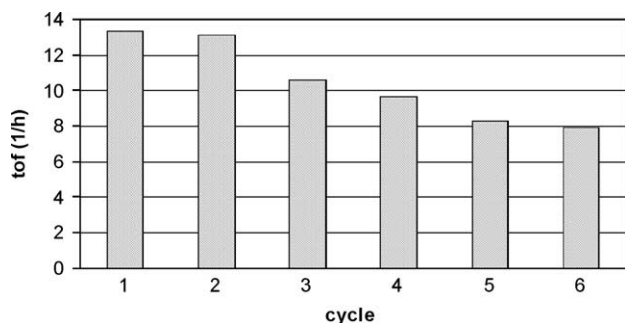Fig. 2. Recyclability of Pd-pol in the Stille reaction between p-iodonitrobenzene and $Sn(CH_3)_4$ in DMF at 70 °C.
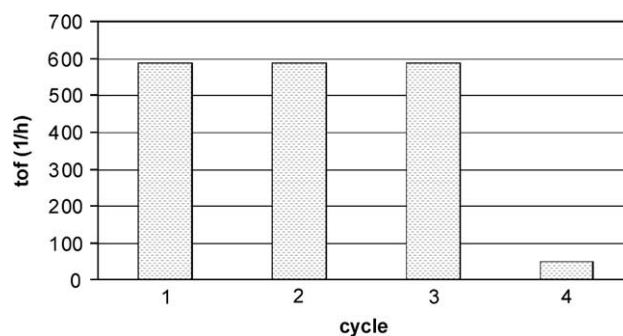

Fig. 4. Recyclability of Pd-pol in the Stille reaction between p-iodonitrobenzene and $^{n}B_3SnC\equiv CPh$ in DMF at 70 °C.
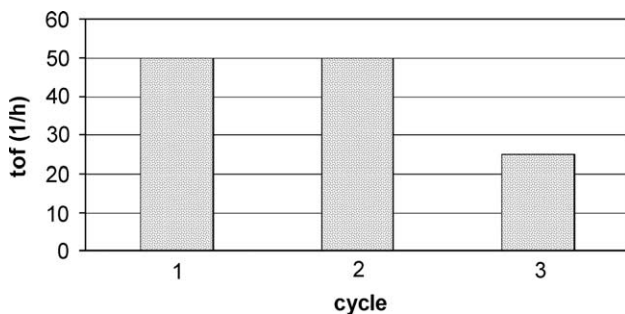

Fig. 3. Recyclability of Pd-pol in the Stille reaction between p-iodonitrobenzene and $^{n}B_3SnPh$ in DMF at 70 °C.

active, selective and recyclable in the coupling between p-bromoacetophenone and $^{n}Bu_3SnPh$ (entries 8-2, 9-2 and 10-2). On the contrary, the reaction between p-bromoacetophenone and $^{n}Bu_3SnCH=CH_2$ stopped at 63% conversion (entry 11-2). This result is in contrast to the better transmetallation ability reported for vinyl respect to phenyl group [26]. However, it has been demonstrated that a nucleophile such as $^{n}Bu_3SnCH=CH_2$, which is able to coordinate Pd(0) species, causes in some catalytic systems the formation of new palladium complexes that do not react with the substrate [27].

Among the tested aryl bromides, bromobenzene was the less reactive: the reaction with $^{n}Bu_3SnPh$ carried out at 120 °C stopped at a 38% yield in biphenyl (entry 12-2).

To improve the activity of Pd-pol, the same reaction was carried out in the presence of TBAB, an additive used in several palladium promoted C–C bond forming

Table 2
Stille reactions of aryl bromides catalysed by Pd-pol[a]
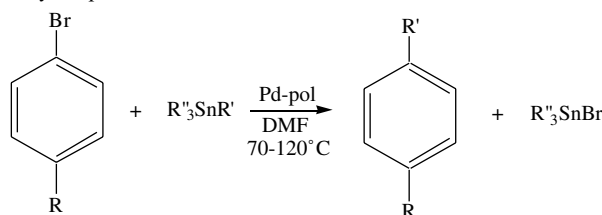
Entry	R	R′	R″	T (°C)	Time (h)	Conv. (%)	Yield (%)
1-2	–NO$_2$	–Ph	–^{n}Bu	70	8	100	>99
2-2[b]	–NO$_2$	–Ph	–^{n}Bu	70	8	100	>99
3-2	–NO$_2$	PhC≡C–	–^{n}Bu	70	13	100	>99
4-2[b]	–NO$_2$	PhC≡C–	–^{n}Bu	70	13	65	65
5-2[b]	–NO$_2$	PhC≡C–	–^{n}Bu	70	22	23	23
6-2	–NO$_2$	–CH$_3$	–CH$_3$	70	4	100	80
7-2[b]	–NO$_2$	–CH$_3$	–CH$_3$	70	6	100	80
8-2	H$_3$C(O)C–	–Ph	–^{n}Bu	120	5	100	98
9-2[b]	H$_3$C(O)C–	–Ph	–^{n}Bu	120	5	82	82
10-2[b]	H$_3$C(O)C–	–Ph	–^{n}Bu	120	8	82	82
11-2	H$_3$C(O)C–	H$_2$C=CH–	–^{n}Bu	120	10	63	63
12-2	–H	–Ph	–^{n}Bu	120	14	38	38
13-2[c]	–H	–Ph	–^{n}Bu	120	6	100	90
14-2[b,c]	–H	–Ph	–^{n}Bu	120	6	52	49
15-2[d]	–H	–Ph	–^{n}Bu	120	6	63	52
16-2[b,d]	–H	–Ph	–^{n}Bu	120	6	49	44

[a] Reaction conditions: 0.50 mmol aryl bromide, 0.55 mmol organo-tin compound, Pd-pol (0.01 mmol of Pd), 2.0 ml DMF.
[b] Recycle of the previous run.
[c] In the presence of TBAB (0.50 mmol).
[d] In the presence of PPh$_4$Cl (0.50 mmol).

reactions [28]. Under these conditions, a quantitative conversion of the substrate with 90% selectivity in biphenyl (entry 13-2) was obtained after 6 h reaction in the first cycle. Unfortunately the catalyst lost part of its activity in the recycle giving 49% yield in biphenyl after 6 h (entry 14-2). The addition of PPh$_4$Cl [29] was less effective in the coupling between bromobenzene and ^{n}Bu$_3$SnPh, since 52% and 44% yields were obtained in the first and in the second cycle respectively (entries 15-2 and 16-2). In both cases a little amount of *n*-butylbenzene was detected in the reaction mixtures.

2. Analysis of the recovered catalysts and activity of the mother liquors

The Stille reaction is a tough benchmark for heterogeneous recyclable systems based on supported catalysts. First of all the catalytic cycle is very responsive to various factors, such as metal ligand, solvent, substrate and type of stannane [2,26,30]. The reaction yields, besides the product, a tin-salt containing the leaving group of the substrate. The salt accumulates in the reaction media and can poison catalyst forming a precipitate.

It is widely recognised that a certain amount of palladium leaching is necessary to promote most of the "het-

erogeneously" catalysed C–C bond forming reactions (such as the Heck reaction, the Sonogashira reaction, etc.). In those cases the supported catalyst acts as reservoir that delivers catalytically active palladium species into solution [20]. Provided that the metal leaching is controlled, supported palladium catalysts are very useful for many reasons, such as the simplification of the work-up procedure, the possibility to carry out the reaction in the absence of phosphanes, a higher air and moisture stability of the insoluble catalysts, the chance to minimise residual palladium in the final coupled products, and, more important, the potential recyclability of the supported catalyst.

It has been demonstrated that also in the Heck reaction catalysed by Pd-pol [24] the catalytic cycle is homogeneous and is started by soluble palladium species that leave the insoluble support after the oxidative addition of the aryl halide [31]. These soluble palladium species (complexes or colloids) remain active until substrate consumption, after which deactivation and precipitation occur. Two evidences revealed the presence of a homogeneous mechanism in the Heck coupling catalysed by Pd-pol. First, although the optimisation of the reaction conditions rendered the palladium leaching very low, a slight decrease of the metal content in the recycled catalyst was detected. Second, more important, in the mother liquor obtained after hot filtration of the solid

catalyst at about 20% conversion of the substrate, the coupling between the aryl halide and the olefin proceeded precisely as fast as it did in the presence of Pd-pol. On the other hand, if the filtration of the supported catalyst was carried out at quantitative substrate conversion, the solution had no more catalytic activity, and no coupling occurred between the freshly added reagents, since the active palladium species precipitated (or deactivated) when the substrate disappeared. The presence of soluble palladium species was revealed also by the colour of the reaction solution, which usually exhibited the typical orange colour of palladium(II) species during the coupling, and became colourless at the end of reaction. Tiny amount of Pd black were observed occasionally.

The catalytic cycle of the Stille reaction [26] implies the same Pd(0)/Pd(II) route of the Heck reaction, and both mechanisms are similar in the oxidative addition step. It has been demonstrated that this stage (i.e. the substrate oxidative addition) is responsible for the formation of soluble palladium species in the Heck reaction promoted by supported palladium complexes [20], hence it is conceivable that also in the Stille reaction similar active species can leach out in solution, performing the catalytic cycle in homogeneous phase. This is substantiated by the observed decrease of Pd content on the supported catalyst after duty (Table 3). A test of the catalytic activity of the clear solutions obtained by hot filtration at ∼30% conversion of the reaction mixture containing $^nBu_3SnPh$ and p-iodonitrobenzene or iodobenzene showed that the mother liquors were almost inactive. In fact, when the substrate was p-iodonitrobenzene the substrate was not consumed even after 24 h

(compare with 1 h necessary to convert all the substrate with the fresh Pd-pol, entry 4-1), giving less than 20% of coupling product. On the other hand, the mother liquor of the reaction between iodobenzene and $^nBu_3SnPh$ kept under stirring at 70 °C for 20 h gave an increase of conversion of only 10% (the conversion of the substrate passed from the initial value of 32% to the final one of 42%). These data could be explained admitting that the reaction is mainly homogeneous, but the lifetime of the leached active palladium species is short, so that a continuous supplying of fresh soluble Pd species is necessary in order to sustain the catalysis.

Table 3 reports the percentage of Pd leached out from the catalyst in selected experiments. Comparing data related to entries 12-2, 14-2 and 16-2 it is apparent that low activity observed with bromobenzene and $^nBu_3SnPh$ in the absence of additives (entry 12-2) is related with negligible leaching of Pd. The increase of activity registered in the presence of additives such as TBAB (entry 14-2) or Ph_4PCl (entry 16-2) is accompanied with a dramatic increase of Pd leaching. Data on reaction 7-1 confirm that the degree of leaching parallels the catalytic activity of Pd-pol.

As to the entries 9-1 and 11-2, the degree of Pd leaching seems excessive, if related only to the catalytic activity as represented by the turnover numbers. However, it should be noted that in these two cases, Pd leaching can be enhanced by the coordinative ability of the double (entry 11-2) or the triple bond (entry 9-1) versus palladium [32].

Another source of deactivation of Pd-pol might be the attachment of tin oxides, hydroxides and salts onto the polymer after duty. In fact, tin analyses carried out

Table 3
Analyses of Pd-pol recovered after Stille reactions[a]
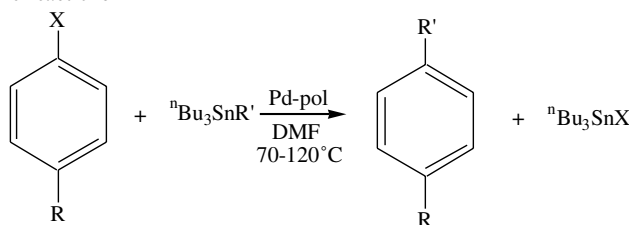
Entry	X	R	R′	T (°C)	Cycles[a]	% of Pd leached out[b]	Total t.o.n.[c]
12-2	Br	H	Ph	120	1	2	19
14-2[d]	Br	H	Ph	120	2	41	69
16-2[e]	Br	H	Ph	120	2	76	48
7-1	I	H	Ph	70	2	38	83
9-1	I	H	Ph–C≡C–	70	2	72	89
11-2	Br	H_3C(O)C–	H_2C=CH–	120	1	31	31

[a] Number of cycles to which Pd-pol was subjected.
[b] Calculated as {(moles of Pd in the fresh Pd-pol – moles of Pd in the recovered resin)/moles of Pd in the fresh Pd-pol} × 100.
[c] Total moles of product/moles of Pd in the fresh catalyst.
[d] In the presence of TBAB.
[e] In the presence of PPh_4Cl.

on the recovered resins submitted to several catalytic cycles revealed that, especially when tributylstannanes were used, significant amounts of tin (ranging from 25 to 30 wt%) remained attached to the resin.

3. Conclusions

Pd-pol is an active catalyst for the Stille coupling of iodoarenes or activated bromoarenes with different organostannanes. Its recyclability was satisfactory when $Sn(CH_3)_4$ or $^nBu_3SnPh$ were used with iodoarenes or activated bromoarenes. The reaction of bromobenzene with $^nBu_3SnPh$ gave fair yields in the coupling product only in the presence of additives such as TBAB or Ph_4PCl but the catalyst could not be recycled. In all cases the catalytic cycle is supposed to be mainly homogeneous as indicated by the parallel between the activity of the catalyst and the degree of Pd leaching. Finally, the lack of activity of the mother liquors indicates a short lifetime of the soluble active species, that do not survive to the hot filtration. All the catalytic experiments did not require the presence of inert and dry atmosphere.

4. Experimental

All 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. 23. Palladium and tin contents in the supported catalyst were determined after sample mineralization by atomic absorption spectrometry using a Perkin Elmer 3110 and a Shimadtzu AA-6701 instrument, respectively. Gas chromatographic analyses were carried out on Hewlett Packard 6890 instruments using a HP-5 crosslinked 5% PH ME siloxane (30.0 m × 0.32 mm × 0.25 μm) column (injector temperature 280 °C, FID temperature 280 °C, carrier: nitrogen or helium). GC-MS data (EI, 70 eV) were acquired on a HP 6890 instrument (injector temperature 280 °C, carrier: helium) using a HP-5MS crosslinked 5% PH ME siloxane (30.0 m × 0.25 mm × 0.25 μm) capillary column coupled with a mass spectrometer HP 5973. The products were identified by comparison of their GLC and GC-MS features with those of authentic samples. Conversions and yields were calculated by GLC using *n*-dodecane as internal standard. In the case of reactions reported in entries 8-1 and 9-1, the isolated yields were assessed as described below.

4.1. General procedure for Stille reactions

A 50 ml tube was charged with Pd-pol (4.50 wt% Pd, 0.01 mmol of Pd), aryl halide (0.50 mmol), organo-tin compound (0.55 mmol), the additive (0.50 mmol TBAB or PPh_4Cl, when present) and DMF (2.0 ml). The mixture was heated under stirring at the desired temperature until reaction completion as monitored by GLC and GC-MS analyses.

After reaction, diethyl ether (10 ml) was added to the reaction mixture and the shrinked catalyst was recovered by filtration, washed with CH_2Cl_2, acetone, water, acetone and diethyl ether, and dried under vacuum.

After separation from the insoluble catalyst, the organic solution was washed with an aqueous 1 M KF solution (3 × 10 ml) and an aqueous 1.0 M NH_4OH solution (3 × 10 ml), dried over Na_2SO_4 and added of the internal standard (*n*-dodecane).

In the cases of entries 8-1 and 9-1 purification of the diphenylacetylene was carried out by silica gel chromatography with petroleum ether (b.p. 40–60°).

4.2. Catalytic test for the determination of the activity of the mother liquor

The reaction solution was separated from the supported catalyst by hot filtration at ∼30% conversion of the substrate (GLC analyses). The clear solution was left under stirring and the reaction course was monitored by GLC.

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