Tuning the Catalytic Efficiency of Palladium Supported Complexes (Pd-NHC-SILLPs): The Cooperative Effect of the Ionic Liquid-Like Groups

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Summary: Gel-type Supported Ionic Liquid-like Phases (*g*-SILLPs) have been employed as medium for the preparation of Palladium carbene (Pd-NHC) complexes. These supported complexes onto ionic liquid-like phases were employed as catalysts for the *phosphine-, copper- and amine-free* Sonogashira reaction showing excellent activity and selectivity. The loading and nature of the ionic liquid-like moieties have proved to have an effect in the reactivity of the different Pd-NHC-*g*-SILLPs prepared, with TOF values ranging from 450 to 25000 h^{-1}.

Keywords: copper-free; green chemistry; Pd; sonogashira coupling reaction; supported ionic liquids phases (SILLPs)

Introduction

The Sonogashira reaction is one of the most widely used tools to form C–C bonds.[1,2] It provides an efficient route to aryl alkyne derivatives, which are useful in different areas ranging from natural product chemistry to materials science.[3–6] Typical procedures for Sonogashira couplings are sensitive to air and moisture and required the use of catalytic palladium species with a metal co-catalyst and a base.[2,7] The most widely employed co-catalysts are copper salts. Unfortunately, most of the alternative procedures require a stoichiometric amount of metal, which is a concern in terms of toxicity, cost, and product purity. In this regard, an interesting approach is to develop copper-free systems.[8] This strategy was of limited success because these copper-free methods often also involve the use of excess amines (even as solvents), which is not deemed to be environmentally friendly and so the ultimate goal lies in developing a copper- and amine-free Sonogashira coupling reaction.[9]

In light of recent developments towards greener chemistry, the development of an insoluble polymer-supported catalytic system is highly attractive approach to overcome those problems. However only few cases have described the copper-free Sonogashira reaction catalyzed by supported catalysts.[10]

We and other have recently reported on the synthesis of supported Pd-NHC complexes on gel-type polymeric materials and its application for the C-C reaction.[11–13] In general, these supported Pd-NHC are designed following the current paradigm for the development of polymer supported catalysts, which establishes that the support must be both electronically and sterically "inert" towards the reaction and/or the catalyst.[14] However, we have demonstrated that it is possible to design the support to play an active role in the catalytic reaction. Indeed, the use of supported ionic liquid phases (SILLPs) in which IL-like moieties are covalently held to polymeric backbone have shown big potential to fine tune the catalytic efficiency

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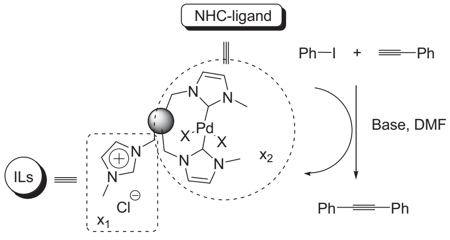


Chart 1.
Benchmark Sonogashira reaction between phenyliodide and phenylacetylene catalysed by Pd-NHC-g-SILLPs (x_1: loading of IL-like units, x_2: loading of Pd-NHC).

of different type of catalyst.[15] The presence of polymers modified with IL-like moieties is an alternative to the use of bulk ILs, overcoming some of the limitations associated to their use.[16] The SILLPs retain many of the properties of bulk ILs, such as polarity and are able to stabilize catalysts.[17] Here we report the use of different Pd-NHC-*g*-SILLPs as efficient *phosphine-*, *copper- and amine-free* catalysts for the Sonogashira reaction (Chart 1) and how the presence of the IL-like unit are used to tune the catalytic behaviour of these supported Pd-NHC complexes.

Results and Discussion

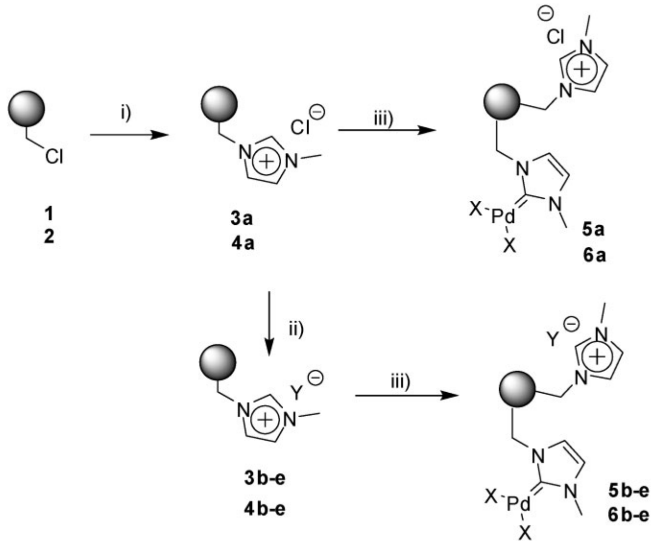
Synthesis of Pd-NHC-*g*-SILLPs 5-6a-e

The *g*-SILLPs, **3a** and **4a** were synthesized through modification of commercially available Merrifield gel-type resins with different chlorine loadings (1.1 meq of Cl/g or 4.3 meq of Cl/g, **1** and **2**, respectively) by covalent attachment of IL-like units (Scheme 1) as it has been recently reported.[12] From **3a** and **4a**, *g*-SILLPs **3-4b-e** with different anions were prepared by the metathesis reaction of the chloride anion by the corresponding salts or acid reactants ($NaBF_4$, CF_3SO_3H, $NaSbF_6$, and $LiNTf_2$ respectively). The corresponding NHC palladium complexes (**5** and **6**) were prepared by reaction of the different *g*-SILLPs with $Pd(OAc)_2$ using Bu^tOK as the base. The same amount of palladium was used in all the different *g*-SILLPs. The Pd loading of complexes was found out by ICP-MS (see Table 1), to be ca. 1.5–3% by weight for all the catalysts prepared.

Our initial studies were focused on determining the influence of different reaction parameters such as type of base, temperature and nature of the catalytic species. The bases used in copper-free palladium-catalyzed Sonogashira reactions play multiple and very role important.[18] Consequently, different bases were tested. The reaction between phenyliodide and phenylacetylene was firstly assayed employing 0.1 mol% of polymer Pd-NHC-*g*-SILLPs **6a** (X = Cl, high loading of IL-like moieties). Highly disappointing results were obtained with low yields (ca. 15%, Figure 1). It seems that Et_3N was unable to accomplish the above mention base function properly, and therefore this would be the limiting step of the reaction. In the search of a efficient base for our catalytic system piperidine and both tetrabutylammonium acetate (TBAA) and tetrabutylammonium benzoate (TBAB) were alternatively tested. Piperidine was chosen as alternative amine base and TBAA and TBAB as non-amine organic bases. The results obtained are summarised in Figure 1.

The use of piperidine clearly improved the yields obtained, compared to Et_3N, 95% of yield is achieved in 95 min (TOF 632 (mol product/mol cat) $\times$ h^{-1}). In good agreement with the observations by Urgaonkar and Verkade,[19] both TBAA and TBAB showed excellent yields and also an improvement in reaction rates. Indeed, 95% yield of product was obtained in less than 20 minutes, with TOF of 9677 and 4959 to TBAB and TBAA, respectively.[20]

In order to study, in more detail, the behaviour our catalytic system the temperature effect was evaluated. The reaction between phenyliodide and phenylacetylene was conducted using 1.2 equivalents of tetrabutylammonium acetate (TBAA) as the base and using Pd-NHC-*g*-SILLPs **6a** (X = Cl, high loading IL-like moieties) as the catalyst at three different temperatures. The use of high temperatures (130 °C and 90 °C) led to very high reaction rates. As it



Scheme 1.
Synthesis of supported Pd-NHC complexes onto *g*-SILLPs. i) 1-methylimidazole, 90 °C (**1**: PS-DVB, 1% cross linking, 1.1 meq Cl/g; **2**: PS-DVB, 2% cross-linking, 4.3 meq Cl/g). ii) metathesis, ZY or HY, MeOH/H_2O. iii) Bu^tOK, $Pd(OAc)_2$, 50 °C, 3h.

would be expected, the reaction rate dropped with temperature. This effect is clearly reflected if the TOF at 50% of conversation ($TOF_{50\%}$) is calculated 31250 h^{-1} (at 130 °C), 1307 h^{-1} (at 90 °C) and 274 h^{-1} (at 70 °C). Moreover, sigmoidal kinetics can be observed (see Figure 2). Indeed, at 90 °C a short induction time was observed, which can be clearly seen already at 70 °C. Significant reactivity differences were observed between TBAA and TBAB at 70 °C as represented in Figure 3. In fact, when TBAB was used as a base, higher activity was achieved than with TBAA, since the reaction had a shorter induction time ($TOF_{50\%}$ are 3947 h^{-1} and 106 h^{-1} for TBAB and TBAA).

The great importance of the nature of TBA salts in the reaction was evidenced when tetrabutyl methanesulfonate (TBAMs) and triflate (TBATfO) were also evaluated. The reaction did not proceed and yields lower than 2% were obtained after 18 hours of reaction. At the same time high levels of leaching were detected (*ca.* 30% of Pd/Pd_0). This proved

Table 1.
Functionalisation of the *g*-SILLPs and the corresponding Pd-NHC-*g*-SILLPs.[12b]

Entry	*g*-SILLPs (X^-)	Loading (mmol SILLP/g)[a] [b]	Pd-NHC-*g*-SILLPs (X^-)	Pd loading (mmol/g)[c]	Ratio Pd/IL-like units
1	**3a** (Cl^-)	0.93	**5a** (Cl^-)	0.17	5.5
2	**4a** (Cl^-)	3.03	**6a** (Cl^-)	0.34	9.0
3	**3b** (BF_4^-)	0.89	**5b** (BF_4^-)	0.16	5.5
4	**4b** (BF_4^-)	2.65	**6b** (BF_4^-)	0.28	9.5
5	**3c** (TfO^-)	0.84	**5c** (TfO^-)	0.20	4.2
6	**4c** (TfO^-)	2.30	**6c** (TfO^-)	0.18	13.0
7	**3d** (NTf_2^-)	0.79	**5d** (NTf_2^-)	0.17	4.6
8	**4d** (NTf_2^-)	1.62	**6d** (NTf_2^-)	0.27	6.0
9	**3e** (SbF_6^-)	0.71	**5e** (SbF_6^-)	0.18	4.0
10	**4e** (SbF_6^-)	1.61	**6e** (SbF_6^-)	0.21	7.7

[a]Determined by elemental analysis.[b]Calculated as g SILLP/g polymer.[c]Determined by ICP-MS.

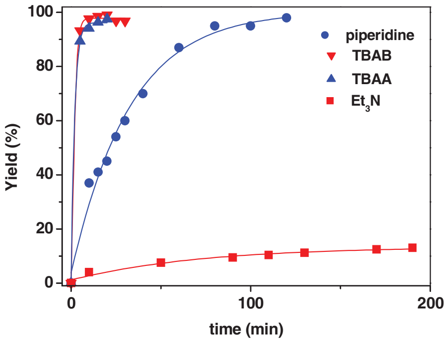


Figure 1.

Plot of yield *vs.* time for the Sonogashira reaction between phenylacetylene and phenyliodide at 130 °C catalysed by 0.1% mol of Pd-NHC-*g*-SILLPs 6a in 5 mL DMF, using different bases: i) ■: Et$_3$N (2 eq.), ii) ●: piperidine (2 eq), iii) ▲: TBAA (1.2 eq.), iv) ▼: TBAB (1.2 eq).

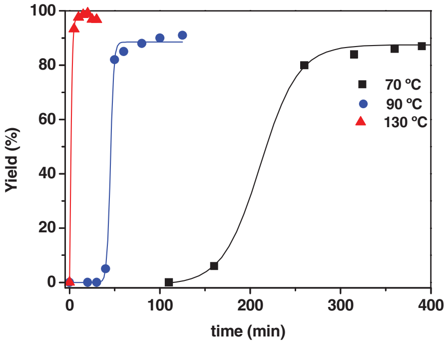


Figure 2.

Plot of yield vs. time for the Sonogashira reaction between phenylacetylene and phenyliodide at different temperatures catalysed by 0.1% mol of Pd-NHC-g-SILLPs 6a in 5 mL DMF, using TBAA (1.2 eq.) as base: i) ■: 70 °C, ii) ●: 90 °C, iii) ▲: 130 °C.

that the base has a large influence in the formation and stabilisation of the palladium soluble species as well as in the deprotonation of the alkyne. In these cases there are two reasonable explanations for the low activity observed. On one hand, the base could be so weak that it was unable to deprotonate the alkyne, thus limiting the reaction. On the other hand, this TBA salt might form very stable clusters that would be unactive in the Sonogashira reaction.

We also studied how nature and loading of *g*-SILLPs can influence on the reaction rate of Sonogashira reaction between phenyliodide and phenylacetylene. The study was performed in DMF at 70 °C using 0.1% of Pd-NHC-*g*-SILLPs **6a–e** as catalysts and dry TBAB as the base. Some of the results achieved are summarised in Figure 3.

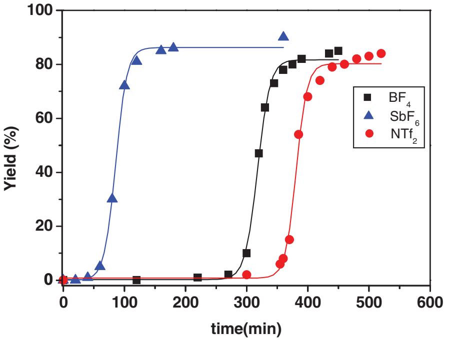


Figure 3.

Anion effect on catalytic activity. Plot of yield *vs.* time for the Sonogashira reaction between phenylacetylene and phenyliodide at 70 °C catalysed by 0.1% mol of different Pd-NHC-*g*-SILLPs with high loading (polymers 6) in 5 mL DMF, using dry TBAB (1.2 eq) as the base: i) ●: ($X = NTf_2$, high-loading IL-like groups) ii) ▲: ($X = SbF_6$, high-loading IL-like groups), iii) ■: ($X = BF_4$, high-loading IL-like groups).

When catalyst Pd-NHC-*g*-SILLP **6a** (X = Cl, high loading of IL-like groups) was used, an induction period of over 10 hours was observed. After 24 hours, 90% yield of the desired product was obtained. However, polymer Pd-NHC-g-SILLP **6c** (X = TfO, high loading of IL-like groups) showed a yield not higher than 3% after 24 hours of reaction time. Thus, under these conditions, the catalytic species derived from **6c** were not activated for the Sonogashira reaction between the phenyliodide and phenylacetylene. The other anions showed a reactivity order similar to that found in the case of the Heck reaction, namely $SbF_6^- > BF_4^- > NTf_2^-$.

This type of kinetic profile observed suggests that the reaction mechanism involves the formation of palladium nanoclusters, in a similar way to that observed for the Heck reaction.[12b] Indeed, if a ligand-free process as in Figure 4 is considered, in which leached palladium

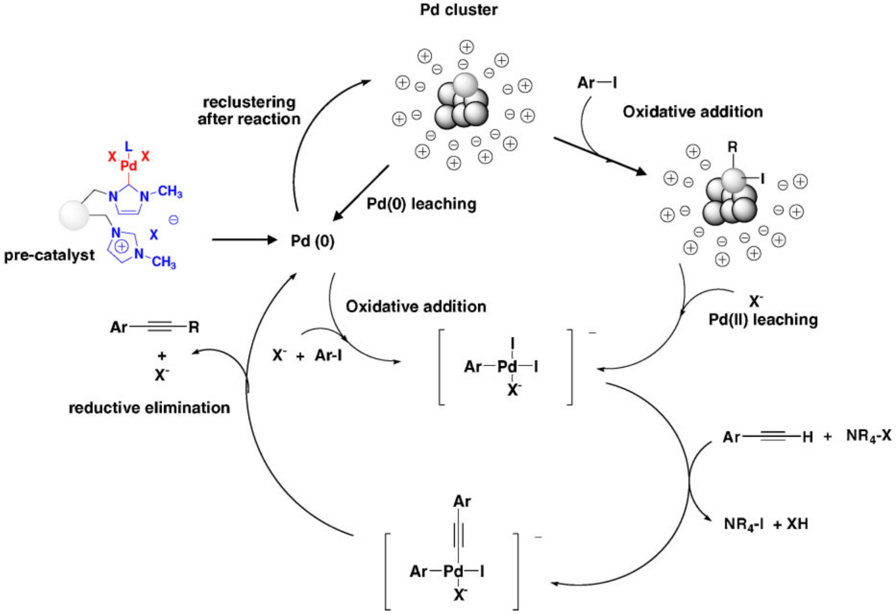


Figure 4.
Proposed mechanism for the Sonogashira reaction involving different possible pathways.

species are involved, the role of both nature of the polymer and ammonium salts should be crucial. The results also suggested that ammonium salt stabilised the active palladium species, thus improving the reaction rate of the process. Rothenberg and co-workers showed that cluster-catalysed Sonogashira reaction can proceed via soluble Pd species.[21]

If the presence of soluble active palladium species in solution is responsible for the catalytic activity in the Sonogashira reaction, the hot filtration test should provide experimental evidence for the true catalytic mechanism. Thus, when the resin was filtered after one hour of reaction, the filtered phase showed pattern similar to that of the control experiment. In this way, the active species are soluble species released from the g-SILLPs. The nature of polymeric Pd-NHC complex has the function to control this release of active species to the reaction medium. The nature of the polymeric is likely to control the mechanism of nucleation and auto-catalytic growth. Therefore, the kinetic data were adjusted using Finke's model of nucleation and auto-catalytic growth.[22] The results obtained are shown in Table 2. In all cases studied, the model describes with accuracy the observed kinetics in the induction period and at the beginning of the auto-catalytic growth period. For all the cases the limiting step of the reaction is

Table 2.
Values of k_1 and k_2 calculated for kinetics corresponding to the Sonogashira reactions catalysed by Pd-NHC-*g*-SILLPs **6a-e**.

Entry	Pd-NHC-*g*-SILLPs	Anion	% weight SILLP	$TOF_{50\%}$	$k_1(min^{-1})$	$k_2\ (M^{-1}\cdot min^{-1})\cdot 10^2$
1	**4a**	Cl	71	–	–	–
2	**4b**	BF_4	69	447	1.4×10^{-10}	6.2
3	**4c**	TfO	80	–	–	–
4	**4d**	NTf_2	78	382	1.2×10^{-13}	6.9
5	**4e**	SbF_6	85	2835	1.1×10^{-4}	7.0

the formation of the active species, thus the kinetics profile shows sigmoidal-shape. However, after about 70% of conversion, the model can not reproduce the experimental results, in contrast with what was observed for the Heck reaction.[12b]

The use of alkyl ammonium salts as the base is likely to help stabilise palladium species in solution. Indeed, the *in-situ* generation of a big excess of $R_4N^+I^-$ salts is likely to help to stabilise the palladium clusters formed. This compound is well known to help stabilise both soluble palladium species and nano-clusters.[23,24] The model applied does not take into account this possible effect. Nevertheless, since the model does offer an accurate fit for the reaction at ca. 50% of conversion, the TOF at this conversion was calculated, together with the values for k_1 and k_2. The obtained results are summarized in Table 2.

The excess of these salts with respect to the imidazolium groups in the polymer neglects the polymer effect observed for the different *g*-SILLPs in the case of the Heck reaction.[12b] Indeed, the observed k_2 value was very similar for all the active catalysts. The stabilisation of the palladium species should be mainly attributed to the ammonium salts, with the imidazolium subunits playing a minor role in the recapture and stabilisation of palladium species. The stabilization of the active species by TBA was evidenced by the lack of activity of the supported species in recycling experiments.

On the other hand, an effect of the type of *g*-SILLP on the reaction kinetics was also observed. Indeed, the induction period, and hence the k_1 value, showed a clear dependence on the nature of the counter-anion. As in the case of the Heck reaction, more strongly coordinating ions led to longer induction periods as slower release of active palladium species.

All these observations were confirmed when the reaction was performed using the polymer with lower loadings Pd-NHC-*g*-SILLPs **5a–e**. In a first attempt, the same conditions were employed. However, the reactions were very fast with about 80% of yield in only 5 minutes. These fast kinetics were not suitable to analyze differences among the different polymers. Therefore, the reaction was carried out with a lower amount of catalyst: 0.02 mol% of palladium. The results obtained are shown in Figure 5.

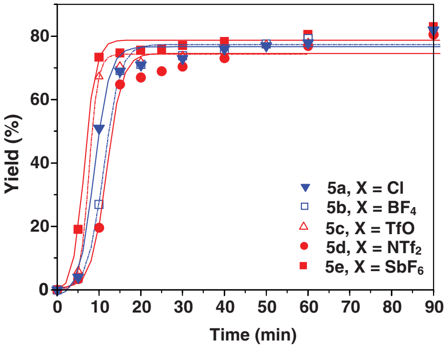


Figure 5.
Anion effect on catalytic activity. Plot of yield *vs.* time for the Sonogashira reaction between phenylacetylene and phenyliodide at 70 °C catalysed by 0.02% mol of different Pd-NHC-*g*-SILLPs with low-loading IL-like groups **5a-e** in 5 mL DMF, dry TBAA (1.2 eq) as the base: i) solid triangles: **5a** (X = Cl) ii) squares empty: **5b** (X = BF_4) iii) empty triangles: **5c** (X = TfO) iv) dots: **5d** (X = NTf_2) v) squares: **5e** (X = SbF_6).

Even with the low amounts of catalysts used, all Pd-NHC-g-SILLPs were catalytically very active, giving good yields in very short reaction times. For catalysts with low-loading of ionic liquid-like units no significant differences were observed for the different counteranions employed. All of them showed similar and very short induction periods. The delivery of the active palladium species took place with similar rate leading to very active catalysts. These results highlight how the presence of the IL-like unit can be used to fine tune the catalytic behavior of these supported Pd-NHC complexes. The reaction was attempted with phenylbromide and phenylacetylene in order to try a more challenging transformation. After 1 hour at 130 °C, 20% of product yield was observed. Afterwards, the reaction did not proceed any further.

This study opens the possibility of designing polymeric supported systems that play multiple roles in the reaction, leading to synergistic effects. The support can play an active role in the release and catch of the active species, but can also participate in stabilizing species of interest, acting as scavengers of by-products or even as supported reagents or precatalyst.

Conclusion

The elimination of both copper and phosphine ligands is an advantage from an economic and environmental standpoint, as a number of useful ligands are considered to be expensive, sensitive and difficult to obtain or have a negative environmental impact. The Pd-NHC-*g*-SILLPs act as efficient and robust catalysts that are tolerant to air and moisture. Furthermore the catalysts are quite sensitive to the presence of additional functional moieties on the polymer backbone. In fact, the TOF values ranging from 450 to 25000 h^{-1} can be tuned by changing the polymer loading and the anion employed. In the system studied, an influence of the loading and nature of the g-SILLP was observed. In the low-loading species, high activity was observed in all the cases studied. However, when higher-loading g-SILLPs were employed, a very different behaviour was observed. In these cases, very different induction times were observed as a function of the anion. More strongly coordinating anions proved to release the palladium at lower reaction rates, leading to higher induction times. When triflate was employed, the reaction was inhibited. Nevertheless, once the active species were released into the reaction medium the kinetic profile was similar in all the cases studied. This is due to the stabilizing effect of the TBA salts that overlapped the effect of the polymers.

Experimental Part

General Procedure for the Synthesis of Pd-NHC-g-SILLP

The *g*-SILLP 2a (300 mg, 0.26 mmol) and BuO^tK (60 mg, 0.53 mmol) were suspended in a flask containing 50 mL of dry THF under N_2 atmosphere. Ultrasounds were applied to the flask for few seconds in order to remove any possible aggregate of the polymer. Then the system was stirred at room temperature for 10 minutes, and later $Pd(OAc)_2$ (58 mg, 0.26 mmol) were introduced and the system was heated at 50 °C in a thermostated bath for 3 hours. After this, the polymer was filtered off and washed with THF, MeOH and CH_2Cl_2. Finally the polymer was dried under vacuum at 60 °C.

The palladium content was determined by ICP-MS. A known amount of the polymer containing palladium (ca. 10 mg.) was introduced in a round bottomed flask and suspended in 5 mL of a mixture $HCl:HNO_3$ (1:1). The flask was heated at 100 °C for 4 hours. Then the polymer was filtered and washed with 10 mL of H_2O. The filtered phases were combined and analyzed by ICP-MS.

General Procedure for the Sonogashira Reaction

In a round-bottomed flask were introduced DMF (5 mL), PhI (1.02 g, 5 mmol), phenylacetylene (0.765 g, 7.5 mmol), Et_3N (1.01 g, 10 mmol), mesitylene (0.45 mL, 3.23 mmol) and the corresponding Pd-NHC-*g*-SILLP (0.05 mmol). The flask was closed with a septum and heated at 70 °C. Periodically, samples of 5 μL were taken, diluted in CH_3CN (1 mL) and analyzed by HPLC. When the reaction was over, the polymer was filtered and washed with THF and MeOH and dried under vacuum. The kinetics were followed by HPLC.

The HPLC conditions employed were analogous to the previously described for the Heck reaction.[12b] Retention times: 3.85 min. phenylacetylene, 5.85 min. phenyliodide, 8.75 min. mesitylene, 10.85 min diphenylacetylene, 18.99 min. diphenyldiacetylene.

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