

Vinylic Addition Polynorbornene as Support for N-Heterocyclic Carbene Palladium Complexes: Use as Reservoir of Active Homogeneous Catalytic Species in C–C Cross–Coupling Reactions

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Abstract: A vinylic addition polynorbornene (VA-PNB) functionalized with imidazolium groups can be used to synthesize a well-defined supported palladium carbene complex. This complex is a suitable precatalyst for Suzuki and Negishi cross coupling reactions, and it can be reused. A close look to how the catalysis work reveals that palladium aggregates form on the polymer surface after the first catalytic reaction. However, they are not easily washed out and serve as a source of a small amount of homogeneous palladium active species (about 0.1% mol) that are responsible for the catalysis. The recovered polymer can be reused several times although increased induction and reaction times are observed in consecutive uses from one run to the next. The reaction was followed up by in situ IR spectroscopy using the $\nu(\text{C-Br})$ absorption of the electrophile, so there is no need of an additional functional group to apply this technique.

Introduction

Vinylic addition polynorbornenes (VA-PNBs, Figure 1) have an aliphatic, robust backbone that has been successfully used as scaffold to support N-heterocyclic carbenes- (NHCs),^[1] or proline-based organocatalysts,^[2] as well as stannyl groups for their application as recyclable reagents in the Stille reaction.^[3] The saturated polymer backbone in VA-PNBs has a clear advantage when compared to ROMP-PNBs, especially in metal-catalyzed reactions (Figure 1). Recently, we have reported the risks of exposing the unsaturated ROMP scaffold to some metal complexes, and we have observed the insertion of the C=C double bond of a ROMP-PNB in a palladium-aryl complex, leading to the formation of an aryl substituted polymer.^[4] Considering the a priori attractive features of VA-PNBs, we decided to test the behavior of the VA-PNB skeleton as support of palladium complexes in two cross-coupling reactions, namely Suzuki and Negishi couplings. We chose our imidazolium functionalized VA-PNBs, previously used as precursors of NHC organocatalyst,^[1] to support Pd-NHC complexes. The aliphatic scaffold allows one to find out the ability of the carbene moiety

(or imidazolium salt) to retain the metal on the support, without interference of the interactions with the polymer backbone.

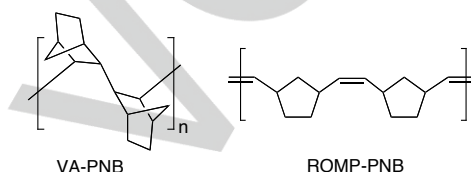


Figure 1. Simplified structure of vinylic addition polynorbornene (VA-PNB) and polynorbornene synthesized by ROMP.

The use of NHCs, especially imidazole-2-ylidenes, as ancillary ligands in Pd-catalyzed processes has become a common practice.^[5] Due to the good performance of these ligands, palladium NHC-complexes have been supported on silica,^[6] polymers,^[7] or other materials,^[8] so the advantages of heterogeneous systems (good separation and catalyst recovery) can be added to the catalytic process. Usually, the supported Pd-NHCs have been assessed in the Suzuki, Sonogashira or Heck reactions. Following the early examples of polymer supported NHC-complexes,^[9] the use of Pd-loaded polymer-bound NHCs in C–C coupling reactions have been reported using polystyrene,^[10] polyethyleneglycol,^[11] polyoxazoline,^[12] polyisobutylene,^[13] and ROMP-polynorbornene matrixes.^[14] Polymeric imidazolium salts,^[15] or NHC-coordination polymers have also been used.^[16] Although many publications report good results, in most cases direct comparison between systems is difficult to make because of the many different conditions used (reagents, reaction times, catalyst loading,...) and the unlike way of presenting data. The characterization of the supported palladium NHC complexes is usually less straightforward than the determination of the structure of the non-supported analogues, especially when insoluble polymers are used. Thus, in many reports, the nature of the metal species attached to a polymer, used as catalysts precursors, is frequently unknown or poorly determined. The operating mechanism in reactions using the supported catalysts has not always been determined. A crucial point is to find out if the catalytic reaction actually occurs on the support or if this is a mere palladium reservoir, the real catalytic species being homogeneous and formed under catalytic conditions. Some reviews have addressed this subject.^[14b,17] Also, conclusions concerning reusability must be cautious if long reaction times are used in the recycling experiments: this may hide the catalyst undergoing partial loss or decomposition in every cycle.

All things considered, some efficient and reusable polymer-

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supported Pd-NHC complexes have been reported. Among those examples that allow moderate reaction times, Lee et al. have synthesized polystyrene-supported NHC-Pd species that can be reused five times in the Suzuki reaction of aryl bromides under mild reaction conditions (1 h, 50 °C, 1% mol of Pd).^[10d] Luis' polystyrene resins functionalized with imidazolium salts have also proved to be reusable in the Heck reaction at high temperature (130 °C, 80-120 min).^[10f] Good results have also been obtained in the Suzuki reaction using the poly-imidazolium salts reported by Ying et al.^[15] Luo et al. reported mild reaction conditions (room temperature) when employing polystyrene-supported NHC palladium species as catalyst in the Suzuki reaction of aryl bromides. The catalyst can be recycled at the expense of increasing the reaction times (24 h).^[10d] In general, it can be said that, among the different types of polymeric matrixes used so far, polystyrene is the support that has allowed the preparation of the best recyclable palladium catalytic species. We report here on the use of VA-polynorbornenes, which also have the potential of being a good choice to support palladium catalytic species in C-C coupling reactions.

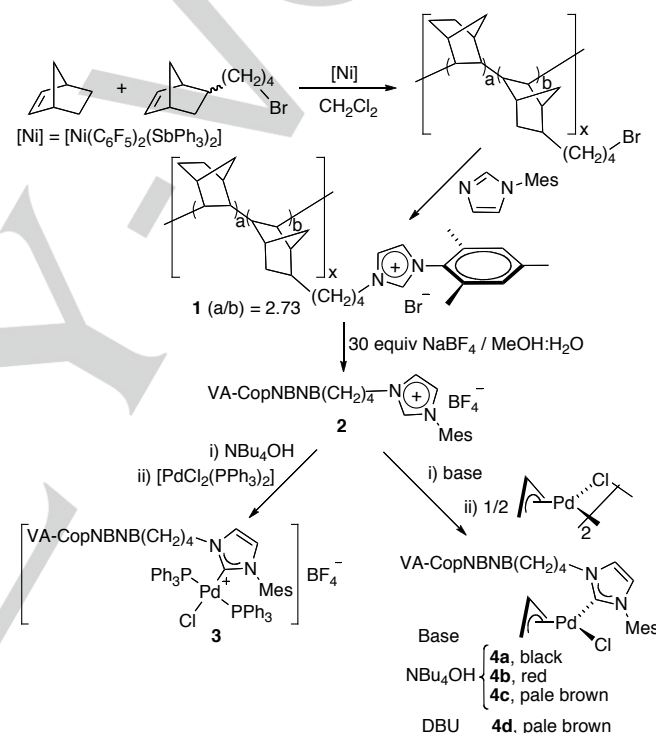
Results and Discussion

A VA-polynorbornene with pendant imidazolium groups (**1**) was synthesized, as previously reported, by nucleophilic substitution of the bromide by an imidazole in a vinylic addition copolymer of norbornene and bromobutyl norbornene (Scheme 1).^[1] We have shown before that a longer alkyl tether leads to more reactive functionalized VA-PNBs,^[3c] and for this reason a bromobutyl group was chosen rather than a shorter ω -bromoalkyl. Polymer **1** is a solid, insoluble in common organic solvents or water, and it was used to synthesize the polymer-supported metal-carbene complexes by addition of a palladium precursor to a suspension of the in situ formed carbene. In order to avoid possible interferences of the bromide, acting as a ligand during the syntheses of the complexes, a change of that anion for a less coordinating one was performed. Thus, polymer **1** was treated with sodium tetrafluoroborate in a mixture of water and methanol and the complete exchange of anions took place to give **2**, as shown by the absence of bromide by quantitative analysis (Scheme 1). Infrared spectra showed the appearance of a strong band associated with the $\nu(\text{B-F})$ at 1053 cm^{-1} .

The imidazolium functionalized polymer **2** was deprotonated with tetrabutylammonium hydroxide in CH_2Cl_2 . After the formation of the polymeric carbene, $[\text{PdCl}_2(\text{PPh}_3)_2]$ was added and the mixture was stirred for 24 hours (Scheme 1). Polymer **3** was insoluble in common solvents and it was characterized by solid state NMR spectroscopy. A ^{31}P MAS NMR experiment showed a broad signal around 26 ppm corresponding to the trans phosphine ligands bound to palladium. The palladium content was determined by ICP-MS and was found to be 5.75 mg Pd/ g polymer.

A different supported palladium complex was synthesized using **2** and $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\mu\text{-Cl})_2]$ giving different results depending on the reaction conditions. When tetrabutylammonium hydroxide was used as a base to deprotonate **2**, the contact time between

this mixture and the organometallic compound was crucial. Even using an equimolar ratio of the base to the imidazolium salt in **2**, incomplete base consumption produces the decomposition of the palladium allyl dimer to form allyl alcohol and palladium black. This was confirmed by an independent experiment where $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\mu\text{-Cl})_2]$ was mixed with $(\text{NBu}_4)\text{OH}$ and the resulting dark suspension was analyzed by ^1H NMR where allyl alcohol was clearly detected. Thus, if the polymeric product of the reaction shown in Scheme 1 (base = $(\text{NBu}_4)\text{OH}$) was filtered 24 hours after the addition of $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\mu\text{-Cl})_2]$ the resulting solid, **4a**, was black and contains 58.1 mg Pd/ g polymer. When shorter reaction times were allowed, we got a dark red polymer **4b** with 27.9 mg Pd/ g polymer in 2 hours, and a pale brown **4c** with 6.70 mg Pd/ g polymer in 30 minutes (Scheme 1).



Scheme 1. Synthesis of VA-PNB supported palladium complexes.

The loading of palladium in the polymer increases with time but the nature of the species formed (probably a mixture of Pd(II) and Pd(0)) are far from being well defined. When a different base such as DBU was employed in the formation of the carbene, $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\mu\text{-Cl})_2]$ did not undergo decomposition even after long reaction times allowing a higher amount of palladium to be attached to the polymer without decomposition of the starting dimer. In this case polymer **4d** was obtained as a brownish solid with 89.4 mg Pd/ g polymer (Scheme 1). The ^{13}C CP-MAS NMR spectrum of **4d** showed a signal at 180 ppm characteristic of the carbene carbon atom bound to palladium, as well as signals for the allyl group at 114 and 70 ppm (Figure 2). Those signals are not visible, either in the ^{13}C CP-MAS NMR

spectrum of **4c** (probably because the amount of NHC-Pd complex formed is too low) or in the spectra of **4a** and **4b**, where the presence of a Pd-NHC bond is dubious.

In order to study the catalytic activity of the VA-PNB-supported palladium complexes synthesized, as well as their reusability, some Suzuki reactions were carried out.^[18]

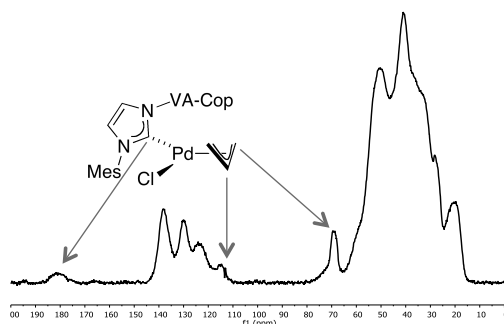


Figure 2. ¹³C CP-MAS NMR spectrum of polymer **4d**.

Initially, all the polymers, **3** and **4a-d**, were tested and their activity compared in the same reaction conditions. In a model reaction the supported palladium precatalyst (1% mol of Pd) was added to a mixture of 4-bromobenzotrifluoride, phenylboronic acid and cesium carbonate in acetonitrile:water (3:1; v/v) (Equation 1). After heating at 80 °C for 20 minutes the reaction was cooled down and checked by ¹⁹F NMR. Subsequently, the polymer was filtered, washed with the same mixture of solvents, air-dried and reused in the same reaction conditions for 30 minutes. The results obtained in both cycles are collected in Table 1.

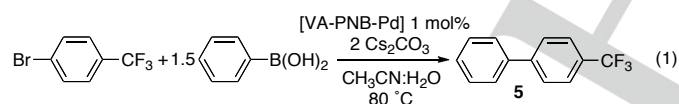


Table 1. Comparative experiments in the Suzuki reaction shown in Equation 1 catalyzed by VA-PNB-supported palladium complexes.^a

Entry	Catalyst	Pd content (mg/g polym)	5, Yield cycle 1/ Yield cycle 2 (%) ^b
1	3	5.75	10/4
2	4a	58.1	0/0
3	4b	27.9	96/21
4	4c	6.70	46/63
5	4d	89.4	87/99

a) Reaction conditions shown in Equation 1. Reaction times: 20 min for the first cycle and 30 min for the second cycle. b) Crude yields determined by ¹⁹F NMR. No byproducts were observed.

Polymer **3** was barely active and, after the first run, its performance was even worse (Table 1, entry 1). The way the

palladium is attached is more important than the amount loaded and, in the case of polymers **4**, quite different results were found. **4a** showed no activity at all (Table 1, entry 2). In spite of being one of the polymers with higher Pd-load, the metal seems to be deposited as inactive palladium black. When the catalyst used was **4b** a very high yield was initially achieved but after the first run the yield notably dropped (Table 1, entry 3). **4c** and **4d** showed similar trends although the complex prepared with DBU gave better yields in the synthesis of **5** (Table 1, entries 4 and 5). In both cases, the second use of the catalyst gave better results due to the increased reaction time (20 and 30 min in the first and second runs respectively). Additionally, other solvent mixtures (dioxane:water or DMF:water) were tested but they were less convenient because either the reaction was slower or the formation of the dehalogenation product, CF₃C₆H₅, was observed (see Supporting information). We have previously reported and thoroughly studied the route that solvents such as DMF follow to induce the formation of ArH from palladium aryl complexes.^[19] On the contrary, this side reaction is absent in acetonitrile.

In view of these results we decided to study the recyclability of polymer **4d**. In order to determine the real reaction time for full conversion in each run, we monitored the reactions by *in situ* infrared spectroscopy. We discarded the use of ¹⁹F NMR spectroscopy, quite useful in homogeneous close-related reactions, since **4d** is insoluble and in this heterogeneous systems mass transfer effects must be considered and stirring happens to be important. Although *in situ* infrared spectroscopy has been known for several decades few examples of its application in palladium catalysis can be found.^[20] The reaction studied was the one depicted in Equation 1. With a React-IR apparatus the ν(C-Br) IR absorption band at 1012 cm⁻¹ belonging to 4-bromobenzotrifluoride could clearly be observed since this signal was not overlapped with the bands of the solvent or any other reagent (Figure 3, a). This methodology allowed us to monitor the disappearance of the aforementioned band and thus to follow the progress of the reaction. The mixture of boronic acid, base, polymer and solvent was introduced in a bath at 80 °C. The aryl bromide was then added and the variation of the ν(C-Br) IR absorption intensity was recorded. When no variation of the band was observed for several minutes the heating was stopped and, after cooling, the yield was determined by ¹⁹F NMR spectroscopy. The same procedure was applied in the four subsequent recycling experiments and the results are collected in Table 2.^[21] In all the reactions an induction time could be observed (Figure 3, b). As a general trend this period as well as the total reaction time increased from one cycle to the next. In the first reaction the induction time was no longer than 5 minutes and the conversion was complete after 26 minutes (Table 2, cycle 1), whereas the last run took about 60 minutes with an induction period around 23 minutes (Table 2, cycle 5).

Palladium leaching was determined by ICP-MS finding a small amount of palladium in the filtrate after every run (Table 2). Since the polymer was losing palladium in every reaction, we performed a hot filtration test to find out whether the catalysis was occurring onto the polymer or in a homogeneous way with

some active palladium species released. In the sixth cycle, after running the reaction at 80 °C for 1 hour, the hot mixture was filtered. At that point, the ^{19}F NMR spectrum showed a 31 % yield. The filtrate was allowed to react at 80 °C for an additional hour affording a yield of 92 %. This result clearly evidences that a homogeneous catalysis is operating for our system. In this case the palladium leaching was determined and showed a value of 1 % of the initial amount added. Comparison of this quantity with those observed in the recycling experiments seems to indicate that the small amount of palladium freed to the solution in every run is enough to catalyze the reaction. This release might account for the induction period observed.

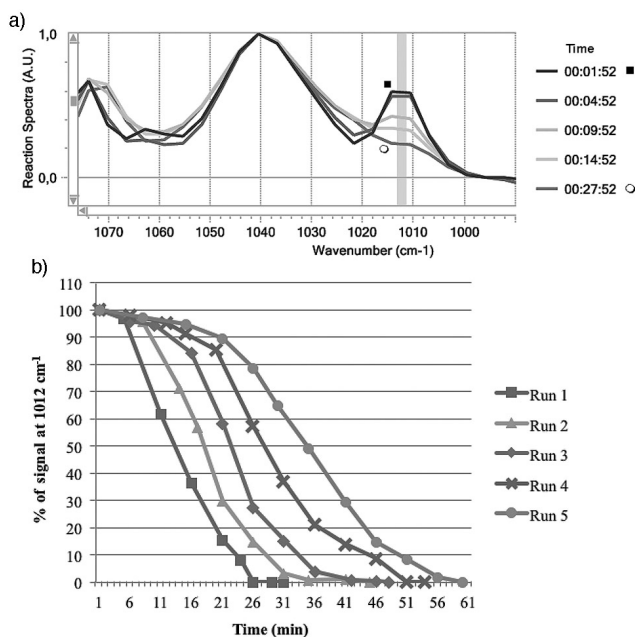


Figure 3. Time evolution of the $\nu(\text{C-Br})$ IR absorption band of the ArBr in Equation 1 followed by in situ IR: a) IR spectra (cycle 1, $\nu(\text{C-Br})$ band marked with shadowed bar) and b) plot of the change of the absorption intensity with time in subsequent reuses.

Table 2. Recycling experiments of **4d** in the Suzuki reaction shown in Equation 1.^a

Cycle	Time (min)	Induction time (min)	5 , Yield (%) ^{b,c}	Pd Leaching (%) ^d
1	26	5	98	3.2
2	35	10	96	0.59
3	41	14	96	0.37
4	51	18	97	0.35
5	60	23	91	1.3

a) Reaction conditions shown in Equation 1. b) Crude yields given were determined by ^{19}F NMR. No byproducts were observed. c) **5** was isolated (see experimental) with 83-87% yields. d) Leaching determined by ICP-MS in the crude product of the reaction. Percentage of Pd leached referred to the total amount initially added.

Scanning electron microscopy (SEM) images of **4d** before and after its use shows a clear change in the distribution of the palladium in the polymer. Before its use **4d** showed a smooth surface (Figure 4, a), whereas after one run aggregates could be observed on the surface (Figure 4, b and c). In order to have a better knowledge of the composition of those particles a microanalysis by Energy Dispersive X-ray Spectroscopy (EDS) was carried out. This technique allowed us to see that the concentration of palladium in the aggregates (29 % weight) was higher than the average concentration in the polymer matrix (9 % weight). These particles have an average size around 65 nm much larger than common palladium nanoparticles useful in catalysis, rarely larger than 10 nm (Figure 4, c). This kind of distribution of the palladium aggregates all over the surface was maintained for the five runs (Figure 4, d).

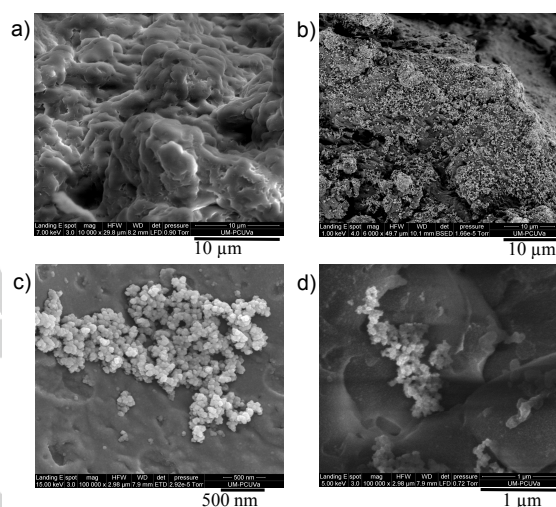


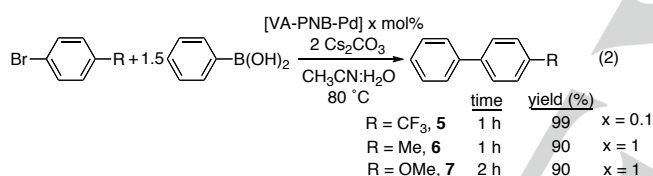
Figure 4. SEM images of polymer **4d**: a) before use; b) after 1 use; c) after 1 use (magnified); d) after 5 uses.

These results show that the complex $[\text{Pd}(\text{allyl})\text{Cl}(\text{NHC-VA-PNB})]$ does not survive after a first catalytic Suzuki reaction, even if linked to the polymer support through a Pd-NHC bond. Nonetheless the palladium aggregates show a strong interaction with the polymer surface, since they are not washed down easily and they just slowly release the very small amount of Pd enough for the catalysis in successive reuses (between 1.5%-0.3% of the initial Pd content from the second cycle on).^[22] We do not have any experimental data that gives information about the nature of this interaction with the polymer. However, we could hypothesize that either the carbene or the imidazolium centers, formed on the support after the decomposition of the complex, must be playing a leading role, since the interaction with the completely saturated VA-PNB skeleton used as support is expected to be weak.

The release of the palladium active species into solution is promoted by the aryl bromide. We run two consecutive catalytic experiments where the polymer was suspended in the solvent and incubated with 4-bromobenzotrifluoride for 5 min at 80 °C before adding the mixture of the boronic acid and the base. No induction period was observed in these runs (see supporting

information, Figure S2). Additionally, a sample of the solution in the reaction mixture, before complete conversion, was drop-casted on a grid. TEM images of this sample showed the presence of nanoparticles in solution of average size 3 nm (see supporting information, Figure S3). Thus, the aryl bromide is playing the main role in transporting the palladium from the aggregates on the polymer surface into solution, most probably by oxidative addition to the metal. In catalytic conditions the solution species form small nanoparticles that could be responsible for the catalysis.

Other haloarenes were also tested. The system is inactive for aryl chlorides. Those reactions of para-substituted aryl bromides with electron donating groups required longer times but high yields were achieved (R = OMe, Equation 2). The model reaction was also effective when only 0.1 mol% of **4d** was used (R = CF₃, Equation 2). Considering all the amount of palladium added, a TOF value of 990 TON/h was achieved, which is a good value in this type of reactions. However, as mentioned above, the actual catalytic species are most probably the homogeneous species released into the reaction medium (around 1%-0.3% of the Pd content, Table 3.2). This means that the TOF number for the actual catalytic species reaches a value of at least 10⁵ TON/h in each run. The polymeric palladium precatalyst **4d**, being recyclable, can reach a very high cumulative TON.



The VA-polynorbornene-supported palladium complex was also tested in the Negishi reaction with organozinc derivatives. This reaction has been well studied and tolerates many functional groups.^[23] Despite its advantages, supported palladium catalysts have seldom been assessed using Negishi reactions and fewer reports can be found,^[24] none of them involving NHCs. In a standard reaction **4d** as catalyst precursor (1 mol% of palladium) and 4-bromobenzotrifluoride were added to a freshly-prepared solution of diphenylzinc in a 1:1 mixture of THF and dibutyl ether (Equation 3). The reaction was heated at 50 °C and monitored by *in situ* infrared spectroscopy. The ν(C-Br) IR absorption band was not overlapped by any other reagent or solvent band and its decrease could be easily followed. In this case, longer reaction times than in the Suzuki reaction were needed to achieve good results (Table 3), but the yields are similar in three consecutive uses. Induction times were also observed (10, 13 and 15 min in consecutive cycles). Furthermore, a significant amount of homocoupling product (4,4'-bis(trifluoromethyl)-1,1'-biphenyl) could be observed as byproduct. The presence of this undesired product can be explained by the reversible aryl exchange between palladium bis-aryl complexes and the zinc species leading to a [Pd(C₆H₄CF₃)₂L₂] complex prior to the reductive elimination, as it

has been shown before.^[25] Leaching measurements showed higher values than those observed in the Suzuki coupling, indicating that the supported catalyst could be acting again as a palladium reservoir of homogeneous catalytic active species. As it happened before, the loss of palladium in the first run was higher (10.7%) than in the subsequent cycles.^[22] After the first use the leaching decreased to 2.5-5% of the Pd added as **4d** in the reaction mixture, so the precatalyst is slowly wasted and useful in several cycles.

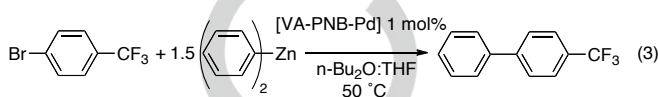


Table 3. Recycling experiments of **4d** in the Negishi reaction.^a

Cycle	Time (h)	Conversion (%) ^b	17 , Yield (%) ^b	Pd Leaching (%) ^c
1	4	98	89	10.7
2	4.5	98	88	4.4
3	6	91	83	2.8

a) Reaction conditions shown in Equation 3. b) Conversions and crude yields determined by ¹⁹F NMR. The formation of the homocoupling product accounts for the differences in these values. c) Leaching determined by ICP-MS in the crude product of the reaction. % of Pd leached from the total amount initially added.

Conclusions

Vinyl addition polynorbornene is a useful catalyst support for C-C coupling reactions. A functionalized VA-PNB with an N-heterocyclic carbene coordinates to palladium to give [(VA-PNB-NHC)Pd(allyl)Cl] which is a well characterized species and a good catalyst precursor in the Suzuki and Negishi reactions. After the first use, the polymeric complex is transformed into palladium aggregates of 65 nm average size attached to the surface of the support. These aggregates are a reservoir of the active homogeneous catalytic species, which are released into the reaction medium in a very small amount every recycling experiment. The polymeric precatalyst can be reused with good yields and activity.

In situ infrared spectroscopy can be applied to the straightforward monitorization of the reaction by following the decrease of the C-Br band of the bromoaryl reagent. This is a useful and general protocol that can be applied to bromoaryl electrophiles, with no need of a specific IR-active substituent on the reagent, as has been common practice so far.

NHC groups on a robust vinyl addition polynorbornene devoid of additional functional groups are enough to retain a heterogeneous source of minute amounts of a homogeneous palladium catalyst. This operation pathway is being recognized now as a common scenario for supported Pd-catalysts, but it has not always looked into and analyzed. The released homogeneous species in our system are very active, with TOF

comparable to some of the most active homogeneous Pd-catalysts in the first run,^[26] and, as it is reusable, the cumulative turnover number can reach very high values. The synthesis of the polymeric NHC-ligand described here is neither cumbersome nor costly so it can compete with some of the monomeric NHC used for the synthesis of mono- or oligomeric complexes.

Experimental Section

General Methods.

¹H, ¹³C and ¹⁹F NMR spectra were recorded using Bruker AV-400 and Agilent MR-500 instruments. Chemical shifts (δ) are reported in ppm and referenced to SiMe₄ (¹H, ¹³C) or CFCl₃ (¹⁹F). All NMR spectra were recorded at 293 K in deuterated solvents or, in the case of the catalytic reactions, in protic solvents using an acetone-d₆ capillary. The solid state NMR spectra were recorded at 293 K under magic angle spinning (MAS) in a Bruker AV-400 spectrometer using a Bruker BL-4 probe with 4 mm diameter zirconia rotors spinning at 8 kHz. ¹³C CP MAS NMR spectra were measured at 100.61 MHz and recorded with proton decoupling (tppm), with a 90° pulse length of 4.5 μ s and a contact time of 3 ms and recycle delay of 3 s. The ¹³C NMR spectra were referred to glycine (CO signal at 176.1 ppm). ³¹P MAS NMR spectra were recorded at 161.97 MHz with proton decoupling (tppm), with a 90° pulse length of 5.45 μ s. ³¹P-NMR chemical shifts are in ppm relative to external 85 % H₃PO₄. IR spectra were recorded on a Perkin-Elmer FT/IR SPECTRUM FRONTIER spectrophotometer with Csl + ATR diamond accessory. Microscopy measurements have been carried out at the Unidad de Microscopía Avanzada de the Parque Científico UVA. Scanning Electron Microscopy (SEM) images were obtained using an Environmental Scanning Electron Microscope (ESEM), model FEI-Quanta 200FEG provided with a Schottky-Field Emission filament. The SEM analyses were performed uncoated at low vacuum mode (Figure 4, a, d), high vacuum mode with Au metalization (Figure 4, c) and BSED detector using the beam deceleration mode (Figure 4, b). Microanalysis by Energy Dispersive X-ray Spectroscopy (SEM-EDS) was carried out using an EDAX Genesis accessory. Transmission Electron Microscopy (TEM) measurements have been carried out using a JEOL JEM-1011 microscope working at 100 KV; samples were prepared by drop-casting of a solution aliquot on a grid. The halogen content in the polymers was determined by oxygen-flask combustion of a sample and analysis of the residue by mercurimetric titration of the bromide.^[27] The palladium content of the polymers and leaching measurements were determined by ICP-MS, using Agilent 7500i equipment; the samples were dissolved in HNO₃ (65%) using an ETHOS SEL Milestone microwave oven. In situ IR spectra were recorded with a ReactIR 15 equipped with a transmission fiber of 6.3 mm AgBr FiberConduit and a probe DiComp with diamond sensor. Solvents were dried prior to use and stored under nitrogen. The reagents used in the synthesis of the monomers and catalytic reactions were purchased from Aldrich, Alfa-Aesar and Acros. Polymer **1** was prepared as described before.^[2] [PdCl₂(PPh₃)₂]^[28] and [Pd(η^3 -C₃H₅)(μ -Cl)]₂^[29] were synthesized according to the literature procedures. Diphenylzinc was prepared by reaction of a solution of ZnCl₂ (1.0 M, THF) and a solution of LiPh (1.9 M Bu₂O).^[30]

Synthesis of [VA-CopNBNB(CH₂)₄IMes]BF₄ (2). A round-bottom flask was charged with copolymer [VA-CopNBNB(CH₂)₄IMes]Br (**1**) (0.8000 g, 1.190 mmol IMes) and MeOH (100 mL). Then a solution of sodium tetrafluoroborate (3.900 g, 35.52 mmol) in H₂O (30 mL) was added slowly and the mixture was stirred at room temperature for 40 h. After that time H₂O (100 mL) was added and the mixture stirred for 2 h. The polymer

was filtered, washed with a mixture MeOH:H₂O (1:1, v/v, 5 x 20 mL) and air-dried. The polymer is a white solid (0.7690 g, 95% yield). Halogen analysis: 0 mg Br/g. IR (Neat), ν : (C=N) 1548, (B-F) 1052. ¹³C CP-MAS NMR (100.61 MHz): 150-120 (br, aromatic protons, NCHN, NCH=CHN), 64-24 (br, polyNB), 24-15 (br, CH₃).

Synthesis of [VA-CopNBNB(CH₂)₄IMes]PdCl(PPh₃)₂]BF₄ (3). NBu₄OH (0.270 g, solution in MeOH, 40% wt, 1.04 mmol) was added to a suspension of **2** (0.604 g, 0.868 mmol) in CH₂Cl₂ (40 mL) under nitrogen. After 30 min [PdCl₂(PPh₃)₂] (0.640 g, 0.911 mmol) was added to the carbene solution and the mixture was stirred at room temperature for 24 h. The polymer was filtered and washed with hot CH₂Cl₂ (5 x 10 mL) until the filtrate showed no yellow color. The product was obtained as a yellow solid (0.605 g, 60% yield). The polymer contains 5.75 mg Pd/g. ¹³C CP-MAS NMR (100.61 MHz): 165-159 (br, NCN), 144-117 (br, aromatic protons, NCH=CHN), 63-23 (br, polyNB), 23-13 (br, CH₃). ³¹P MAS NMR (161.97 MHz): 32-20 (br, PPh₃).

Synthesis of [VA-CopNBNB(CH₂)₄IMes]PdCl(η^3 -C₃H₅)] (4d). In a Schlenk tube in a nitrogen atmosphere polymer **2** (0.400 g, 0.589 mmol of IMes), DBU (0.134 g, 0.883 mmol) and THF (10 mL) were stirred at reflux for 8 hours. After cooling to room temperature [Pd(η^3 -C₃H₅)(μ -Cl)]₂ (0.108 g, 0.294 mmol) was added and the mixture was stirred at room temperature for 12 hours. The polymer was then filtered, washed with THF (5 x 10 mL) and air-dried. The product was obtained as a pale brown powder (0.415 g, 91% yield). The polymer contains 89.4 mg Pd/g. IR (neat), cm⁻¹: ν (C=C) 1648, ν (C=N st) 1604. ¹³C CP-MAS NMR (100.61 MHz): 184-177 (br, NCN), 142-117 (br, aromatic protons, NCH=CHN), 117-111 (br, allyl C¹), 77-65 (br, allyl C², allyl C³), 64-24 (br, polyNB), 24-15 (br, CH₃). **4a**, **4b**, and **4c** were synthesized in a similar way, but treating the polymer with NBu₄OH (solution in MeOH, 40% wt) as base for 2 h at room temperature before stirring with the palladium complex different times (24 h, 2 h and 30 min respectively).

General procedure for the Suzuki reactions. Synthesis of 5. (Table 1, entry 5, cycle 1). Polymer **4d** (0.0024 g, 0.0020 mmol Pd), phenylboronic acid (0.0370 g, 0.300 mmol) and cesium carbonate (0.1410 g, 0.400 mmol) were introduced in Schlenk tube in a nitrogen atmosphere. Then 4-bromobenzotrifluoride (0.0450 g, 0.200 mmol) and a mixture of CH₃CN:H₂O (2.0 mL, 3:1; v/v) were added and the mixture was kept in a heat-bath at 80 °C for 20 min. The reaction mixture was then cooled to room temperature and checked by ¹H NMR and ¹⁹F NMR. The polymer was then filtered, washed with a mixture of CH₃CN:H₂O (5 x 2.0 mL, 3:1; v/v) and air dried. The polymer was stored for further use. The acetonitrile was removed under vacuum and the residue was dissolved in CH₂Cl₂ (10.0 mL). The organic phase was washed with water (5 x 5.0 mL) and a saturated aqueous solution of NH₄Cl (2 x 5.0 mL) and dried over MgSO₄. After evaporating the solvent the residue was chromatographed on silica gel (hexane as eluent) to afford the pure product as a colorless solid (**5**, 0.037 g, 83 % yield). The other experiments showed in Table 1 and Equation 2 were carried out in the same way. Crude yields are given in Equation 2 and isolated yields for compounds **6** and **7** are 78 and 81% respectively. The identity of the products **5**, **6** and **7** was confirmed by comparison of the characterization data with those found in the literature.^[31]

General procedure for the Suzuki reactions followed by in situ IR (Table 2, entry 1). Polymer **4d** (0.0100 g, 0.00840 mmol Pd), phenylboronic acid (0.154 g, 1.26 mmol) and cesium carbonate (0.547 g, 1.68 mmol) were introduced in a pear-shaped flask with three necks. It was equipped with the IR-probe in the central neck, a gas inlet with stopcock and a septum. Then, in a nitrogen atmosphere, a mixture of CH₃CN:H₂O (4.0 mL, 3:1; v/v) was added and the mixture was introduced in a heated bath at 80 °C. After 5 min 4-bromobenzotrifluoride (0.189 g,

0.840 mmol) was added and the reaction was immediately monitored by IR, following the decrease of the $\nu(\text{C-Br})$ band at 1012 cm^{-1} . When no increase of conversion was observed the reaction was cooled down to room temperature and checked by ^1H NMR and ^{19}F NMR. The polymer was then filtered and washed with a mixture of $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ (5 x 2.0 mL, 3:1; v/v). The polymer was stored for further use. The other experiments showed in Table 2 were carried out in a similar way. IR monitoring can also be applied to the other bromoarenes in Equation 2 by following the disappearance of the $\nu(\text{C-Br})$ band at 1003 cm^{-1} for $p\text{-BrC}_6\text{H}_4\text{OMe}$ and at 1010 cm^{-1} for $p\text{-BrC}_6\text{H}_4\text{Me}$.

General procedure for Negishi reactions followed by in situ IR. Polymer **4d** (0.0200 g, 0.0168 mmol) and THF (4.0 mL) were introduced in a pear-shaped flask with three necks. It was equipped with the IR-probe in the central neck, a gas inlet with stopcock and a septum. The mixture was kept in a heated bath at $50\text{ }^\circ\text{C}$ for 5 min. Then 4-bromobenzotrifluoride (0.378 g, 1.68 mmol) and a solution of ZnPh_2 (5.0 mL, 2.5 mmol in $\text{THF}:\textit{n}\text{-Bu}_2\text{O}$ 0.5 M) were added and the reaction was immediately monitored by IR. When no increase of the conversion was observed the reaction was cooled down to room temperature and checked by ^1H NMR and ^{19}F NMR. The polymer was then filtered, washed with THF (5 x 5.0 mL), air dried and stored for further use. Compound **5** was obtained as described above.

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Keywords: supported catalysts • polynorbornene • palladium carbenes • cross coupling •

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- [21] A parallel set of experiments was performed by carrying out the reaction in a conventional Schlenk flask and determining the conversion and crude yields by ^{19}F NMR at the same reaction times as those collected in Table 2. The results obtained reproduced those in Table 2 (see Supporting Information).
- [22] The loss of palladium in the first run was higher (3.2 %), probably because in the reaction conditions some starting palladium complex in the synthesis of **4d** or other weakly supported species were removed.
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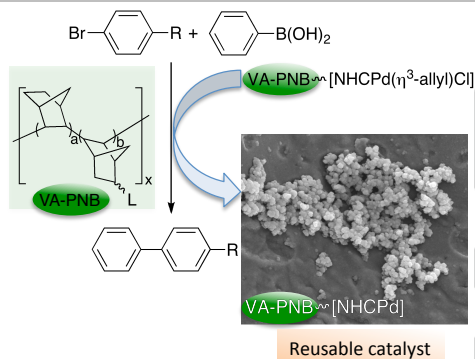
Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

A small dose of palladium

released from a Pd-loaded vinylic addition polynorbornene (VA-PNB) is enough to catalyze a Suzuki or a Negishi reaction in a homogeneous way; the polymer contains Pd aggregates formed when a VA-PNB supported NHC palladium complex is used as precatalyst and it is reusable.



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