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α-Diimine-Palladium Complexes Incorporated in Vinylic Addition Polynorbornenes: Synthesis and Catalytic Activity

Jesús A. Molina de la Torre,[a] and Ana C. Albéniz*[a]

Abstract: α-Diimine polymeric ligands have been synthesized using the bicyclic norbornane structure, present in vinylic addition polynorbornene (VA-PNB). The VA-PNB-diimine ligands have been prepared by functionalization of the copolymer obtained by the Ni-catalyzed polymerization of norbornene and norbornenylcarbonate. Immobilized palladium complexes of the type VA-PNB-diimine-PdX$_2$ have been prepared and their catalytic activity tested. The trifluoroacetato complex (X = CF$_3$COO) can be used as a recyclable precatalyst in the Suzuki reaction. It is the source of minute amounts of homogeneous palladium active species that carry out the catalysis with high turnover numbers. The recovered polymeric complex can be reused several times with no significant loss of activity. The polymeric analogue to Brookhart´s catalyst, VA-PNB-diimine-PdMeCl, can also polymerize ethylene, although it is less active than their monomeric counterparts.

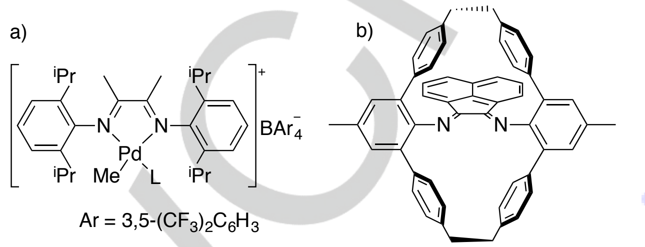

Figure 1: a) An example of Brookhart's type catalyst. b) Cyclophane-based diimine.

Introduction

α-Diimines (or 1,4-diazadienes) are a particular class of Schiff base ligands that have been used for a long time. They experienced a surge in the 90s when Brookhart and coworkers discovered that cationic diimine complexes of nickel or palladium with bulky non-coordinating anions are excellent catalysts for olefin polymerization.[1] The use of late transition metals with α-diimine ligands (Figure 1a) allowed the synthesis of highly branched low density polyethylene or other poly(α-olefins), thus expanding the type of microstructure and properties of polyethylene that can be obtained by metal-catalyzed polymerization. Mechanistic studies to have a better knowledge of the reaction pathway were carried out and new types of catalysts were tested soon after.[2] These studies showed that bulky diimine substituents are crucial to ensure polymer formation. Palladium and nickel diimine complexes were also tested in the insertion copolymerization of ethylene with polar olefins, such as acrylates or vinyl acetate. These late transition metals are less oxophilic than traditional metallocene-type catalysts formed with early transition metals, and therefore less susceptible to poisoning with most polar olefins. However, complete control of the incorporation of both polar and non-polar monomers remains a challenge. Brookhart's catalysts that are very active in the polymerization of ethylene usually give copolymers of ethylene and polar olefins with low yields and low incorporation of the polar monomer (around 10%). Interestingly, the modification of the diimine ligand architecture has proved to be a useful approach for improvement,[3] and, for example, the use of cyclophane-based Pd(II) diimine catalysts increases the amount of polar monomer in the final copolymer (Figure 1b).[4]

In the last years, we have been using vinylic addition polynorbornenes (VA-PNBs, Figure 2, a) as supports of catalysts or reagents in several organocatalytic,[5] and palladium-catalyzed processes.[6,7] In contrast to the materials resulting from ring opening metathesis polymerization of norbornene (ROMP-PNB, Figure 2, b),[8] these VA-PNB materials have an aliphatic backbone that keeps the bicyclic structure of norbornene. This cyclic structure is ideal to accommodate a diimine fragment, as has been shown for comparable [2.2.1] bicyclic molecules such as norbornane,[9] or camphor,[10,11] and we decided to incorporate this ligand in the structure of VA-PNBs as shown in Figure 2 (c). With this approach, we reasoned that if the steric hindrance of the polymeric structure is to have an influence on the ligand, and as a result in the behavior of the catalysts derived from it, this would be larger than that of a pendant ligand bound to the polymer skeleton with a tether.

Immobilization of diimine ligands on solid supports has been tried a few times in the context of developing catalysts for olefin polymerization. Most cases show diimines attached to inorganic solid supports such as SiO$_2$,[12] MgCl$_2$[13] or clays like montmorillonite.[14] Activated multiwalled carbon nanotubes (MWNTs) have also been used to support diimines covalently forming palladium and nickel complexes tested in olefin polymerization.[15] In the case of polymer-supported diimines fewer examples can be found and most of them involve Merrifield type resins.[12b,d,16] Jin and Zhang described nickel-diimine catalysts with pendant allyl groups that, when reacted with ethylene, were incorporated in the polyethylene chain (self-supported).[17]

Although olefin polymerization has been their most remarkable application, palladium-diimine complexes are also useful catalysts in different C-C cross-coupling reactions such as the Heck reaction,[18] Kumada, Negishi or Stille reactions,[19] the Suzuki reaction,[20] as well as carbonylation processes.[21]

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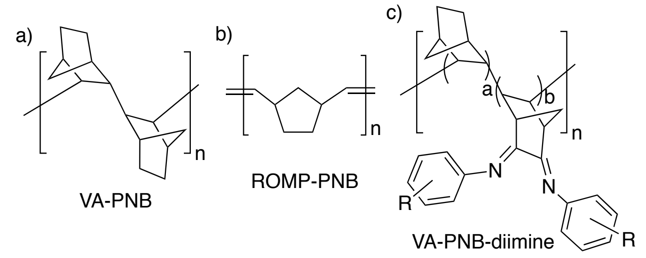
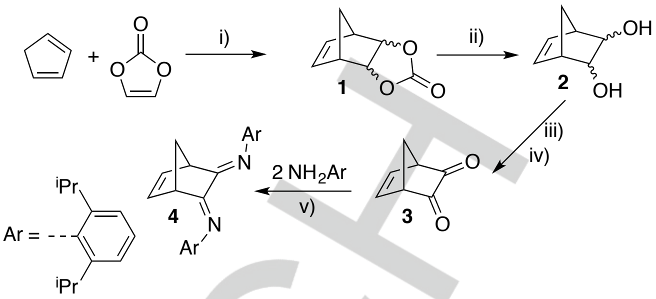


Figure 2: a) Vinylic addition polynorbornene (VA-PNB); b) Ring opening metathesis polynorbornene (ROMP-PNB); c) VA-PNB incorporated α-diimine.



Scheme 1. Synthetic route to diimine **4**. Reaction conditions and reagents: i) Toluene, 180 ˚C, 20 h; ii) NaOH (aq); iii) $(CF_3CO)_2O$, DMSO, –78 ˚C, 2 h; iv) NEt_3, –78 ˚C to room temperature; v) MeOH/HCOOH.

Both the ability of this type of ligand to support palladium in different oxidation states and its utility in coupling reactions has been demonstrated.[22] However, the effort to develop supported catalysts that can be recycled,[23] has not been extended to diimine palladium complexes and only a report of a silica-anchored catalyst of this type in the Suzuki reaction has been disclosed. The catalyst can be reused four times before undergoing an important loss of activity.[24]

Thus, encouraged by the stability that the aliphatic and robust backbone of VA-PNB has shown in former catalytic applications,[5-7] and its suitable bicyclic structure to support a chelating diimine fragment, we report here on the preparation of such VA-PNB-diimine ligand (Figure 2, c) and the performance of the palladium complexes derived from it as catalyst in the polymerization of olefins and as recyclable catalyst in Suzuki couplings.

Results and Discussion

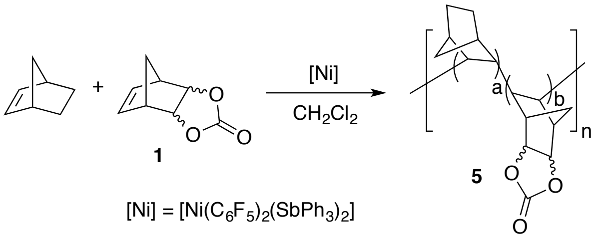
Synthesis of the vinylic addition polynorbornene precursors. In order to obtain diimine VA-PNBs of the type shown in Figure 2c, it is necessary to copolymerize norbornene with a substituted norbornene that, once incorporated in the polymer, can be transformed easily into the diimine ligand. In contrast to ROMP, the vinylic addition polymerization of functionalized norbornenes is not straightforward. Many catalysts which are useful in the VA polymerization of norbornene, shown a dramatic decrease of activity when substituted norbornenes are used, and this is especially serious for polar O- or N-containing substituents. Our group has obtained good results in the polymerization of bromoalkyl or bromoaryl substituted norbornenes,[25] as well as stannylated norbornenes,[7a] using $[Ni(C_6F_5)_2(SbPh_3)_2]$ as catalyst. Thus, we decided to test this complex in the polymerization of a series of substituted norbornenes that could be intermediates in the synthesis of the norbornane-diimine fragment.

Norbornene derivatives **1**-**4** were synthesized as shown in Scheme 1. No examples of norbornene bearing diimines can be found in the literature, and we followed the method reported by Kobayashi et al. for the synthesis of **3**.[26] The first step is a Diels-Alder reaction of cyclopentadiene and vinylene carbonate,[27] which gives **1** in high yield as a mixture of isomers endo:exo = 97:3. Subsequent hydrolysis and a Swern oxidation of the diol **2**, afforded the diketone **3**. This is a viable route to the diimine since condensation of **3** with 2,4-diisopropylaniline in a mixture of methanol and formic acid led to **4**,[2b] albeit in a low yield due to the high solubility of the diimine. Once the precursors of the diimine were synthesized we studied which one showed the best results in the copolymerization with norbornene. The diimine **4** was not tested because it is a good ligand for Ni, capable of substituting $SbPh_3$ in the polymerization catalyst $[Ni(C_6F_5)_2(SbPh_3)_2]$. Complexes $[Ni(C_6F_5)_2L_2]$ show very low activity in the polymerization of norbornene when L has a higher coordinating ability that $SbPh_3$.[28]

Copolymerization experiments of norbornene with carbonate **1** were initially conducted using a 1:1 ratio of monomers in CH_2Cl_2 in the presence of 1% mol of the Ni-catalyst (Scheme 2). The mixture was stirred for 24 h at room temperature and copolymer **5** (VA-PNB-NBCO$_3$) was obtained as a white powder after precipitation in MeOH. Copolymerization reactions with the diol **2** or the diketone **3** were carried out in the same way to form copolymers **6** and **7** respectively (Table 1, entries 1-3). Only **1** afforded a copolymer in moderate yield for the copolymerization reaction (Table 1, entry 1). Polymer **5** was soluble and its composition could be determined by ^{1}H NMR by comparison of the integrals of the protons bound to C^2 and C^3 of the carbonate and the broad signal associated to the aliphatic protons, showing a ratio NB/**1** (a/b) = 16.8. The infrared spectrum of the polymer showed a strong band corresponding to the ν(C=O st) IR absorption at 1809 cm^{-1}, typical of carbonates.

The copolymerization of monomers **2** and **3** yielded poorly (Table 1, entries 2 and 3). Both polymers were insoluble and their composition could not be determined. IR spectra showed a broad band at 3400 cm^{-1} characteristic of ν(O-H st) for **6** and a weak band at 1746 cm^{-1} ν(C=O st) for **7**, characteristic of a carbonyl moiety. According to these results the synthesis of the diimine polymer needs to be carried out from polymer **5** by postpolymerization functionalization.

The composition of polymer **5** obtained as shown in Table 1, entry 1, indicates that the reactivity of norbornene is much higher than that of monomer **1** (cf. a/b = 16.8 vs. NB:**1** = 1:1 in the monomer feed). In fact, the homopolymerization of **1** does not occur as shown by ^{1}H NMR monitorization of the reaction of **1** and the catalyst $[Ni(C_6F_5)_2(SbPh_3)_2]$ in $CDCl_3$ for 72 hours. This is not unexpected considering the low reactivity of O-substituted norbornenes and the fact that this catalyst proved to be useless before in the polymerization of other O-functionalized



Scheme 2. Copolymerization reaction of **1** and norbornene.

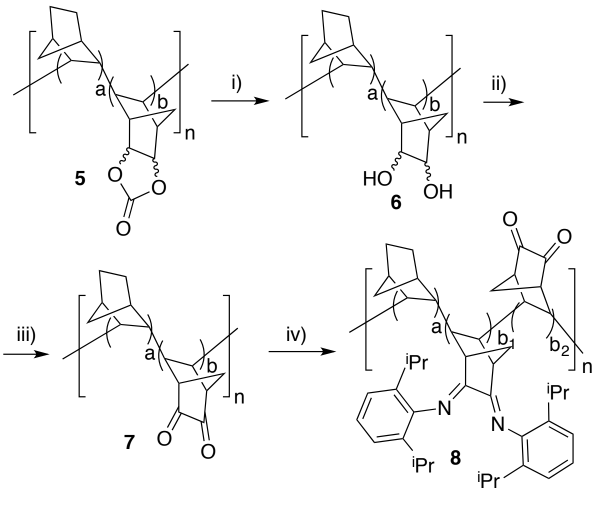
Table 1. Copolymerization of norbornene (NB) with O-functionalized norbornenes (NBO), precursors of the diimine.[a]

Entry	NBO	NB:NBO:[Ni]	Polymer (Yield, %)[b]	Composition, a/b[c]
1[d]	**1**	50:50:1	**5** (54)	16.8
2[d]	**2**	50:50:1	**6** (8)	-
3[d]	**3**	50:50:1	**7** (17)	-
4[d]	**1**	100:100:1	**5** (30)	25.2
5[d]	**1**	1000:1000:1	**5** (1.5)	58.2
6[e]	**1**	50:50:1	**5** (44)	4.8
7[e]	**1**	100:50:1	**5** (73)	5.7
8[e]	**1**	150:50:1	**5** (67)	10
9[f]	**1**	150:50:1	**5** (38)	6.4

a) Reactions performed under nitrogen atmosphere, in CH_2Cl_2 at 25 ˚C for 24 h. b) Yields are referred to the total monomer mass. c) Ratio of monomers in the copolymer (a/b = NB/NBO) determined by ^{1}H-NMR. d) [Ni(C_6F_5)$_2$($SbPh_3$)$_2$] was added to a solution of both monomers in CH_2Cl_2. e) Norbornene (5.9 M in CH_2Cl_2) was added dropwise to a mixture of **1** and the catalyst for 1 h. f) Norbornene (2.7 M in CH_2Cl_2) was added dropwise to a mixture of **1** and the catalyst for 3 h.

norbornenes like 5-norbornene-2-carboxaldehyde.[28] However, unlike **1**, the coordinating ability of the oxygen in that monomer is strong enough to avoid copolymerization with norbornene. In order to reach better yields and higher incorporation of the functionalized monomer, additional polymerization reactions were performed in different conditions. The results show that the catalyst loading affects not only the yields but also the incorporation of the carbonate monomer. The lower the amount of catalyst, the lower the presence of **1** in the copolymer (Table 1, entries 1, 4 and 5). Since no homopolymerization of **1** was observed, we decided to test the slow addition of the more reactive norbornene to a solution of **1** and [Ni(C_6F_5)$_2$($SbPh_3$)$_2$] in CH_2Cl_2 in order to increase the incorporation of the carbonate in polymer **5**. As can be seen in Table 1, when norbornene was slowly added over a period of 1 hour, this protocol leads to a higher amount of carbonate in the copolymer, although a small reduction of yield is also observed (Table 1, entries 1 and 6).[29] We studied the influence of the monomer feed ratio when using this methodology (Table 1, entries 6-8). The best balance between yield and functionalization was obtained when the monomer ratio was NB:**1** = 2:1 and this mixture allowed us to obtain a polymer with moderate incorporation of the carbonate monomer and good yield (Table 1, entry 7). A slower addition of norbornene (3 hours) led to a higher incorporation of **1** but to a significant decrease of the yield (Table 1, entry 8). While studying the ^{1}H-NMR spectra of polymer **5** we observed in some experiments the presence of a small olefinic signal at 5.7 ppm, specially in those polymers synthesized with slow addition of norbornene. This olefinic signal is not a product of the ring opening polymerization of norbornene (signals around 5.3-5.2 ppm) and it is not observed in other vinylic addition copolymers of norbornene. We are currently studying the origin of this unsaturation in the polymer structure. Hydrogenation of the polymer with p-toluenesulfonylhydrazide led to its total disappearance without modification of the carbonate moiety (see supporting information), and this procedure, if needed, ensures the presence of an aliphatic backbone in **5**, with the carbonate group as the only reactive moiety.

Functionalization of VA-PNB-NBCO$_3$ (5) to synthesize a VA-PNB supported diimine. We chose as starting material for the synthesis of the VA-PNB-diimine, polymer **5** of composition a/b = 5.7, synthesized according to entry 7 (Table 1). It has a molecular weight $M_w = 3.19 \times 10^4$ and a moderate polydispersity (M_w/M_n = 1.75). The polymer shows a strong ν(C=O st) IR absorption band at 1809 cm^{-1} as well as characteristic signals in solid state ^{13}C CP-MAS NMR at 161 and 85 ppm corresponding to C^8 (carbonate) and C^2 and C^3 respectively. The synthetic route followed to the diimine polymer was analogous to that used with the monomeric compounds and it is shown in Scheme 3. Hydrolysis of **5** was carried out using a solution of NaOH in a mixture H_2O:MeOH to facilitate the contact between the polymer and the base. Although the polymer remained undissolved in that mixture it got completely soaked and the reaction goes to completion. The resulting polymer VA-PNBNB(OH)$_2$ (**6**) is insoluble but can be characterized by IR spectroscopy and solid state NMR. The ν(C=O st) band at 1809 cm^{-1} typical of carbonates, visible in **5**, disappears completely and a new broad signal ν(O-H st) at 3405 cm^{-1} appears. ^{13}C CP-MAS NMR of **6** shows a signal at 76 ppm associated with the carbon atoms

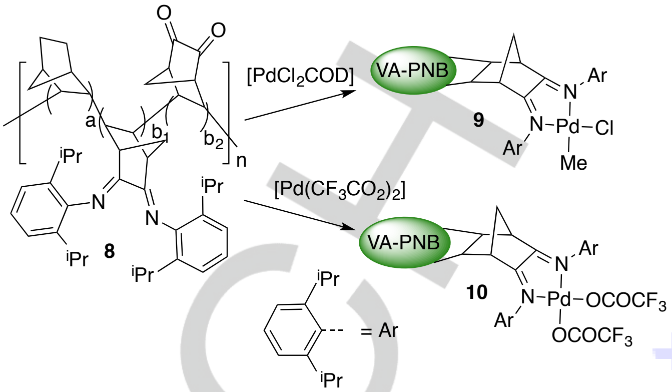


Scheme 3. Synthesis of polymer **8**. Reaction conditions: i) NaOH (aq)/MeOH; ii) $(CF_3CO)_2O$, DMSO, –78 ˚C, 2 h; iii) NEt_3, –78 ˚C to room temperature; iv) 2,6-diiopropylaniline (neat), MW, 200 ˚C, 4 h. MeOH/HCOOH.

bound to the hydroxyl groups (C^2 and C^3) and there are no traces of those signals observed in **5** at 161 and 85 ppm, characteristic of the carbonate group. Swern oxidation of **6** was performed in the same conditions used for diol **2**. The infrared spectrum of the resulting **7** shows a strong absorption at 1755 cm^{-1} corresponding to the ketone moiety ν(C=O st). In this case the solid state ^{13}C CP-MAS NMR spectrum shows no signal around 200 ppm in the ketone region, but the diol signal at 76 ppm has disappeared. The final step in the synthesis of the VA-PNB incorporated diimine is the condensation of **7** with 2,6-diisopropylaniline. Unlike the former steps, when this reaction was attempted in similar conditions to those described in the synthesis of **4**, only a small amount of imine was formed. We tried different methods and reaction conditions and the best results were obtained when polymer **7** was heated in neat aniline at 200 ºC for 4 hours in a microwave oven (Scheme 3). The resulting polymer **8** (VA-CopNBNB(C=N-Ar)$_2$) was soluble in chlorinated solvents and the amount of diimine formed could be determined by ^1H NMR, by comparing the integral of the aromatic protons to the broad signal that comprehends all the backbone protons. 46% of aniline was incorporated into the polymer ($a:b_1:b_2$ = 5.7:0.46:0.54, Scheme 3), giving a diimine content of 0.570 mmol per gram of polymer. The IR spectrum of **8** still shows a signal at 1755 cm^{-1} ν(C=O st) with lower intensity than in **7**, along with a new signal at 1677 cm^{-1} corresponding to the ν(C=N st). The ^{13}C CP-MAS NMR spectrum shows a signal at 175 ppm for the imine carbons as well as signals between 157-124 ppm associated with the aromatic carbons and at 30 ppm typical of the methyl groups of the aryl substituents.

Use of VA-PNB-NB(C=N-Ar)$_2$ as ligand in olefin polymerization. Substitution of cyclooctadiene in [PdMeCl(COD)] led to [{VA-PNB-NB(C=N-Ar)$_2$}PdClMe]) (**9**), a precursor of a cationic methylpalladium complex similar to those used by Brookhart et al. in olefin polymerization (Scheme 4). Polymer **9** has a palladium content of 8.1 mg Pd/ g polymer, 15% of the maximum Pd-content if complete coordination to the diimine fragment had occurred. Due to the small amount of palladium incorporated in **9**, clear differences can be seen neither in the IR spectrum nor in the NMR spectra when comparing **9** and **8**.

Polymer **9** was used as a precatalyst in the polymerization of ethylene in a similar way to that described by Brookhart et al.[1a] We generated the cationic complex *in situ* by treating the palladium complex with the sodium salt of the bulky-non coordinating anion $[B[3,5\text{-}(CF_3)_2C_6H_3]_4]^-$ (BARF). The results show that the supported complex **9** is a less active catalyst (about 10.9 g/ mmol Pd) than the analogous monomeric catalysts (about 450 g/mmol Pd).[1a] The polyethylene obtained has a similar structure to those obtained with Brookhart's catalysts. It has a high molecular weight (M_w = 2.97 x 10^4) and a polydispersity of 2.4. Analysis of its ^1H-NMR spectrum shows that it is a highly branched polyethylene, with 91 branches per 1000 carbon atoms (see Figure S1, supporting information).[2d] After the polymerization reaction, the separation of the supported catalyst can be carried out removing the solvent and washing the resulting solid with pentane. In this solvent, **9** is insoluble and can be easily separated by filtration whereas polyethylene is soluble and can be collected after removing the filtrate. The recovered catalyst was reused in an ethylene polymerization reaction under the same conditions. A polymer with a similar size and structure was obtained but the activity of the catalyst was clearly lower (3.5 g/ mmol Pd).



Scheme 4. Synthesis of VA-PNB-diimine supported palladium complexes.

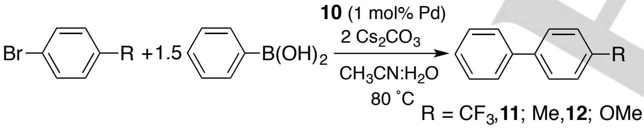
We also tested the copolymerization of ethylene and methyl acrylate (MA), a combination of interest that has been shown to benefit, as far as higher incorporation of polar monomer in the copolymer is concerned, from bulky axial diimine ligands.[4] This experiment could assess the influence of the polymeric backbone on the steric features of the diimine fragment. A copolymerization of ethylene (6 atm) and MA (molar ratio MA:Pd = 5800:1) was carried out and we found that two different polymerizations were taking place. A polyethylene with no MA was obtained (1.75 g/ mmol Pd) as well as a copolymer MA-ethylene with a low content of polyethylene (75% mol MA, 1.31 g/ mmol Pd), and the yield of both processes was very low. The high amount of MA in the copolymer suggests a radical polymerization mechanism, which can be initiated by palladium complexes.[30] Thus, either monomer polymerizes by its preferred mechanism and no control of the copolymerization process can be achieved.

The polymerization results show that the palladium coordination sphere attained using polymer **8** as a ligand is analogous to that in monomeric molecular catalysts, as shown by the similar size and structure of the polyethylene obtained. Unfortunately, the polymer backbone does not introduce any advantageous steric feature useful in non-polar/polar olefin copolymerization processes.

Use of VA-PNB-NB(C=N-Ar)$_2$ as ligand in the Suzuki reaction The ability of polymer **8** to anchor palladium complexes useful as catalysts in C-C coupling reactions was tested using the Suzuki reaction. A new polymeric palladium complex [{VA-PNB-NB(C=N-Ar)$_2$}Pd(OOCCF$_3$)$_2$] (**10**), was synthesized by reaction of Pd(OOCCF$_3$)$_2$ with **8** (Scheme 4). The palladium loading in **10** was 29.6 mg Pd/ g polymer, 58% yield considering the maximum possible content that could be introduced. Trifluoromethylacetate, instead of the most common acetate, was chosen because the characteristic signals of the CF_3 moieties in infrared spectroscopy and ^{19}F NMR would allow us an easier characterization of the polymer. Polymer **10** is insoluble in common solvents. Its IR spectrum shows two bands at 1182 and 1146 cm^{-1} characteristic of the trifluoromethyl group. Furthermore, the band at 1677 cm^{-1}, corresponding to the ν(C=N st) in **8**, is partially overlapped by another band at 1686 cm^{-1}, associated with the ν(CO_2 asym) absorption of the acetate. This ν(CO_2 asym) resonance has a high value, higher than the parent palladium trifluoroacetate, which is consistent with a monodentate coordination fashion.[31] ^{19}F MAS NMR shows a signal at -73 ppm slightly shifted from the signal of the starting complex $Pd(CF_3CO_2)_2$ (-76 ppm). The ^{13}C CP MAS NMR spectrum shows new signals at 167 ppm, corresponding to the carbon in the carboxylate group, and a quartet for the CF_3 with an average chemical shift of 120 ppm and a coupling constant $^1J_{C\text{-}F}$ = 280 Hz.

The catalytic activity of polymer **10** was tested using the reaction of 4-bromobenzotrifluoride and phenylboronic acid as a model one. This reaction, shown in Equation 1 (R = CF_3), was complete in 15 min (Table 2, entry 1). Polymer **10** was also used with other para-substituted aryl bromides such as 4-bromotoluene or 4-bromoanisole. These haloarenes, less activated towards oxidative addition to Pd(0), required longer times but high yields were also obtained (Table 2, entries 6, 7).

In order to evaluate the performance of the catalyst and its recyclability the reaction in Eq. 1 (R = CF_3) was monitored by *in situ* infrared spectroscopy. The ν(C-Br) IR absorption band at 1012 cm^{-1} of 4-bromobenzotrifluoride was not overlapped with the bands of the solvent or other reagents and its intensity variation was recorded with time, indicating the progress of the reaction (Figure S2, supporting information). When no variation of the band was observed for several minutes the heating was stopped and, after cooling, the yield was determined by ^{19}F NMR spectroscopy. The same procedure was applied in the four recycling experiments collected in Table 2 (entries 2-5).



(1)

Table 2. Suzuki reactions catalyzed by **10**.[a]

Entry	ArBr	Cycle	Time (min)	Crude yield (%)
1	*p*-CF_3-C_6H_4Br	1	15	**11** (97)[b]
2	*p*-CF_3-C_6H_4Br	2	20	**11** (98)[b]
3	*p*-CF_3-C_6H_4Br	3	25	**11** (96)[b]
4	*p*-CF_3-C_6H_4Br	4	30	**11** (98)[b]
5	*p*-CF_3-C_6H_4Br	5	30	**11** (99)[b]
6	*p*-Me-C_6H_4Br	1	60	**12** (95)[c]
7	*p*-OMe-C_6H_4Br	1	120	**13** (91)[c]

[a] Reaction conditions shown in Eq. 1. [b] Crude yields determined by ^{19}F NMR. [c] Crude yields determined by ^1H NMR.

The activity of polymer **10** decreases in the two first recycling experiments (Table 2, entries 2, 3), as there is an increase of the reaction times. However the reaction time stays almost constant (around 30 min) from the fourth use on, reaching high yields in every case (Table 2, entries 4, 5). Leaching measurements showed that some palladium is being released to the solution. In the first run 4.3 % of the initial amount of the palladium added as supported catalyst was leached, as determined by ICP-MS, but in the next runs leaching was around 0.4-0.2 %. The higher value in the first use indicates that it is possible that some of the palladium trifluoroacetate precursor used in the synthesis of **10** is trapped in the polymer backbone, not coordinated to the diimine moiety, and gets released in the first catalytic use. Although a transformation of the nature of the palladium diimine complex on the polymer after the first reaction is possible, we do not observe important changes in the SEM images of the polymer before or after the catalytic use (see Figure S3, supporting information). We have reported before the behavior of polymeric complexes where palladium is coordinated to VA-PNB-N-heterocyclic carbenes; in that case the nature of the palladium moiety changes dramatically after the first Suzuki reaction and palladium aggregates can be clearly seen by electron microscopy. In contrast to the system described here, the activity of those polymers steadily decreases in every run.[6]

In order to determine if the actual active catalytic species was acting homogenous or heterogeneously, we performed a hot filtration test in the sixth reuse cycle of the catalyst in the Suzuki reaction with 4-bromobenzotrifluoride. After running the reaction at 80 ºC for 20 minutes, the hot mixture was filtered. ^{19}F NMR spectrum at that point showed an 80% yield. When the filtrate was allowed to react other 30 minutes at 80 ˚C the yield increased to 99%. This points to a soluble palladium species as the active catalyst and, as a result, a homogeneous catalytic system where the polymer is acting as a reservoir of a small amount of palladium. The determination of the amount of palladium in solution in this experiment by ICP-MS showed that 0.26% of the initial amount added is leached, similar to the other recycling experiments. Thus, the amount of catalyst bringing about the reaction is equivalent to a 0.0026% molar amount of added catalyst (26 mol ppm) and a TON in the reaction close to $4x10^4$ in each cycle (TOF close to $5x10^4$ TONs/h). Considering the catalyst can be reused with little or no loss of activity after the third cycle, the cumulative TON can reach very high values and makes polymer **10** a useful catalyst precursor playing the role of a source of very active species in solution.

Conclusions

Vinylic addition polynorbornenes provide a suitable backbone to introduce a diimine fragment, leading to polymeric diimine ligands that can be coordinated to palladium. The polymer backbone does not introduce any remarkable steric feature that can be of use in the Pd-catalyzed polymerization of ethylene or copolymerization of this olefin with polar alkenes. However, it is a good support of palladium complexes that have proved to be excellent catalyst precursors in cross coupling reactions. The actual catalysis is homogeneous and the Pd-loaded polymer is a source of a very small amount of palladium active species in solution (about 25 mol ppm of Pd; TOF close to 5x10^4 TONs/h). The polymer precatalyst can be reused without significant loss of activity, so the number of cumulative TONs is very high.

A homogeneous catalysis by metal leaching is a common scenario when using supported palladium catalysts, probably more common than previously anticipated.[23c, 32] It is very important to evaluate this point, but it does not make the metal-loaded materials useless. On the contrary if, as it is the case of the example described here, the dosage of soluble palladium species remains very small, steady, and active upon reuse, the supported precatalyst is a convenient, easy to use source of catalyst. It becomes equivalent to use extremely active homogeneous palladium species each time, without the need of precise quantity measurement, and comparing well as far as TONs reached.

Experimental Section

General Methods

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded using Bruker AV-400 and Agilent MR-500 instruments. Chemical shifts (δ) are reported in ppm and referenced to $SiMe_4$ (^{1}H, ^{13}C) or $CFCl^3$ (^{19}F). 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-d$_6$ 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 4mm diameter zirconia rotors spinning at 8 kHz. ^{13}C CP MAS NMR spectra were measured at 100.61 MHz and recorded with proton decoupling (tppm), with a 90º pulse length of 4.5 μs and a contact time of 3 ms and recycle delay of 3 s. The ^{13}C NMR spectra were referred to glycine (CO signal at 176.1 ppm). ^{19}F MAS NMR spectra were recorded at 376.5 MHz with a 90º pulse length of 5.5 μs. ^{19}F NMR chemical shifts are in ppm relative to external $CFCl_3$. IR spectra were recorded on a Perkin-Elmer FT/IR SPECTRUM FRONTIER spectrophotometer with CsI + ATR diamond accessory. The palladium content of the polymers and leaching measurements were determined by ICP–MS, using Agilent 7500i equipment; the samples were dissolved in HNO_3 (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. Size exclusion chromatography (SEC) was carried out using a Waters SEC system on a three-column bed (Styragel 7.8x300 mm columns: 50-10^5, 5x10^3-5x10^5 and 2x10^3-4x10^6 Da) and a Waters 410 differential refractometer. SEC samples were run in $CHCl_3$ at 313 K and calibrated to polystyrene standards. Controlled addition of norbornene in the copolymerization reaction was done with a Thermo Scientific Orion M365 Sage Syringe Pump. 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. $[Ni(C_6F_5)_2(SbPh_3)_2]$, [PdMeCl(COD)],[33] $[Pd(CF_3CO_2)_2]$[34] and $NB(C{=}O)_2$ (**3**)[26] were prepared according to the literature procedures. Compounds **1** and **2** have been prepared with slight modifications of the procedure described by Neumman et at.[27,35]

Synthesis of norbornene-diimine precursors.

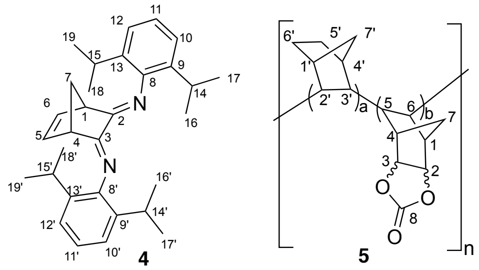
Synthesis of NBCO$_3$ (1). A Schlenk flask with J Young Teflon tap was charged with vinylene carbonate (25 g, 290.5 mmol), dicyclopentadiene (6.401 g, 48.42 mmol), hydroquinone (0.01 g, 0.0908 mmol) and toluene (8.0 mL). The reaction was heated at 180 ºC for 20 hours. After removing the volatiles under vacuum at 65 ºC a pale brown solid was obtained (the excess of dienophile can be recovered from the volatiles in this step). The solid was dissolved in CH_2Cl_2 (15 mL) and crystallized with cold hexane (60 mL). Then it was filtered, washed with cold hexane (3 x 10 mL) and air dried. The product was obtained as a pale yellow solid (13.43 g, 91% yield). It is a mixture of isomers endo:exo = 97.6:2.4. **1** *endo*: ^{1}H NMR (300.13 MHz, δ, $CDCl_3$): 6.21 (m, 2H, H^5, H^6), 4.98 (m, 2H, H^2, H^3), 3.27 (m, 2H, H^1, H^4), 1.75 (d, J = 10.4 Hz, 1H, H^7), 1.26 (d, J = 10.4 Hz, 1H, $H^{7'}$). $^{13}C\{^1H\}$ NMR (75.4 MHz, δ, $CDCl_3$): 155.59 (s, C^8), 134.35 (s, C^5 C^6), 78.96 (s, C^2, C^3), 45.57 (s, C^1, C^4), 42.55 (s, C^7). **1** *exo*: ^{1}H NMR (300.13 MHz, δ, $CDCl_3$): 6.1 (m, 2H, H^5, H^6), 4.55 (m, 2H, H^2, H^3), 3.13 (m, 2H, H^1, H^4), 1.84 (m, 1H, H^7), 1.7 (m, 1H, $H^{7'}$). $^{13}C\{^1H\}$ NMR (75.4 MHz, δ, $CDCl_3$): 155.59 (s, C^8), 135.95 (s, C^5, C^6), 78.81 (s, C^2, C^3), 45.57 (s, C^1, C^4), 40.94 (s, C^7). MS (EI) m/z (relative intensity): 152 (0.5) [M]+, 107 (2), 79 (34), 77 (24), 66 (100), 65 (13).

Synthesis of NB(OH)$_2$ (2). **1** (3.650 g, 24 mmol) was dissolved in a solution of NaOH in H_2O (1.0 M, 50 mL, 50 mmol). The mixture was stirred at room temperature for 5 hours and the product was extracted with Et_2O (5 x 15 mL). The organic phase was washed with saturated $NaHCO_3$ aqueous solution (20 mL), water (20 mL) and dried over $MgSO_4$ The solvent was removed and the product was obtained as a white solid. (2.658 g, 88% yield). **2** was obtained as a mixture of isomers in a ratio endo:exo = 97.6:2.4 that parallel the starting material (**1**). **2** *endo*: ^{1}H NMR (400.13 MHz, δ, $CDCl_3$): 6.26 (m, 2H, H^5, H^6), 4.18 (m, 2H, H^2, H^3), 3.02 (m, 2H, H^1, H^4), 2.25 (br, 2H, -O*H*), 1.51 (d, J = 9.7 Hz, 1H, H^7), 1.22 (d, J = 9.7 Hz, 1H, $H^{7'}$). $^{13}C\{^1H\}$ NMR (100.6 MHz, δ, $CDCl_3$): 135.04 (s, C^5, C^6), 70.92 (s, C^2, C^3), 47.59 (s, C^1, C^4), 41.81 (s, C^7). **2** *exo*: ^{1}H NMR (400.13 MHz, δ, $CDCl_3$): 6.04 (m, 2H, H^5, H^6), 3.71 (m, 2H, H^2, H^3), 2.7 (m, 2H, H^1, H^4), 2.25 (br, 2H, -O*H*), 1.89 (d, J = 9.2 Hz, 1H, H^7), 1.62 (d, J = 9.2 Hz, 1H, $H^{7'}$). $^{13}C\{^1H\}$ NMR (100.6 MHz, δ, $CDCl_3$): 136.29 (s, C^5, C^6), 68.80 (s, C^2, C^3), 47.85 (s, C^1, C^4), 42.11 (s, C^7). MS (EI) m/z (relative intensity): 126 (0.6) M]+, 116 (100), 101 (25), 79 (8), 77 (8), 67 (50), 66 (76), 60 (29).

Synthesis of NB(C=N-Ar)$_2$, Ar = 2,6-diisopropylphenyl (4). Diketone **3** (0.2853 g, 2.336 mmol) and 2,6-diisopropylaniline (0.8283 g, 4.672 mmol) were dissolved in a mixture of MeOH (2.5 mL) and formic acid (0.25 mL). The mixture was stirred at room temperature for 24 hours. Volatiles were removed and MeOH (1.0 mL) was added and cooled to -78 ºC. The solid formed was filtered and air dried. (0.1164 g, 11% yield). ^{1}H NMR (400.13 MHz, δ, $CDCl_3$): 7.19-7.07 (m, 6H, H^{10}-H^{12}, $H^{10'}$-$H^{12'}$), 6.36 (m, 2H, H^5, H^6), 3.27 (m, 2H, H^1, H^4), 2.95 (qq, J = 6.8 Hz, 2H, H^{14}, $H^{14'}$), 2.70 (spt, J = 6.8 Hz, 2H, H^{15}, $H^{15'}$), 2.32 (d, J = 9.6 Hz, 1H, H^7), 1.97 (d, J = 9.6 Hz, 1H, $H^{7'}$), 1.23, 1.22, 1.19, 1.15 (four d, J = 6.8 Hz, 24H, H^{16}-H^{19}, $H^{16'}$-$H^{19'}$). $^{13}C\{^1H\}$ NMR (100.6 MHz, δ, $CDCl_3$): 168.27 (s, C^2, C^3), 146.13 (s, C^8, $C^{8'}$), 137.44 (s, C^5, C^6), 136.70, 136.53 (2 s, C^9, $C^{9'}$, C^{13}, $C^{13'}$), 124.04, 122.82, 122.76 (three s, C^{10}- C^{12} $C^{10'}$-$C^{12'}$), 48.9 (s, C^7), 46.08 (s, C^1, C^4), 28.31, 27.91 (2 s, C^{14}, $C^{14'}$, C^{15}, $C^{15'}$), 23.78, 23.70, 23.46, 23.15 (4 s, C^{16}-C^{19}, $C^{16'}$-$C^{19'}$). MS (EI) m/z (relative intensity): 440 (1) [M]+, 397 (13), 253 (100), 238 (26), 207 (14), 188 (46), 186 (31), 157 (11), 146 (19), 130 (14), 117 (7), 91 (12), 66 (87).

Syntheses of functionalized VA-polynorbornenes.

Synthesis of copolymer VA-PNB-NBCO$_3$ (5). *Method A* (Table 1, entry 1): In a Schlenk flask under a nitrogen atmophere **1** (0.49 g, 3.22 mmol) and norbornene (0.85 mL, 3.80 M in CH_2Cl_2, 3.22 mmol) were dissolved in CH_2Cl_2 (5 mL). To this mixture, a solution of $[Ni(C_6F_5)_2(SbPh_3)_2]$ (0.0708 g, 0.0644 mmol) in CH_2Cl_2 (5 mL) was slowly added.



4 5

Figure 3. Examples of the numbering scheme for NB-derived compounds.

After stirring 24 h at room temperature the viscous solution was poured into MeOH (30 mL). The resulting polymer was filtered, washed with MeOH (5 x 5 mL) and air dried. The product was obtained as a white solid (0.4278 g, 54% yield). a/b = 16.8 (0.58 mmol $–CO_3$/g polymer).[36] Direct syntheses of copolymers **6** and **7** (Table 1) were carried out following this method. They are insoluble in common organic solvents.

Method B (Table 1, entry 7): To a solution of **1** (4 g, 26.29 mmol) in CH_2Cl_2 (20 mL) a mixture of $[Ni(C_6F_5)_2(SbPh_3)_2]$ (0.5778 g, 0.5258 mmol) and triphenylstibine (0.074 g, 0.2103 mmol) in CH_2Cl_2 (15 mL) was added. Then norbornene (5.89 M in CH_2Cl_2, 8.9 mL, 52.58 mmol) was added in a controlled flow of 0.15 mL / min for 1 h. The resulting reaction mixture was stirred at room temperature for 24 hours. After this time it was poured into MeOH (250 mL) where a solid appeared, which was filtered, washed with MeOH (5 x 20 mL) and air dried. The copolymer is a white powder. (6.491 g, 73% yield). a/b = 5.7 (1.45 mmol $–CO_3$/g polymer).[36]

5 (a/b = 5.7). M_w (Daltons) = 3.19 x 10^4. M_w /M_n = 1.7. IR (neat), cm^{-1}: 1809 ν(C=O st), 1127 ν(C-O st as), 1085 ν(C-O-C st as). ^1H NMR (500.15 MHz, δ, $CDCl_3$): 5.1-4.3 (br, 2H, H^2, H^3), 3-0.3 (br, 16H). ^{13}C NMR (125.72 MHz, δ, $CDCl_3$): 155 (br, C^8), 79 (br, C^2, C^3), 54-50 and 48-45 (br, C^5, C^6, $C^{2'}$, $C^{3'}$), 44-38 (br, C^1, $C^{1'}$, C^4, $C^{4'}$), 37-34 (br, C^7, $C^{7'}$), 33-28 (br, $C^{5'}$, $C^{6'}$).

Synthesis of VA-PNBNB(OH)$_2$ (6). Copolymer **5** (5.6 g, 8.174 mmol of carbonate) was dissolved in THF (120 mL). Tetrabutylammonium hydroxide (1 M solution in MeOH, 81.74 mL, 81.74 mmol) was added and the reaction was refluxed for 9 hours. After cooling to room temperature the mixture was poured into a mixture of MeOH:H_2O (1:1, v/v, 300 mL) and stirred overnight. The solid was filtered, washed with MeOH (5 x 20 mL) and dried in a vacuum oven at 35 ºC for 24 hours. The polymer is a white powder barely soluble in common solvents (5.255 g, 98% yield). IR (neat), cm^{-1}: 3240 ν(O-H st), 1110 and 1076 ν(C-O st). ^{13}C CP-MAS NMR (100.61 MHz): 74-65 (br, C^2, C^3), 63-18 (br, polyNB).

Synthesis of VA-PNBNB(C=O)$_2$ (7). A two-necked round-bottom flask under a nitrogen atmosphere was charged with copolymer **6** (5 g, 7.586 mmol diol), CH_2Cl_2 (200 mL) and cooled to -78 ºC. To another Schlenk flask containg a stirring mixture of dimethyl sulfoxide (7.112 g, 91.03 mmol) and CH_2Cl_2 (50 mL) at -78 ºC, was added trifluoroacetic anhydride (15.93 g, 75.86 mmol) dropwise. Ten minutes later this solution was added slowly via cannula to the polymer suspension at -78 ºC. After 4 hours triethylamine (15.35 g, 151.7 mmol) was added. The reaction was stirred for 3 hours and allowed to warm up to room temperature. CH_2Cl_2 was removed to about half the initial volume and the mixture was poured into MeOH:H_2O (3:1, v/v, 400 mL) and stirred overnight. The polymer was filtered, washed with a mixture of MeOH:H_2O (1:1, v/v, 5 x 20 mL), then MeOH (5 x 20 mL) and it was dried in a vacuum oven at 35 ºC for 24 hours. The polymer was obtained as a yellowish powder (4.440 g, 89% yield). IR (neat), cm^{-1}: 1755 ν(C=O st). ^{13}C CP-MAS NMR (100.61 MHz): 63-18 (br, polyNB).

Synthesis of VA-PNBNB(C=N-Ar)$_2$, Ar = 2,6-diisopropylphenyl (8). Copolymer **7** (1 g, 1.527 mmol diketone) and 2,6-diisopropylaniline (11.28 g, 63.62 mmol) were placed in a 30 mL microwave reaction vessel. The mixture was heated to 200 ºC and stirred for 4 hours in the microwave oven. The reaction mixture was then poured into MeOH (100 mL) and stirred for 3 hours at room temperature. The solid was filtered, washed with MeOH (3 x 20 mL) and CH_3CN (3 x 20 mL) and dried in a vacuum oven at 35 ºC for 24 hours. The polymer is a pale orange powder (1.14 g, 77%, 45% incorporation of aniline; 0.570 mmol of diimine/g polymer). IR (neat), cm^{-1}: 1755 ν(C=O st), 1677 ν(C=N st). ^1H NMR (500.15 MHz, δ, $CDCl_3$): 7.3-6.7 (br, 6H, H^{10}, H^{11}, H^{12}), 3.2-0.3 (br, $CH(CH_3)_2$, $CH(CH_3)_2$ polyNB). ^{13}C NMR (125.72 MHz, δ, $CDCl_3$): 146 (br, C^8), 135-133 (br, C^9, C^{13}), 125-121 (br, C^{10}, C^{11}, C^{12}) 54-50 and 48-45 (br C^5, C^6, $C^{2'}$, $C^{3'}$), 44-38 (br, C^1, $C^{1'}$, C^4, $C^{4'}$), 37-34 (br, C^7, $C^{7'}$), 33-28 (br, $C^{5'}$, $C^{6'}$), 28 (br, $CH(CH_3)_2$), 24-21 (br, $CH(CH_3)_2$).

Synthesis of polymer-supported diimine-palladium complexes.

Synthesis of [{VA-PNB-NB(C=N-Ar)$_2$}PdClMe]) (9). [PdClMeCOD] (0.0344 g, 0.1296 mmol) was added to a solution of copolymer **8** (0.25 g, 0.1426 mmol diimine) in CH_2Cl_2 (20 mL). The reaction was stirred for 24 hours at room temperature. After that time the mixture was poured into acetone (100 mL). The solid was filtered, washed with acetone (4 x 20 mL) and air dried. The polymer was obtained as a pale brown solid (0.1892 g, 70% yield). Analysis ICP-MS Pd 8.080 mg Pd/g. The NMR spectra of **9** are indistinguishable from those of **8**. No characteristic signals of the complex could be observed.

Synthesis of [{VA-PNB-NB(C=N-Ar)$_2$}Pd(OOCCF$_3$)$_2$] (10). Palladium(II) trifluoroacetate (0.0431 g, 0.1296 mmol) was added to a solution of copolymer **8** (0.2500 g, 0.1426 mmol diimine) in CH_2Cl_2 (20 mL). The reaction was stirred for 24 hours at room temperature and poured into acetone (100 mL). The solid was filtered, washed with acetone (4 x 20 mL) and air dried. The polymer was obtained as a brown solid insoluble in common solvents (0.2776 g, 95% yield). Analysis ICP-MS Pd 29.58 mg Pd/g. IR (neat), cm^{-1}: 1755 ν(C=O st, polymer ketone), 1686 ν(COO st as), 1677 ν(C=N st), 1182 and 1146 ν(CF_3 st). ^{13}C CP-MAS NMR (100.61 MHz): 175 (br, C^2, C^3), 168 (br, CF_3CO_2), 155-126 (br, aromatic), 120 (q, CF_3CO_2, $^1J_{C\text{-}F}$ = 280 Hz), 63-18 (br, $CH(CH_3)_2$, $CH(CH_3)_2$, polyNB) ^{19}F MAS NMR (376.50 MHz): -72.9 (br, CF_3).

Polymerization reactions with 9. Polymerization of ethylene. A Fischer-Porter flask with **9** (0.06 g, 4.56 x 10^{-3} mmol Pd) and NaB[3,5-$(CF_3)_2C_6H_3]_4$ (0.0041 g, 4.56 x 10^{-3} mmol), was cooled at -78 ºC. Upon cooling CH_2Cl_2 (4.0 mL) was added and the system was evacuated and it was purged with ethylene. The pressure was then raised to 2.5 atm and the mixture was stirred for 24 h while the temperature rose to room temperature. After that time, the pressure was released and the volatiles were removed. The solid obtained was extracted with pentane (5 x 5 mL) The undissolved solid was separated by filtration and the solution was evaporated to dryness. Polyethylene was obtained as a white solid (54 mg, 10.9 g/ mmol Pd). M_w (Daltons) = 3.19 x 10^4. M_w/ M_n = 2.4.). ^1H NMR (500.15 MHz, δ, $CDCl_3$): 1.53-1.03 (br, CH_2), 0.93-0.80 (br, CH_3). 91 branches/1000 carbon atoms.[37]

Copolymerization of ethylene with methyl acrylate. A Fischer-Porter flask was protected from light and charged with **9** (0.06 g, 4.56 x 10^{-3} mmol Pd) and NaB[3,5-$(CF_3)_2C_6H_3]_4$ (0.0041 g, 4.56 x 10^{-3} mmol). The system was cooled to -78 ºC and, after being evacuated and refilled with ethylene. Methyl acrylate (2.242 g, 26.4 mmol) and CH_2Cl_2 (2.1 mL) were added and the pressure of ethylene was elevated to 6.0 atm. After 20 h the pressure was released and the mixture was evaporated to remove the solvent and the unreacted methyl acrylate. The residue was extracted with pentane (5 x 5 mL) to separate the polyethylene formed

(8.0 mg, 1.75 g/ mmol Pd). The remaining solid, insoluble in pentane, was extracted with acetone (5 x 5mL) to separate the copolymer of ethylene and methyl acrylate, which was obtained as a colorless gum-like solid (6.0 mg, 1.31 g/ mmol Pd, 75% mol content of MA). In addition to the typical methyl, methylene and methyne signals of polyethylene new signals can be observed. ^{1}H NMR (400.15 MHz, δ, $CDCl_3$): 3.66 (s, 6H, OCH_3), 2.3 (br, 2H, $CH(CO_2CH_3)^{s}$, $CH(CO_2CH_3)^{i}$),* 1.9 (a, 1H, CHH^{i}),* 1.69 (a, 2H, CH_2^{s}), 1.5 (a, 1H, CHH^{i}).* ^{13}C{^{1}H} NMR (100.6 MHz, δ, $CDCl_3$): 174.9 (s, CO_2CH_3), 51.7 (s, OCH_3), 41.3 (m, $CH(CO_2CH_3)$)). * i = isotactic, s = syndiotactic.

General procedure for the Suzuki reactions followed by in situ IR (Table 2, entry 1). Polymer **10** 0.03 g, 0.0084 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 $CH_3CN:H_2O$ (4.0 mL, 3:1; v/v) was added and the mixture was introduced in a heated bath at 80 ºC. After 5 min, 4-bromobenzotrifluoride (0.189 g, 0.840 mmol) was added and the reaction was immediately monitored by IR, flowing the decrease of the ν(C-Br) band at 1012 cm^{-1}. When no further decrease of the IR absorption intensity was observed, the reaction was cooled down to room temperature and checked by ^{1}H NMR and ^{19}F NMR. The polymer was then filtered and washed with a mixture of $CH_3CN:H_2O$ (5 x 2.0 mL, 3:1; v/v). It was stored for further use. In the experiments collected in Table 2 (all of them carried out in the same way described above), the filtrate and solvents employed to wash the polymer were combined and used to determine the amount of Pd leached by ICP-MS (see supporting information for details). In an additional experiment (7th cycle), the collected filtrate (crude yield 98%) and solvents used to wash the polymer were combined and evaporated to c.a. 8 mL. A solution of Na_2CO_3(aq) (20 mL) was added and the mixture was extracted with Et_2O (20 mL). The organic phase was washed with water (3 x 10 mL), dried with $MgSO_4$ and evaporated to dryness. This procedure afforded pure *p*-CF_3-C_6H_4Ph (0.176 g, 94% yield).

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Keywords: supported catalysts• polynorbornene • palladium • diimine • cross-coupling

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[35] No spectroscopic data for these compounds were reported before; for this reason characterization data are included here.

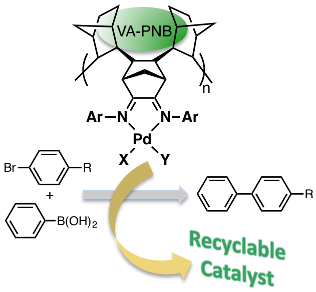
[36] The functionalization content of the polymer **5** (x = mmol carbonate/g) and the polymer composition given as a ratio of monomers incorporated (a/b = NB/$NBCO_3$) are related by the equation: x = 1000/(94.16(a/b)+152.155), where 94.16 and 152.155 are the molecular weights of norbornene and $NBCO_3$ (**1**) respectively.

[37] Calculated following the formula: branches/1000 C = (CH_3 integral x 2 x 1000)/(total integral x 3). See supporting information and reference 2e.

Entry for the Table of Contents

FULL PAPER

Vinylic addition polynorbornene embraces α-diimine ligands, incorporated in the polycyclic backbone of the polymer, and leads to palladium complexes that can be used as recyclable catalysts in cross-coupling reactions.



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Page No. – Page No.

α-Diimine-Palladium Complexes Incorporated in Vinylic Addition Polynorbornenes: Synthesis and Catalytic Activity