

Polymer-Supported Pd Catalysts

 α -Diimine–Palladium Complexes Incorporated in Vinylic-Addition Polynorbornenes: Synthesis and Catalytic ActivityJesús 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 Ni-catalyzed polymerization of norbornene and norbornenylcarbonate. Immobilized palladium complexes of the type VA-PNB–diimine–PdX₂ have been prepared, and their catalytic activity has been tested. The trifluoroacetato complex (X =

CF₃COO) can be used as a recyclable precatalyst in the Suzuki reaction. It is the source of minute amounts of homogeneous palladium active species, which 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 its monomeric counterparts.

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 1990s, when Brookhart and co-workers discovered that cationic diimine complexes of nickel or palladium with bulky noncoordinating 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 designed to improve the 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 for ensuring 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, they are less susceptible to poisoning with most polar olefins. However, complete control of the incorporation of both polar and nonpolar monomers remains a challenge. Brookhart's catalysts, which 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 proven 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]

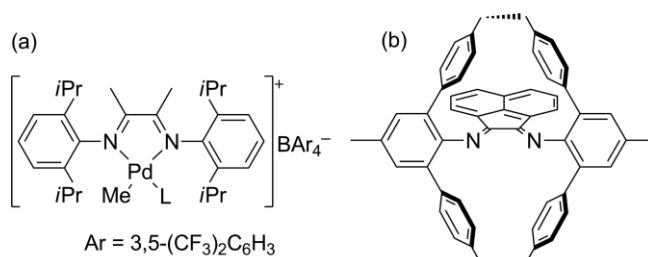


Figure 1. (a) Example of a Brookhart-type catalyst. (b) Cyclophane-based diimine.

In the last few years, we have been using vinylic-addition polynorbornenes (VA-PNBs) (Figure 2a) 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 2b),^[8] these VA-PNB materials have an aliphatic backbone that keeps the bicyclic structure of norbornene. This cyclic structure is ideal for the accommodation of a diimine fragment, as has been shown for comparable bicyclo[2.2.1] molecules, such as norbornane^[9] or camphor,^[10,11] and we decided to incorporate this ligand into the structure of the VA-PNBs, as shown in Figure 2c. 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, on 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 in-

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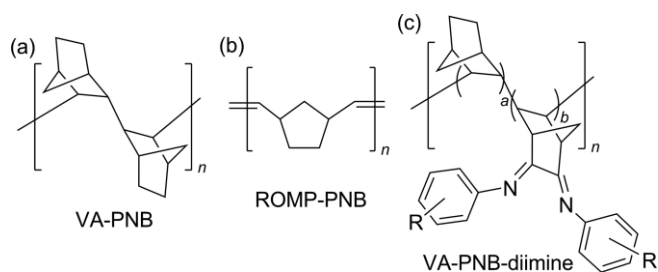


Figure 2. (a) Vinylic-addition polynorbornene (VA-PNB). (b) Ring-opening metathesis polynorbornene (ROMP-PNB). (c) VA-PNB-incorporated α -diimine.

organic 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,12d,16] Jin and Zhang described nickel–diimine catalysts with pendant allyl groups that, when reacting with ethylene, were incorporated into 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] and the Suzuki reaction,^[20] as well as carbonylation processes.^[21]

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 a significant 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 for supporting a chelating diimine fragment, we report here on the preparation of such a VA-PNB–diimine ligand (Figure 2c) and the performance of the palladium complexes derived from it as a catalyst in the polymerization of olefins and as a recyclable catalyst in Suzuki couplings.

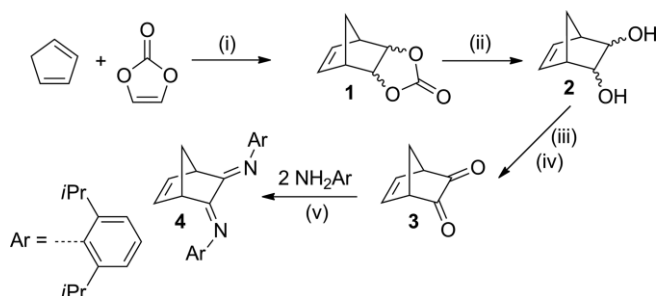
Results and Discussion

Synthesis of the Vinylic-Addition Polynorbornene Precursors

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 that are useful in the VA polymerization of norbornene, show a dramatic decrease of activity when substituted norbornenes are used, and this is espe-

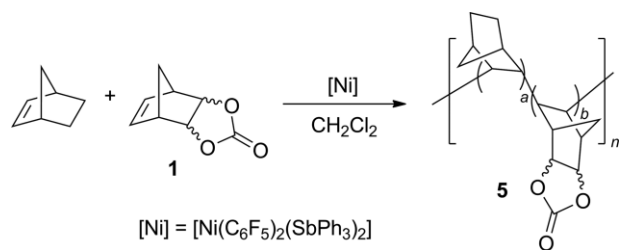
cially serious for polar O- or N-containing substituents. Our group has obtained good results in the polymerization of bromoalkyl- or bromoaryl-substituted norbornenes,^[25] as well as stannylated norbornenes,^[7a] using $[\text{Ni}(\text{C}_6\text{F}_5)_2(\text{SbPh}_3)_2]$ as the catalyst. Thus, we decided to test this complex in the polymerization of a series of substituted norbornenes that could be intermediates in the synthesis of the norbornene–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 $[\text{Ni}(\text{C}_6\text{F}_5)_2(\text{SbPh}_3)_2]$. Complexes $[\text{Ni}(\text{C}_6\text{F}_5)_2\text{L}_2]$ show very low activity in the polymerization of norbornene when L has a higher coordinating ability than SbPh_3 .^[28]



Scheme 1. Synthetic route to diimine **4**. Reaction conditions and reagents: (i) toluene, 180 °C, 20 h; (ii) NaOH (aq.); (iii) $(\text{CF}_3\text{CO}_2)_2\text{O}$, DMSO, –78 °C, 2 h; (iv) NEt_3 , –78 °C to room temperature; (v) MeOH/HCOOH.

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 at room temperature for 24 h, and copolymer **5** (VA-PNB-NBCO₃) 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 ¹H NMR spectroscopy by comparison of the signal integrals of the protons bound to C² and C³ of the carbonate and the broad signal associated with the aliphatic protons, showing a ratio of NB/**1** (*a/b*) = 16.8. The IR spectrum of the polymer showed a strong band corresponding to the $\nu(\text{C}=\text{O}$ st) absorption at 1809 cm^{-1} , which is typical of carbonates.



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 <i>a/b</i> ^[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, in CH₂Cl₂ 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 ¹H NMR spectroscopy. [d] [Ni(C₆F₅)₂(SbPh₃)₂] was added to a solution of both monomers in CH₂Cl₂. [e] Norbornene (5.9 M in CH₂Cl₂) was added dropwise to a mixture of **1** and the catalyst for 1 h. [f] Norbornene (2.7 M in CH₂Cl₂) was added dropwise to a mixture of **1** and the catalyst for 3 h.

The copolymerization of monomers **2** and **3** gave poor yields (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 for **7**, characteristic of a carbonyl moiety [ν(C=O st)]. According to these results, the synthesis of the diimine polymer needs to be carried out from polymer **5** by postpolymerization functionalization.

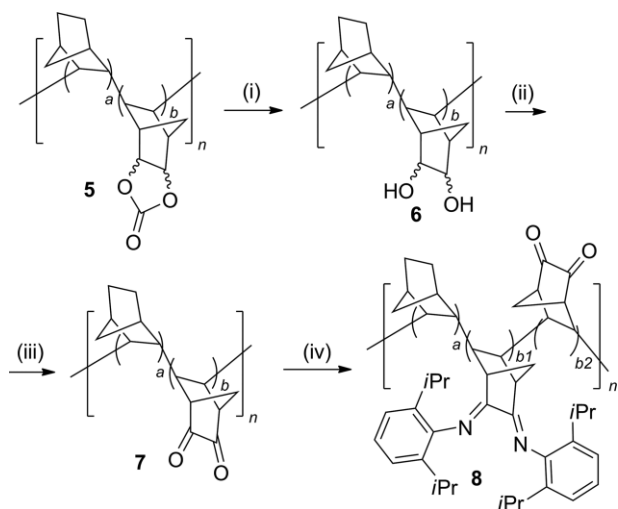
The composition of polymer **5**, obtained as shown in Table 1 (Entry 1), indicates that the reactivity of norbornene is much higher than that of monomer **1** (cf. *a/b* = 16.8 vs. NB/**1** = 1:1 in the monomer feed). In fact, the homopolymerization of **1** does not occur, as shown by ¹H NMR spectroscopic monitoring of the reaction of **1** and the catalyst [Ni(C₆F₅)₂(SbPh₃)₂] in CDCl₃ for 72 h. This is not unexpected, considering the low reactivity of O-substituted norbornenes and the fact that this catalyst previously proved to be useless in the polymerization of other O-functionalized norbornenes like 5-norbornene-2-carbaldehyde.^[28] However, unlike **1**, the coordinating ability of the oxygen atom in that monomer is strong enough to avoid copolymerization with norbornene. To reach better yields and higher incorporation of the functionalized monomer, additional polymerization reactions were performed under 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(C₆F₅)₂(SbPh₃)₂] in CH₂Cl₂, in order to increase the incorporation of the carbonate in polymer **5**. As can be seen in Table 1, when norbornene is slowly added over a period of 1 h, 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; 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 h) led to a higher incorporation of **1**, but also to a significant decrease of the yield (Table 1, Entry 8). While studying the ¹H NMR spectra of polymer **5**, we observed, in some experiments, the presence of a small olefinic signal at δ = 5.7 ppm, especially in those polymers synthesized with the slow addition of norbornene. This olefinic signal is not a product of the ring-opening polymerization of norbornene (signals at δ ≈ 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*-toluenesulfonyl hydrazide 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-NBCO₃ (**5**) To Synthesize a VA-PNB-Supported Diimine

As the starting material for the synthesis of the VA-PNB–diimine, we chose polymer **5**, of composition *a/b* = 5.7, synthesized according to Entry 7 (Table 1). It has a molecular mass of *M_w* = 3.19 × 10⁴ Da and 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 the solid-state ¹³C CP-MAS NMR spectrum at δ = 161 and 85 ppm, corresponding to C⁸ (carbonate) and C² and C³, respectively. The synthetic route for 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 H₂O/MeOH mixture to facilitate the contact between the polymer and the base. Although the polymer remained undissolved in that mixture, it became completely soaked and the reaction went to completion. The resulting polymer VA-PNB-NB(OH)₂ (**6**) is insoluble, but can be characterized by IR spectroscopy and solid-state NMR spectroscopy. The ν(C=O st) band at 1809 cm⁻¹, typical of carbonates, visible for **5**, disappears completely, and a new broad signal ν(O–H st) at 3405 cm⁻¹ appears. The ¹³C CP-MAS NMR spectrum of **6** shows a signal at δ = 76 ppm, associated with the carbon atoms bound to the hydroxy groups (C² and C³), and there are no traces of those signals observed in **5** at δ = 161 and 85 ppm, characteristic of the carbonate group. Swern oxidation of **6** was performed un-

der the same conditions used for diol **2**. The IR spectrum of the resulting compound **7** shows a strong absorption at 1755 cm^{-1} , corresponding to the ketone moiety $\nu(\text{C}=\text{O}\text{ st})$. In this case, the solid-state ^{13}C CP-MAS NMR spectrum shows no signal at $\delta \approx 200$ ppm in the ketone region, and the diol signal at $\delta = 76$ 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 under conditions similar 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 $200\text{ }^\circ\text{C}$ in a microwave oven for 4 h (Scheme 3). The resulting polymer **8** [VA-PNB-NB(C=N-Ar)₂] was soluble in chlorinated solvents, and the amount of diimine formed could be determined by ^1H NMR spectroscopy, by comparing the signal integral of the aromatic protons to the broad signal that includes all the backbone protons. Aniline was incorporated into the polymer at a rate of 46% ($a/b_1/b_2 = 5.7:0.46:0.54$; Scheme 3), giving a diimine content of 0.570 mmol per gram of polymer. The IR spectrum of **8** still shows a band at 1755 cm^{-1} $\nu(\text{C}=\text{O}\text{ st})$, with a lower intensity than that of **7**, along with a new signal at 1677 cm^{-1} , corresponding to $\nu(\text{C}=\text{N}\text{ st})$. The ^{13}C CP-MAS NMR spectrum shows a signal at $\delta = 175$ ppm for the imine carbon atoms, as well as signals between $\delta = 157$ and 124 ppm, associated with the aromatic carbon atoms, and at $\delta = 30$ ppm, which is typical of the methyl groups of the aryl substituents.

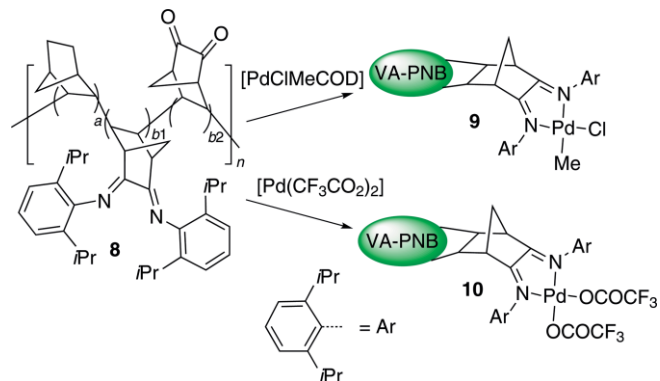


Scheme 3. Synthesis of polymer **8**. Reaction conditions: (i) NaOH (aq.)/MeOH; (ii) $(\text{CF}_3\text{CO})_2\text{O}$, DMSO, $-78\text{ }^\circ\text{C}$, 2 h; (iii) NEt_3 , $-78\text{ }^\circ\text{C}$ to room temperature; (iv) 2,6-diisopropylaniline (neat), microwave heating, $200\text{ }^\circ\text{C}$, 4 h.

Use of VA-PNB-NB(C=N-Ar)₂ as a Ligand in Olefin Polymerization

Substitution of cyclooctadiene in $[\text{PdMeCl}(\text{COD})]$ led to $[\{\text{VA-PNB-NB}(\text{C}=\text{N-Ar})_2\}\text{PdClMe}]$ (**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 cannot be seen, neither in the IR spectrum nor in the NMR spectra, when comparing **9** and **8**.



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

Polymer **9** was used as a precatalyst in the polymerization of ethylene in a way similar 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 noncoordinating anion $[\text{B}\{3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3\}_4]^-$ (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 structure similar to those obtained with Brookhart's catalysts. It has a high molecular mass ($M_w = 2.97 \times 10^4$ Da) 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 solvent from 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).

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. 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. Polyethylene with no MA was obtained (1.75 g/mmol Pd), as well as copolymer MA-ethylene, with a low content of polyethylene (75 mol-% MA, 1.31 g/mmol Pd); 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, each 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 nonpolar/polar olefin copolymerization processes.

Use of VA-PNB-NB(C=N-Ar)₂ as a 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(OOCCF₃)₂] (**10**) was synthesized by reaction of Pd(OOCCF₃)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. Trifluoromethyl acetate, instead of the most common acetate, was chosen, because the characteristic signals of the CF₃ moieties in IR and ¹⁹F NMR spectroscopy 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, which are characteristic of the trifluoromethyl group. Furthermore, the band at 1677 cm⁻¹, corresponding to the ν(C=N st) absorption in **8**, is partially overlapped by another band at 1686 cm⁻¹, associated with the ν(CO₂ asym) absorption of the acetate. This ν(CO₂ asym) absorption has a high value, higher than that of the parent palladium trifluoroacetate, which is consistent with a monodentate coordination fashion.^[31] The ¹⁹F MAS NMR spectrum shows a signal at δ = -73 ppm, slightly shifted from the signal of the starting complex Pd(CF₃CO₂)₂ (δ = -76 ppm). The ¹³C CP-MAS NMR spectrum shows new signals at δ = 167 ppm, corresponding to the carbon atom in the carboxylate group, and a quartet for the CF₃ group, with an average chemical shift of δ = 120 ppm, and a coupling constant of ¹J_{C,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 = CF₃), 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 Pd⁰, required longer times, but high yields were also obtained (Table 2, Entries 6, 7).

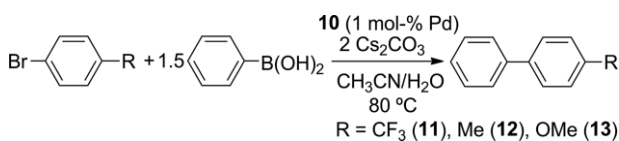


Table 2. Suzuki reactions catalyzed by **10**.^[a]

Entry	ArBr	Cycle	Time [min]	Polymer (crude yield [%])
1	<i>p</i> -F ₃ C-C ₆ H ₄ Br	1	15	11 (97) ^[b]
2	<i>p</i> -F ₃ C-C ₆ H ₄ Br	2	20	11 (98) ^[b]
3	<i>p</i> -F ₃ C-C ₆ H ₄ Br	3	25	11 (96) ^[b]
4	<i>p</i> -F ₃ C-C ₆ H ₄ Br	4	30	11 (98) ^[b]
5	<i>p</i> -F ₃ C-C ₆ H ₄ Br	5	30	11 (99) ^[b]
6	<i>p</i> -Me-C ₆ H ₄ Br	1	60	12 (95) ^[c]
7	<i>p</i> -MeO-C ₆ H ₄ Br	1	120	13 (91) ^[c]

[a] Reaction conditions shown in Equation (1). [b] Crude yields determined by ¹⁹F NMR spectroscopy. [c] Crude yields determined by ¹H NMR spectroscopy.

To evaluate the performance of the catalyst and its recyclability, the reaction in Equation (1) (R = CF₃) was monitored by in situ IR 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). 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 recycling experiments collected in Table 2 (Entries 2–5).

The activity of polymer **10** decreases in the first two 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 a 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 is 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). We have previously reported the behavior of polymeric complexes in which 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]

To determine whether the actual active catalytic species was acting homogeneously 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 °C for 20 min, the hot mixture was filtered. The ¹⁹F NMR spectrum at that point showed an 80 % yield. When the filtrate was allowed to react another 30 min 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, in which the polymer is acting as a reservoir of a small amount of palladium. The ICP-MS determination of

the amount of palladium in solution in this experiment 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 0.0026 mol-% of added catalyst (26 mol-ppm), and the TON of the reaction is close to 4×10^4 in each cycle (TOF close to 5×10^4 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 it makes polymer **10** a useful catalyst precursor, playing the role of a source of very active species in solution.

Conclusion

Vinyl- addition polynorbornenes provide a suitable backbone for the introduction of 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 in the 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 5×10^4 TONs/h). The polymer precatalyst can be reused without significant loss of activity, so the number of cumulative TONs is very high.

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 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 using extremely active homogeneous palladium species each time, without the need of precise quantity measurement, and it compares well, as far as the TONs achieved are concerned.

Experimental Section

General Methods: ^1H , ^{13}C , and ^{19}F NMR spectra were recorded with Bruker AV-400 and Agilent MR-500 instruments. Chemical shifts (δ) are reported in ppm and referenced to SiMe_4 (^1H , ^{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, with an $[\text{D}_6]$ acetone capillary. The solid-state NMR spectra were recorded at 293 K under magic-angle spinning (MAS) with a Bruker AV-400 spectrometer using a Bruker BL-4 probe with 4 mm diameter zirconia rotors spinning at 8 kHz. The ^{13}C CP-MAS NMR spectra were measured at 100.61 MHz and recorded with proton decoupling (tpmm), with a 90° pulse length of 4.5 μs , a contact time of 3 ms, and a recycle delay of 3 s. The ^{13}C NMR spectra were referenced to glycine (CO signal at $\delta = 176.1$ ppm). The ^{19}F MAS NMR spectra were recorded at 376.5 MHz with a 90° pulse length of 5.5 μs ; the ^{19}F NMR chemical shifts are in ppm relative to external CFCl_3 . IR

spectra were recorded with a Perkin–Elmer FT/IR spectrum Frontier™ spectrophotometer with a 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 Fiber-Conduit and a probe DiComp with diamond sensor. Size-exclusion chromatography (SEC) was carried out with a Waters SEC system on a three-column bed (Styragel 7.8 \times 300 mm columns: 50– 10^5 , 5×10^3 – 5×10^5 , and 2×10^3 – 4×10^6 Da) and a Waters 410 differential refractometer. SEC samples were run in CHCl_3 at 313 K, and were 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. $[\text{Ni}(\text{C}_6\text{F}_5)_2(\text{SbPh}_3)_2]$, $[\text{PdMeCl}(\text{COD})]$,^[33] $[\text{Pd}(\text{CF}_3\text{CO}_2)_2]$ ^[34] and $\text{NB}(\text{C}=\text{O})_2$ (**3**)^[26] were prepared according to literature procedures. Compounds **1** and **2** were prepared with slight modifications of the procedure described by Newman et al.^[27,35]

Synthesis of Norbornene–Diimine Precursors

Synthesis of NBCO₃ (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 mixture was heated at 180 °C for 20 h. After removing the volatiles under vacuum at 65 °C, a pale-brown solid was obtained (the dienophile excess could 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 (3×10 mL), and air-dried. The product was obtained as a pale-yellow solid (13.43 g, 91 % yield), containing a mixture of isomers *endo/exo* = 97.6:2.4. **1** *endo*: ^1H NMR (300.13 MHz, CDCl_3): $\delta = 6.21$ (m, 2 H, H^5 , H^6), 4.98 (m, 2 H, H^2 , H^3), 3.27 (m, 2 H, H^1 , H^4), 1.75 (d, $J = 10.4$ Hz, 1 H, H^7), 1.26 (d, $J = 10.4$ Hz, 1 H, H^7) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, 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) ppm. **1** *exo*: ^1H NMR (300.13 MHz, CDCl_3): $\delta = 6.1$ (m, 2 H, H^5 , H^6), 4.55 (m, 2 H, H^2 , H^3), 3.13 (m, 2 H, H^1 , H^4), 1.84 (m, 1 H, H^7), 1.7 (m, 1 H, H^7) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, CDCl_3): $\delta = 155.59$ (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) ppm. MS (EI): m/z (%) = 152 (0.5) $[\text{M}]^+$, 107 (2), 79 (34), 77 (24), 66 (100), 65 (13).

Synthesis of NB(OH)₂ (2): Compound **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 h, and the product was extracted with Et_2O (5×15 mL). The organic phase was washed with saturated aqueous NaHCO_3 solution (20 mL), water (20 mL), and dried with 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 paralleled the starting material (**1**). **2** *endo*: ^1H NMR (400.13 MHz, CDCl_3): $\delta = 6.26$ (m, 2 H, H^5 , H^6), 4.18 (m, 2 H, H^2 , H^3), 3.02 (m, 2 H, H^1 , H^4), 2.25 (br., 2 H, OH), 1.51 (d, $J = 9.7$ Hz, 1 H, H^7), 1.22 (d, $J = 9.7$ Hz, 1 H, H^7) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, 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) ppm. **2** *exo*: ^1H NMR (400.13 MHz, CDCl_3): $\delta = 6.04$ (m, 2 H, H^5 , H^6), 3.71 (m, 2 H, H^2 , H^3), 2.7 (m, 2 H, H^1 , H^4), 2.25 (br., 2 H, OH), 1.89 (d, $J = 9.2$ Hz, 1 H, H^7), 1.62 (d, $J = 9.2$ Hz, 1 H, H^7) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3): $\delta = 136.29$ (s, C^5 , C^6), 68.80 (s, C^2 , C^3), 47.85 (s, C^1 , C^4), 42.11 (s, C^7) ppm. MS (EI): m/z (%) = 126 (0.6) $[\text{M}]^+$, 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 h. Volatiles were removed, MeOH (1.0 mL) was added, and the mixture cooled to -78 °C. The solid formed was filtered and air-dried (0.1164 g, 11 % yield). ¹H NMR (400.13 MHz, CDCl₃): δ = 7.19–7.07 (m, 6 H, H¹⁰-H¹², H^{10'}-H^{12'}), 6.36 (m, 2 H, H⁵, H⁶), 3.27 (m, 2 H, H¹, H⁴), 2.95 (qq, *J* = 6.8 Hz, 2 H, H¹⁴, H^{14'}), 2.70 (sept, *J* = 6.8 Hz, 2 H, H¹⁵, H^{15'}), 2.32 (d, *J* = 9.6 Hz, 1 H, H⁷), 1.97 (d, *J* = 9.6 Hz, 1 H, H^{7'}), 1.23, 1.22, 1.19, 1.15 (4 d, *J* = 6.8 Hz, 24 H, H¹⁶-H¹⁹, H^{16'}-H^{19'}) ppm. ¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ = 168.27 (s, C², C³), 146.13 (s, C⁸, C^{8'}), 137.44 (s, C⁵, C⁶), 136.70, 136.53 (2 s, C⁹, C^{9'}, C¹³, C^{13'}), 124.04, 122.82, 122.76 (3 s, C¹⁰-C¹², C^{10'}-C^{12'}), 48.9 (s, C⁷), 46.08 (s, C¹, C⁴), 28.31, 27.91 (2 s, C¹⁴, C^{14'}, C¹⁵, C^{15'}), 23.78, 23.70, 23.46, 23.15 (4 s, C¹⁶-C¹⁹, C^{16'}-C^{19'}) ppm. MS (EI): *m/z* (%) = 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-NBCO₃ (5). Method A (Table 1, Entry 1): In a Schlenk flask under nitrogen, **1** (0.49 g, 3.22 mmol) and norbornene (0.85 mL, 3.80 M in CH₂Cl₂, 3.22 mmol) were dissolved in CH₂Cl₂ (5 mL). A solution of [Ni(C₆F₅)₂(SbPh₃)₂] (0.0708 g, 0.0644 mmol) in CH₂Cl₂ (5 mL) was slowly added to this mixture. After stirring at room temperature for 24 h, the viscous solution was poured into MeOH (30 mL). The resulting polymer was filtered, washed with MeOH (5 × 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 CO₃/g polymer).^[36] Direct syntheses of copolymers **6** and **7** (Table 1) were carried out according to this method. They were insoluble in common organic solvents. **Method B** (Table 1, entry 7): A mixture of [Ni(C₆F₅)₂(SbPh₃)₂] (0.5778 g, 0.5258 mmol) and triphenylstibine (0.074 g, 0.2103 mmol) in CH₂Cl₂ (15 mL) was added to a solution of **1** (4 g, 26.29 mmol) in CH₂Cl₂ (20 mL). Then norbornene (5.89 M in CH₂Cl₂, 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 h. After this time, it was poured into MeOH (250 mL), upon which a solid appeared, which was filtered, washed with MeOH (5 × 20 mL), and air-dried. The copolymer was obtained as a white powder (6.491 g, 73 % yield); *a/b* = 5.7 [1.45 mmol CO₃/g polymer].^[36] **5** (*a/b* = 5.7); *M_w* = 3.19 × 10⁴ Da; *M_w*/*M_n* = 1.7. IR (neat): $\tilde{\nu}$ = 1809 [ν(C=O st)], 1127 [ν(C-O st as)], 1085 [ν(C-O-C st as)] cm⁻¹. ¹H NMR (500.15 MHz, CDCl₃): δ = 5.1–4.3 (br, 2 H, H², H³), 3–0.3 (br, 16 H) ppm. ¹³C NMR (125.72 MHz, CDCl₃): δ = 155 (br, C⁸), 79 (br, C², C³), 54–50 and 48–45 (br, C⁵, C⁶, C^{2'}, C^{3'}), 44–38 (br, C¹, C^{1'}, C⁴, C^{4'}), 37–34 (br, C⁷, C^{7'}), 33–28 (br, C^{5'}, C^{6'}) ppm. Figure 3 shows the numbering scheme for NB derivatives.

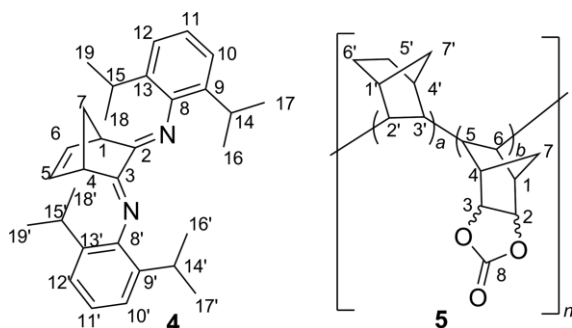


Figure 3. Examples of the numbering scheme for NB-derived compounds.

Synthesis of VA-PNB-NB(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 mixture was refluxed for 9 h. After cooling to room temperature, the mixture was poured into a mixture of MeOH/H₂O (1:1, v/v; 300 mL) and stirred overnight. The solid was filtered, washed with MeOH (5 × 20 mL), and dried in a vacuum oven at 35 °C for 24 h. The polymer was obtained as a white powder, barely soluble in common solvents (5.255 g, 98 % yield). IR (neat): $\tilde{\nu}$ = 3240 [ν(O-H st)], 1110 [and 1076 ν(C-O st)] cm⁻¹. ¹³C CP-MAS NMR (100.61 MHz): δ = 74–65 (br, C², C³), 63–18 (br, polyNB) ppm.

Synthesis of VA-PNB-NB(C=O)₂ (7): A two-necked round-bottom flask under nitrogen was charged with copolymer **6** (5 g, 7.586 mmol diol) and CH₂Cl₂ (200 mL), and cooled to -78 °C. Tri-fluoroacetic anhydride (15.93 g, 75.86 mmol) was added dropwise to another Schlenk flask containing a stirring mixture of dimethyl sulfoxide (7.112 g, 91.03 mmol) and CH₂Cl₂ (50 mL) at -78 °C. Ten minutes later, this solution was added slowly, through a cannula, to the polymer suspension at -78 °C. After 4 h, triethylamine (15.35 g, 151.7 mmol) was added. The reaction mixture was stirred for 3 h and warmed to room temperature. CH₂Cl₂ was removed to about half the initial volume, and the mixture was poured into MeOH/H₂O (3:1, v/v; 400 mL) and stirred overnight. The polymer was filtered, washed with a mixture of MeOH/H₂O (1:1, v/v; 5 × 20 mL), then MeOH (5 × 20 mL), and it was dried in a vacuum oven at 35 °C for 24 h. The polymer was obtained as a yellowish powder (4.440 g, 89 % yield). IR (neat): $\tilde{\nu}$ = 1755 [ν(C=O st)] cm⁻¹. ¹³C CP-MAS NMR (100.61 MHz): δ = 63–18 (br, polyNB) ppm.

Synthesis of VA-PNB-NB(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 °C and stirred in the microwave oven for 4 h. The reaction mixture was then poured into MeOH (100 mL) and stirred at room temperature for 3 h. The solid was filtered, washed with MeOH (3 × 20 mL) and CH₃CN (3 × 20 mL) and dried in a vacuum oven at 35 °C for 24 h. The polymer was obtained as a pale-orange powder [1.14 g, 77 %, 46 % incorporation of aniline; 0.570 mmol diimine/g polymer]. IR (neat): $\tilde{\nu}$ = 1755 [ν(C=O st)], 1677 [ν(C=N st)] cm⁻¹. ¹H NMR (500.15 MHz, CDCl₃): δ = 7.3–6.7 (br, 6 H, H¹⁰, H¹¹, H¹²), 3.2–0.3 [br, CH(CH₃)₂, CH(CH₃)₂ polyNB] ppm. ¹³C NMR (125.72 MHz, CDCl₃): δ = 146 (br, C⁸), 135–133 (br, C⁹, C¹³), 125–121 (br, C¹⁰, C¹¹, C¹²) 54–50 and 48–45 (br, C⁵, C⁶, C^{2'}, C^{3'}), 44–38 (br, C¹, C^{1'}, C⁴, C^{4'}), 37–34 (br, C⁷, C^{7'}), 33–28 (br, C^{5'}, C^{6'}), 28 [br, CH(CH₃)₂], 24–21 [br, CH(CH₃)₂] ppm.

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 CH₂Cl₂ (20 mL). The reaction mixture was stirred at room temperature for 24 h. After that time, the mixture was poured into acetone (100 mL). The solid was filtered, washed with acetone (4 × 20 mL), and air-dried. The polymer was obtained as a pale-brown solid (0.1892 g, 70 % yield). ICP-MS: 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(OOCF₃)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 CH₂Cl₂ (20 mL). The reaction mixture was stirred at room temperature for

24 h and then poured into acetone (100 mL). The solid was filtered, washed with acetone (4 × 20 mL), and air-dried. The polymer was obtained as a brown solid insoluble in common solvents (0.2776 g, 95 % yield). ICP-MS: 29.58 mg Pd/g. IR (neat): $\tilde{\nu}$ = 1755 [v(C=O st, polymer ketone)], 1686 [v(COO st as)], 1677 [v(C=N st)], 1182 [and 1146 v(CF₃ st)] cm⁻¹. ¹³C CP-MAS NMR (100.61 MHz): δ = 175 (br., C², C³), 168 (br., CF₃CO₂), 155–126 (br., aromatic), 120 (q, ¹J_{C,F} = 280 Hz, CF₃CO₂), 63–18 [br., CH(CH₃)₂, CH(CH₃)₂, polyNB] ppm. ¹⁹F MAS NMR (376.50 MHz): δ = -72.9 (br., CF₃) ppm.

Polymerization Reactions with 9. Polymerization of Ethylene: A Fischer–Porter flask with **9** (0.06 g, 4.56 × 10⁻³ mmol Pd) and NaB[3,5-(CF₃)₂C₆H₃]₄ (0.0041 g, 4.56 × 10⁻³ mmol) was cooled to -78 °C. Upon cooling, CH₂Cl₂ (4.0 mL) was added, and the system was evacuated and 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 × 5 mL). The undissolved solid was separated by filtration, and the solution was concentrated to dryness. Polyethylene was obtained as a white solid (54 mg, 10.9 g/mmol Pd). *M_w* = 2.97 × 10⁴ Da. *M_w*/*M_n* = 2.4. ¹H NMR (500.15 MHz, CDCl₃): 1.53–1.03 (br., CH₂), 0.93–0.80 (br., CH₃) ppm. There were 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 × 10⁻³ mmol Pd) and NaB[3,5-(CF₃)₂C₆H₃]₄ (0.0041 g, 4.56 × 10⁻³ mmol). The system was cooled to -78 °C, and after being evacuated, was refilled with ethylene. Methyl acrylate (2.242 g, 26.4 mmol) and CH₂Cl₂ (2.1 mL) were added, and the ethylene pressure was elevated to 6.0 atm. After 20 h, the pressure was released and the mixture was concentrated to remove the solvent and the unreacted methyl acrylate. The residue was extracted with pentane (5 × 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 × 5 mL) 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 were observed. ¹H NMR (400.15 MHz, CDCl₃): δ = 3.66 (s, 6 H, OCH₃), 2.3 [br., 2 H, CH(CO₂CH₃)^[s], CH(CO₂CH₃)^[i]], 1.9 (a, 1 H, CHH^[i]), 1.69 (a, 2 H, CH₂^[s]), 1.5 (a, 1 H, CHH^[i]) ppm ([i] = isotactic, [s] = syndiotactic). ¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ = 174.9 (s, CO₂CH₃), 51.7 (s, OCH₃), 41.3 [m, CH(CO₂CH₃)] ppm.

General Procedure for the Suzuki Reactions Followed by In Situ IR Spectroscopy (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 into a pear-shaped flask with three necks. It was equipped with the IR spectroscopic probe in the central neck, a gas inlet with stopcock, and a septum. Then, under nitrogen, a mixture of CH₃CN/H₂O (3:1, v/v; 4.0 mL) was added, and the mixture was placed 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 spectroscopy, following the decrease of the v(C-Br) band at 1012 cm⁻¹. When no further decrease of the IR absorption intensity was observed, the reaction mixture was cooled to room temperature and checked by ¹H and ¹⁹F NMR spectroscopy. The polymer was then filtered and washed with a mixture of CH₃CN/H₂O (3:1, v/v; 5 × 2.0 mL). It was stored for further use. In the experiments collected in Table 2 (all of them carried out in the same way as 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 concentrated to ca. 8 mL. A solution of Na₂CO₃ (aq.; 20 mL) was added, and the mixture was extracted with Et₂O (20 mL). The organic phase was washed with water (3 × 10 mL), dried with MgSO₄, and the solvents were evaporated to dryness. This procedure afforded pure *p*-CF₃-C₆H₄Ph (0.176 g, 94 % yield).

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