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Mono and diphosphine borane complexes grafted on polypyrrole matrix: direct use as supported ligands for Rh and Pd catalysis

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Abstract

A new versatile method for the synthesis of supported mono and diphosphines on polypyrrole matrix is described, based on the protective borane complexation of the phosphorus atom. For the first time, the unknown alkylation of a diphosphine ethano bridge, was obtained with near yield close to 70%, leading to its derivative **8** bearing the polymerizable pyrrole group on a side chain. The different supported mono and diphosphine boranes **12**–**15** have been applied with success in palladium-catalyzed allylation, cross-coupling reaction and in rhodium-catalyzed hydrogenation. It is of particular interest that supported phosphine boranes can be used without previous decomplexation, forming in situ the catalytically active species from $Pd(OAc)_2$ or $RhCl_3$. Moreover, the recoverable polymer could be used again in rhodium-catalyzed hydrogenation with a very good efficiency after several turn-overs. Nethertheless, we may point out that with palladium catalysis, the addition of $Pd(dba)_2$ was necessary to recover the catalytic activity. These results demonstrate that the phosphine borane complexes are key precursors for the synthesis of functionalized mono and diphosphines, and for their direct use in generating catalysts. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Phosphine boranes; Supported ligands; Polypyrrole; Rhodium catalysts; Palladium catalysts; Hydrogenation; Allylic alkylation; Coupling reaction

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1. Introduction

Homogeneous catalysis via organometallic complexes is a topic of current interest in organic synthesis, and spectacular progresses have been obtained toward selectivity and reactivity [1]. Furthermore, selective reactions under mild conditions giving few by-products and which satisfy the atom economy criteria, have a great potential for modern organic synthetic methods [2]. Nevertheless, the cost of the catalytic process and the presence of traces of transition metals in the final product, require the salvage and the recycling of the catalyst which are key points, for applications in medicinal-chemistry, agro-chemistry or food industry. Moreover, the recycling of chiral ligand which represents generally the more important part of the catalytic system is a major problem, for new industrial asymmetric processes [3].

In the recent past, one of the most noteworthy progresses can be illustrated by the use of hydrosoluble or amphiphilic ligands, which allow to realize biphasic catalysis [4,5] or to recover the catalyst by an acid-base work up ([5]k). The economic interest of catalytic biphasic reactions is demonstrated by the industrialization of a propene hydroforming process using an hydrosoluble rhodium complex associated with $P(m\text{-}NaSO_3Ph)_3$ (TPPTS) ([5]c, e). More recently, supercritical carbon dioxide [6], perfluorinated solvents [7] or molten salts [8] were used to realize biphasic catalysis for oxidation, hydrogenation or palladium-coupling reactions.

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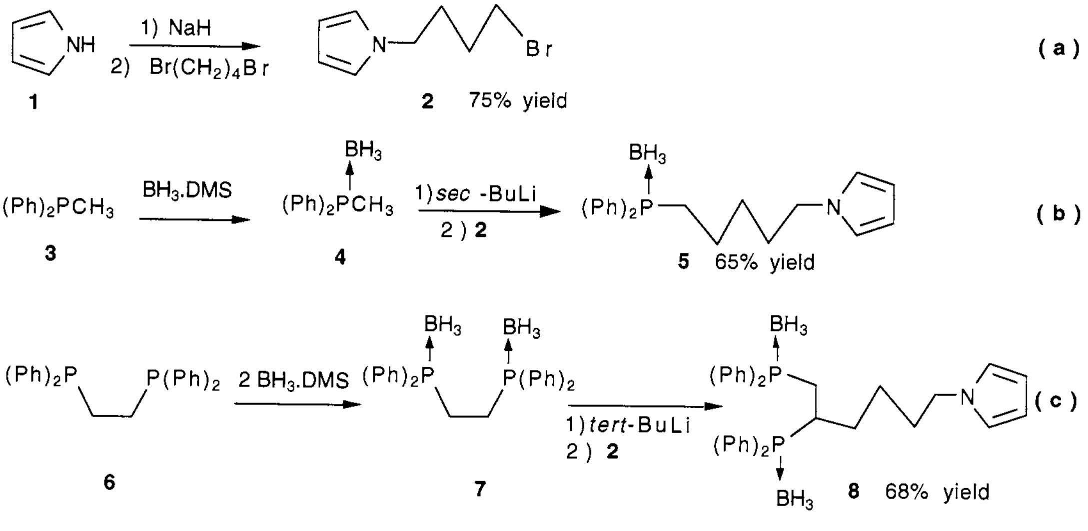


Scheme 1.

However, another alternative to recover the catalyst is to adsorb or graft it on an inorganic matrix [9,10], a polymer [11–13] or a dendrimer [14]. In this case, it is possible to combine the conditions of the heterogeneous catalysis with the interest of the homogeneous catalysts, which allow wide steric or electronic modifications. Up today, the synthesis of functionalized organic and mineral matrixes has been largely reported, in view of their applications for solid support chemistry [15], high technology materials or surface modifications [16,17]. Recently, the spectacular booming of the combinatorial chemistry on solid support retained much attention, due to the spectacular progress in drug discovery ([15]a, d). In the case of phosphines grafted on polymer, there are not many examples of this kind of supported ligands and only few are commercially available. This could be explained by the relative difficulty to functionalize organophosphorus P(III) compounds, or the problems of purification and easy oxidation. Until now, the preparation of supported-phosphine ligands is often achieved by reacting phosphorus reagents (i.e. secondary phosphines, phosphides, phosphine chlorides...) with a functionalized matrix [11] or with an olefin precursor ([12]d, e). Another approach is based in the polymerization of a phosphine monomer containing a polymerizable function such as styrene or acrylate ([11]a).

As part of our program on the synthesis of chiral mono and diphosphine ligands via their borane complexes [18], we have investigated a new way for the synthesis of phosphinated polymers. In this aim, we have studied the linkage of mono and diphosphines on a polypyrrole matrix. Up today, very few examples of phosphine ligands bound to polypyrrole are known ([18]e, [19]a), and furthermore only few examples of supported catalysts on this matrix have been applied in the field of organic catalysis.

We wish to report herein the preparation of diphenylphosphine and dppe borane complexes grafted to a polypyrrole matrix, and their direct use to generate Pd or Rh catalysts applied in C–C or C–H bond formation.

2. Results and discussion

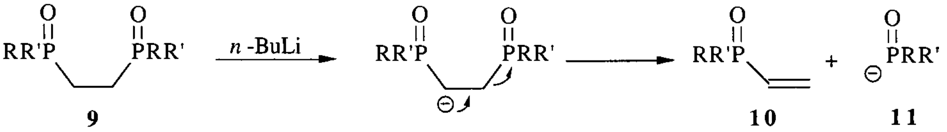
2.1. Synthesis of mono and diphosphine boranes ***5***,***8*** bearing a polymerizable pyrrole group

The use of borane as protective group of the phosphorus center, is an efficient method for the synthesis of achiral or chiral organophosphorus compounds [18,21–23]. Indeed, phosphine borane complexes present many advantages in the organophosphorus synthesis, as they possess an interesting reactivity and do not require any purification or storage problems. It is also particularly easy to prepare the carbanion of a methylphosphine borane, and consequently to introduce a functionalized group on the side chain ([18]c, [21]a, [22,23]).

We have used this methodology to functionalize the methyldiphenylphosphine borane **4** and the dppe-diborane **7** complexes, with a chain bearing a polymerizable pyrrole group (Scheme 1).

The borane complexes **4**, **7** were easily obtained in high yields (91 and 95%, respectively) as crystalline solids, by simple addition of $BH_3 \cdot DMS$ to the corresponding phosphines **3** and **6**. Then **4** was treated with *sec*-BuLi to form an α-anion, which reacted with the bromide **2** previously prepared from pyrrole **1**, to produce the monomer **5** with 65% yield (Scheme 1a, b).

Following the same procedure, reaction of the dppe diborane **7** with *tert*-BuLi led to the α-anion of the ethano bridge, which reacted with **2** to provide the compound **8** with 68% yield. As far as we know,



Scheme 2.

reaction of the diphosphine dioxide **9** with *n*-BuLi entailed its decomposition into the vinylphosphine oxide **10** and phosphide **11** [24], and the alkylation of the ethano bridge of a 1,2-diphosphine has never been reported (Scheme 2).

*2.2. Chemical polymerization of the substituted mono and diphosphine borane complexes **5** and **8***

The polymerization of the monomers **5** and **8** has been achieved by the two classical ways leading to polypyrroles: by chemical oxidation [20,25] or electrochemical preparation [17,19]. In the first case, reaction of the phosphine borane monomers **5** or **8** with anhydrous $FeCl_3$ in ether, led rapidly to the polymers **12** and **13** as insoluble black powders (Scheme 3a, c).

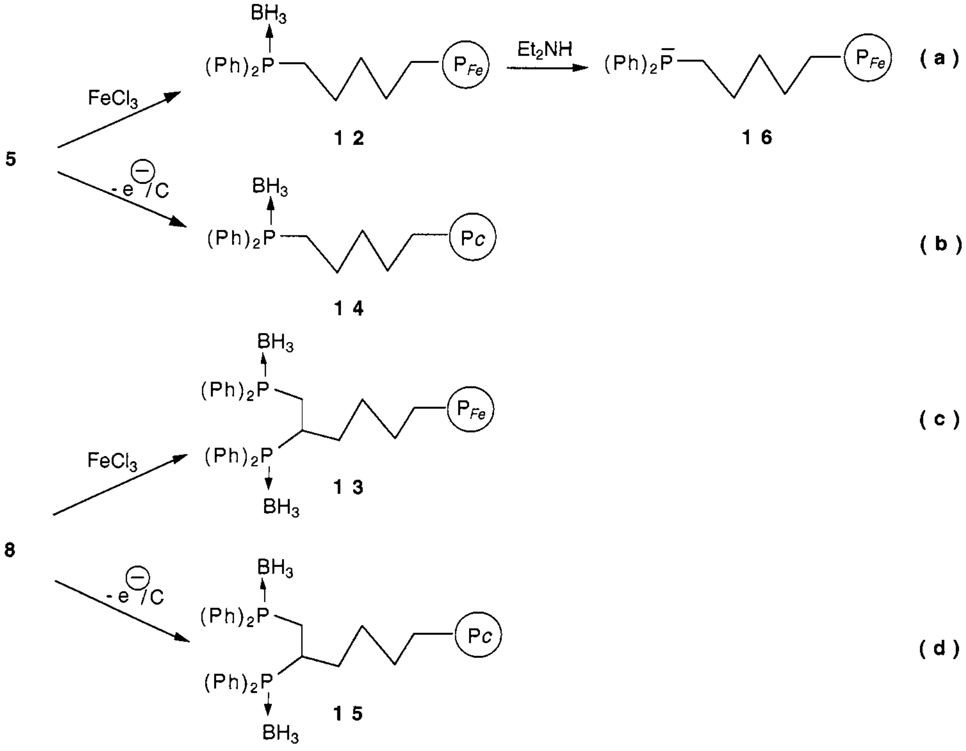
The FT-IR spectra of these polymers **12** and **13**, exhibited caracteristic B–H bands in the 2300–2400 cm^{-1} region, which indicated the presence of phosphine borane groups in the polypyrrole matrix. The elemental analyses of polypyrroles **12** and **13** displayed an important quantity of chlorine and iron (more than 50% of the material weight, Table 1, entries 1, 3), which proved that a large part of the ferric (III) chloride used for the polymerization, was aggregated to the matrix. The phosphorus analysis of the polypyrroles **12** and **13** gave 3.10 and 4.06%, respectively, in good agreement with the grafting of a mono and a diphosphine per pyrrole unit, with respect to the corresponding calculated values of 3.00 and 4.35 (Table 1, entries 1, 2 and 3, 4). On the other hand, the boron elemental analysis for **13** gives 1.13% which is lower than the calculated value of 1.52% (Table 1, entries 3, 4). Although we have observed significant variation in the elemental analyses of various prepared samples, a partial loss of the borane group during the polymerization cannot be excluded. Finally, the elemental analyses of **12** and **13** are in good agreement with the molecular formulas of $C_{21}H_{39}NPFe_{4.2}Cl_{10}BO_6$ and $C_{34}H_{55}NP_2Fe_{4.8}Cl_{13.6}B_2O_7$, respectively. The formulas are normalized to 21 and 34 carbon atoms per nitrogen, and the oxygen contents is determined by difference. These results clearly indicate that a solid solution of polymer has been generated with mineral salts, moisture and eventually solvents. It will be seen later, that the composition of the matrix have no consequence on their application as supported-ligands for organometallic catalysis.

*2.3. Electrochemical polymerization of the substituted mono and diphosphine borane complexes **5** and **8***

In a preliminary communication, we have described the electrochemical polymerization of the diphosphine borane monomer **8** ([18]e). According to this methodology, the polymer is obtained in an oxidated state with approximatively one in three pyrrole ring carrying positive charge. In order to maintain electroneutrality, perchlorate anion which came from the electrolytic media are incorporated in the polymer matrix [19,20]. Nevertheless, if this methodology is particularly adapted to analytical study, only low quantities (few mg) of product were obtained under these experimental conditions. So, in order to obtain easy handled polymer, the monomers **5** and **8** were polymerized on macroporous carbon electrodes to form the polypyrroles **14** and **15** (Scheme 3b, d). After crushing carbon electrodes, the polypyrroles **13** and **14** were obtained as a powder for their applications in catalysis.

*2.4. Preparation of supported diphosphine **16** on polypyrrole by decomplexation of the corresponding borane complexe **12***

The decomplexation of borane complexes is usually realized by reaction with an amine to give the free P(III) phosphines and the corresponding amine borane, in high yields [26]. In order to obtain the decomplexation of the phosphine borane grafted on polypyrrole, the compound **12** has been warmed at 50°C overnight in diethylamine. After filtration and washing with ether, the polypyrrole phosphine **16** was obtained as a red brown powder (Scheme 3a), which showed a new FT-IR B–N band at 1047 cm^{-1}. Likely the observed B–N band, corresponded to the presence of diethylamine borane in the polymeric matrix, in spite of the washing of the solid with solvent. The elemental analysis of **16** confirmed this adsorption of amine by the polypyrrole, since an important increase of the initial carbon, hydrogen and nitrogen percentages was observed, comparatively to the corresponding borane complex polymer **12** (Table 1, entries 5 and 2). Finally, the calculated elemental analysis of $C_{66}H_{159}PFe_{4.5}Cl_{11}BO_{13}$ was in good agreement with the values obtained for **16** (Table 1, entries 5, 6). We have shown that such material can be used with success in catalysis.



Scheme 3.

*2.5. Application of the supported phosphine and phosphine boranes **12–16** in catalysis*

Up to now, few examples of organometallic complex preparations by the direct use of phosphine boranes were known [27]. In our group, we had shown that it was possible to prepare palladium(0) complexes, by reaction of $Pd(OAc)_2$ with phosphine boranes. The mechanism of this reaction is not well established, but we think that borane reduces Pd(II) into Pd(0) leading to complexation of the free phosphine formed as described on the Scheme 4.

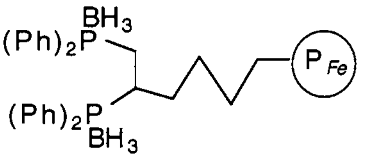
The possibility of generating low oxidating state catalytic systems from phosphine borane complexes is of particular interest, since until now, the preparation of Pd(0) and Rh(I) complexes from Pd(II) or Rh(III) salts was obtained using an excess of free phosphine as reducing agent [28,29]. Consequently, the phosphine boranes grafted on polypyrrole have been tested toward the well known Pd(0)-catalyzed reactions, without prior decomplexation. The supported catalysts have been applicated to the well known catalyzed allylation reaction with methyl acetoacetate **18** and benzylamine **20**, and to the Heck cross coupling reactions ([30] [31]a) (Schemes 5 and 6).

*2.5.1. Application of the supported phosphine boranes **12–15** to Pd(0)-catalyzed allylation reaction*

In the allylation reaction, the catalyst was prepared from $Pd(OAc)_2$ and polypyrrole supported phosphine borane complexes **12–15**, using a phosphorus/palladium ratio of 2:1. After addition of the allylic substrate **17a** (or **17b**) and the nucleophilic agent **18** (or **20**), the reaction was carried out at r.t. for at least 24 h, before filtration of the polymer and work up (Scheme 5a, b). The results are summarized in the Table 2.

In order to verify that the formation of the allylated product **19** was not due to a catalysis with metallic palladium, or to the presence of nitrogen complex with polypyrrole matrix, we have prepared the non-functionalized polymer **25** [33], and used it in the previous reaction. The mixture of allyl acetate **17a** and methylacetoacetate **18** in presence of Pd/C, $Pd(dba)_2$, or $Pd(OAc)_2$ and polypyrrole **25**, gave no reaction under these conditions (Table 2, entries 1 and 2). In contrast, the same reaction between **17a** and **18** in presence of complexes obtained from $Pd(OAc)_2$ and supported mono or diphosphine boranes **12**, **13** or **15**, led to the monoallylated product **19a** in 55–85% yields [32] (Table 2, entries 3, 5, 7, 8). It is noteworthy that the methodology of polypyrroles **12**, **13** and **15** preparation or their chemical composition, have not a dramatic influence on the catalysis despite of the salt inclusion. As the surface area of the polypyrrole **12** is surprisingly low (3.40 ± 0.05 m^2 g^{-1}) [35], the efficiency of the supported ligand must be explained by the high rate of available P(III) phosphine, linked on the matrix by the alkyl chain.

Table 1
Elemental analyses of phosphines and phosphine boranes supported on polypyrrole, prepared from **5** or **8** by oxidation with $FeCl_3$

Entries	Elemental Analyses of Polypyrroles							
		C %	H%	N%	P%	Fe%	Cl%	B%
1	Found for  **12**	23.97	3.78	1.50	3.10	22.80	34.24	-
2	calcd for $C_{21}H_{39}NPFe_{4.2}Cl_{10}BO_6$	24.43	3.81	1.36	3.00	22.72	34.34	-
3	Found for  **13**	28.73	4.07	1.02	4.06	18.76	33.73	1.13
4	calcd for $C_{34}H_{55}NP_2Fe_{4.8}Cl_{13.6}B_2O_7$	28.69	3.89	0.98	4.35	18.83	33.87	1.52
5	Found for  **16**	39.21	7.71	8.83	1.50	12.48	19.71	-
6	calcd for $C_{66}H_{159}N_{13}PFe_{4.5}Cl_{11}BO_{13}$	39.12	7.91	8.99	1.53	12.40	19.25	-

After reaction, the polypyrrole removed from the reaction medium can be used again in catalysis, but it is necessary to add $Pd(dba)_2$ in order to recover the catalytic properties (Table 2, entries 4, 6, 9). In order to prevent the oxidation of the free P(III) group, the $Pd(dba)_2$ used as Pd(0)-source for the recycled ligand was preferred to $Pd(OAc)_2$. So, it appeared that under the conditions of the palladium catalysis without any particular care for the recovery of the supported catalyst, only the polypyrrole supported P(III) ligand was removed. On the other hand, when the supported diphosphines **13** and **15** were used again, the allylated product **19a** was then obtained with 35 and 63% yields, respectively, thus reveling a better efficiency for the recovered diphosphine polypyrrole **15** prepared by electropolymerization (Table 2, entries 6, 9).

In neutral media, the allylation of methylacetoacetate **18** with carbonate **17b** was performed in presence of the catalyst prepared with the supported diphosphine borane **13**. This result indicates that the corresponding polymer prepared via the chemical way using $FeCl_3$, was inert toward the catalytic base formed during the reaction (Table 2, entry 7). Finally, reaction of benzylamine **20** with allylacetate **17a** in presence of the catalyst prepared with the supported monophosphine borane **12**, gave the *N*,*N*-diallylamine **21** in 74% yield (Table 2, entry 10), when the monoallylated product was not detected under these conditions. The recovered ligand **12** was used again in this reaction after addition of $Pd(dba)_2$, leading to the formation of *N*,*N*-diallylamine **21** with 69% isolated yield (Table 2, entry 11).

*2.5.2. Application of supported phosphine boranes **12** and **13** to Pd-catalyzed coupling reactions*

For the Heck coupling reaction described here, the catalysts were generated in situ from the supported mono and diphosphine boranes **12**, **13**, following the same procedure described in Section 2.5.1 for the allylation. The reactions were performed at 65°C between aromatic iodides **22a**,**b** and olefinic derivatives **23a**,**c** (Scheme 6), and the results are summarized in Table 3.

$$Pd(OAc)_2 + 4\,PPh_3.BH_3 \longrightarrow Pd(PPh_3)_4 + 2\,BH_2OAc + 2BH_3 + H_2$$

Scheme 4.

When the supported monophosphine borane **12** was used, the iodobenzene **22a** and the unsaturated compounds **23a**, **23c** led to the coupling products **24a**, **24c** in 72 and 64% yields, respectively (Table 3, entries 1, 4). The recovered polymer **12** can be used again with an addition of $Pd(dba)_2$, in a new coupling reaction of acrylic acid **23a** with the iodide **22a**, to provide the product **24a** with 60% yield (Table 3, entry 2). In the case of the cyclohexenone **22b**, the catalysis with the iodobenzene led to the addition product **24b** with 50% yield (Table 3, entry 3). Otherwise, when the supported diphosphine borane **13** was used with palladium salt or $Pd(dba)_2$, the coupling reaction between iodobenzene **22a** and **23a** gave poor yields in cinnamic acid **24a** (Table 3, entries 5, 6). These results can be attributed to the presence of numerous diphosphine groups in the polypyrrole matrix, which stabilize the palladium(0) species as a $Pd(P-P)_2$ complex analogous of $Pd(dppe)_2$, well known to prevent the oxidative addition with aryl iodide [36].

*2.5.3. Application of supported phosphine boranes **12–16** in rhodium catalysis*

Finally, the supported mono and diphosphine boranes were used in the classical hydrogenation catalysis of α-acetamidocinnamic acid **26** to *N*-acetylphenylalanine **27**, with rhodium complexes [37] (Scheme 7).

As for palladium complexes, the rhodium catalysts were obtained directly by reaction of $RhCl_3$ with the supported phosphine boranes **12–15** (ratio $P/Rh = 3$), by refluxing in ethanol for 1 h. On the other hand, formation of the catalyst with the free supported phosphine **16** was achieved by exchange with the neutral rhodium (I) complex $[Rh(COD)Cl]_2$, in order to prevent the oxidation of the free phosphine groups with $RhCl_3$ as for the preparation of the Wilkinson catalyst [29]. The hydrogenation has been performed with 1–3 mol% of catalyst depending on the polypyrrole preparation were prepared, i.e. either by electrochemical or chemical polymerization; The results are summarized in Table 4.

All hydrogenation reactions involving the supported phosphines were achieved with very good yields, ranging from 75 to 100% yields for the *N*-acetylphenylalanine **27** (Table 4, entries 1, 4, 6, 8, 10). When the supported ligands prepared either by electropolymerization or chemical oxidation were used, the yields of hydrogenation were similar (Table 4, entries 1–6 and 4–8). For the supported free phosphine **16**, the hydrogenation reaction took place also with satisfactory 75–100% yields (Table 4, entry 10, 11). It is noteworthy, that in all cases the catalyst was recovered by simple filtration without loss of activity, because hydrogenation by means of the recovered catalyst gave the product **27** in a near quantitative yield (Table 4, entries 2, 5, 7, 9, 11). Thus after three turn-overs, catalysts initially prepared from the supported phosphines **12** and **16**, kept the same efficiency (Table 4, entries 3, 12).

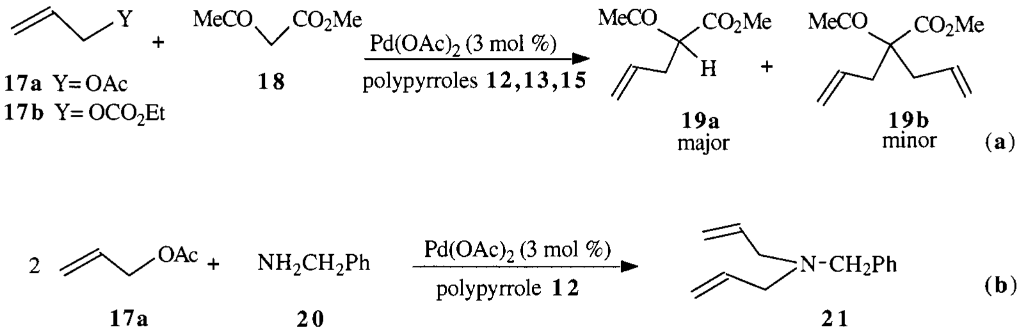
Finally, when the rhodium catalyst was prepared by complexation of $[Rh(COD)Cl]_2$ with the non-functionalized polypyrrole **25** [33], quantitatively *N*-acetylphenylalanine **27** is obtained (Table 4, entry 13). Nethertheless after filtration, the recovered polymer exhibits no more catalytic activity (Table 4, entry 14). This result clearly demonstrated that the phosphine groups grafted on polypyrrole are crucial for rhodium(I) complex stabilization, and that allow efficient recovery.

3. Conclusion

In summary, we have reported a new versatile method for the synthesis of supported mono and diphosphines on polypyrrole matrix, without significally degradation of the P(III) phosphorus group, resulting from the protective borane complexation. For the first time, the diphosphine ethano bridge alkylation, was achieved here on a borane complex serie in about 70% yield, which allows now to envisage the structural modification of the numerous existing chiral or achiral ligands.

The various supported mono and diphosphine boranes **12–15** have been applied with success in palladium-catalyzed allylation, the Heck cross-coupling reactions as well as in the rhodium-catalyzed hydrogenation. It is noteworthy that supported phosphine boranes can be used without previous decomplexation, to form in situ the catalytically active species either from $Pd(OAc)_2$ or from $RhCl_3$. Furthermore, the recovered polymer can be reused in the rhodium-catalyzed hydrogenation with a very good efficiency after several turn-overs, while in the case of the palladium catalysis the addition of $Pd(dba)_2$ was necessary to recover a suitable catalytic activity.

In conclusion, these results demonstrate clearly that the borane P(III) complexes provide key precursors both for the synthesis of mono and diphosphines grafted on a polypyrrole matrix, and for their direct reuse to generate the catalysts. The extensions of this methodology and its application to the preparation of supported chiral catalysts, are currently under investigation in our laboratory.



Scheme 5.

4. Experimental part

4.1. General

All reactions were carried out under argon atmosphere in glassware dried overnight. All solvents were dried and purified according to standard methods. *n*-butyllithium, *s*-butyllithium, *tert*-butyllithium, 1,4-dibromobutane, allylacetate, methylacetoacetate, α-acetamidocinnamic acid **26**, pyrrole **1**, $FeCl_3$, $Pd(OAc)_2$, $RhCl_3$, $BH_3.S(CH_3)_2$ in toluene, diphenylmethylphosphine **3** and 1,2-diphenylphosphinoethane **6** (dppe) were purchased from Aldrich or Acros Organics. The $[Rh(COD)Cl]_2$ complex has been prepared according to the previously described procedure [38], and used without further purification. Thin-layer chromatography and flash chromatography were performed on Silicagel 60 (35–70 μm) and silica gel (230–400 mesh; Merck), respectively.

NMR spectra data were recorded on Bruker AM 200 (^1H, ^{13}C), AM and DPX 250 (^1H, ^{13}C, ^{31}P) spectrometers with TMS as internal reference for ^1H- and ^{13}C-NMR and 85% H_3PO_4 as external reference for ^{31}P-NMR. All NMR coupling values are given in Hertz. IR spectra were recorded on a Perkin Elmer 1600 FT and a Bruker FT 45 spectrometers.

Melting points were measured on a Buchi melting point apparatus and are uncorrected. Optical rotations were measured at 20°C with a Perkin Elmer 241 polarimeter. Mass spectra analyses were performed on a NERMAG R10-10C and a KRATOS MS-50 for exact mass at the 'Laboratoire de Spectroscopie de Masse de l'ENSCP (Paris)' and the 'Laboratoire d'Analyses Structurales' of the University Pierre and Marie Curie (Paris) respectively. The major peak *m/z* is mentionned with the intensity as percent of the base peak in brackets. Elementary analysis were recorded by the 'Service d'Analyses du C.N.R.S.-Vernaison' and the 'Laboratoire de micronalyses' of the University Pierre et Marie Curie-Paris.

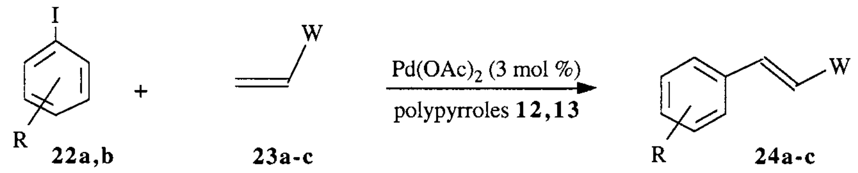
4.2. N-(4-bromobutyl)pyrrole 2

A solution of freshly distilled pyrrole (5.20 ml, 75.0 mmol) in anhydrous THF (50 ml) containing NaH (1.44 g, 60 mmol), was stirred at r.t. for 3 h; then, 75 ml of dry THF were added. In a two necked flask equipped with a condenser, a solution of 1,4-dibromobutane (21.50 ml, 180 mmol, 3 equiv.) in anhydrous THF (10 ml) was heated at 65°C under argon, and the anion previously prepared was added dropwise. The reaction mixture was stirred at r.t. overnight. Then, the reaction was quenched with a saturated aqueous NH_4Cl solution (30 ml), THF was removed under vacuum and the mixture was extracted with dichloromethane (3 × 50 ml). The combinated extracts were washed twice with water (2 × 50 ml), dried ($MgSO_4$) and concentrated. The residue was purified by flash chromatography with a mixture cyclohexane/toluene as eluent (1:1) to give the product **2** as a pink oil (9.05 g, 75% yield). This compound must be kept under inert atmosphere and in dark.

$R_f = 0.54$ (toluene/cyclohexane 1/1); IR (KBr): $\bar{\nu}$ 3098 (w), 2931 (m), 2871 (w), 1499 (s), 1281 (s), 1089 (s), 725 (s) cm^{-1}; ^1H-NMR ($CDCl_3$): δ 6.64 (2H, t, $J = 2.1$ Hz, $NC\underline{H}$), 6.14 (2H, t, $J = 2.1$ Hz, $NCC\underline{H}$), 3.90 (2H, t, $^3J = 6.6$ Hz, $C\underline{H}_2Br$), 3.36 (2H, t, $^3J = 6.4$ Hz, $C\underline{H}_2N$), 1.96–1.78 (4H, m, $(C\underline{H}_2)_2$); ^{13}C-NMR ($CDCl_3$): δ 122.3 ($N\underline{C}HC$), 110.0 ($NC\underline{C}H$), 50.5 ($\underline{C}H_2Br$), 34.9 ($\underline{C}H_2N$), 31.9 ($C\underline{C}H_2C$), 31.7 ($C\underline{C}H_2C$).

4.3. Diphenylmethylphosphine borane 4

The borane dimethylsulfide complex (5.22 ml, 55.0 mmol, 1.1 equiv.) was added dropwise under argon to a solution of diphenylmethylphosphine **3** (10.00 g, 49.9 mmol) in anhydrous THF (100 ml), at r.t.. The reaction was stirred at 25°C for 1 h, and the excess of dimethylsulfide borane was removed by a stream of bubbling argon. Then, the solvent was removed under vacuum and the resulting solid was recrystallized from cyclohexane, to give the borane complex **4** (9.74 g, 91% yield) as colorless crystals.



Scheme 6.

M.p. 55°C (cyclohexane; lit. ([26]a) m.p. 51°C); $R_f = 0.61$ (toluene); IR (KBr): $\bar{\nu}$ 3054 (w), 2365 (s), 2337(s), 2237 (w), 1483 (m), 1484 (s), 1059 (s), 887 (s), 754 (s) cm^{-1}; ^1H-NMR ($CDCl_3$): δ 7.71–7.62 (4H, m, $\underline{H}$ arom), 7.51–7.40 (6H, m, $\underline{H}$ arom), 1.86 (3H, d, $^2J_{PH} = 10.1$ Hz, $C\underline{H}_3$), 1.50–0.23 (3H, q, $^1J_{BH} = 93.5$ Hz, $B\underline{H}_3$); ^{13}C-NMR ($CDCl_3$): δ 132.2–129.1 ($\underline{C}$ arom), 12.3 (d, $^1J_{PC} = 40.3$ Hz, $P\underline{C}H_3$); ^{31}P-NMR ($CDCl_3$): δ 9.99 (q, $^1J_{PB} = 52.8$ Hz).

4.4. 1,2-bis-(diphenylphosphino)ethane-bis-borane 7

To a solution of 1,2-bis-(diphenylphosphino)ethane **6** (10.00 g, 25.1 mmol) in anhydrous THF (150 ml), was added under argon dimethylsulfide borane (5.22 ml, 55.0 mmol, 2.2 equiv.) at r.t. The reaction mixture was stirred at 25°C for 4 h and the solvent was removed under vacuum. The residue was recrystallized from toluene to give the compound **7** as colorless crystals (10.10 g, 94% yield).

M.p. 166–168°C (toluene; lit. [39] m.p. 162–167.5°C); $R_f = 0.82$ (toluene); IR (KBr): $\bar{\nu}$ 3056 (w), 2916 (w), 2380 (s), 2340 (s), 2252 (w), 1482 (m), 1436 (s), 1108 (s), 1059 (s), 756 (s), 692 (s) cm^{-1}; ^1H-NMR ($CDCl_3$): δ 7.67–7.60 (8H, m, $\underline{H}$ arom), 7.50–7.39 (12H, m, $\underline{H}$ arom), 2.37 (4H, dl, $^2J_{PH} = 3.2$ Hz, $C\underline{H}_2$), 1.70–0.20 (6H, q, $^1J_{BH} = 94.0$ Hz, $B\underline{H}_3$); ^{13}C-NMR ($CDCl_3$): δ 132.6–128.1 ($\underline{C}$ arom), 19.9 (d, $^1J_{PC} = 37.7$ Hz, $P\underline{C}H_2$); ^{31}P-NMR ($CDCl_3$) δ 18.0 (m, $^1J_{PB} = 40.9$ Hz).

4.5. N-[5-(diphenylphosphinoborane)pentyl]pyrrole 5

To a solution of methyldiphenylphosphine borane **4** (2.00 g, 9.34 mmol) in anhydrous THF (10 ml) and under argon, was added dropwise at −10°C *sec*-butyllithium (1.3 M in cyclohexane, 7.90 ml, 10.27 mmol). The reacting mixture was stirred at this temperature for 1.5 h, and the *N*-4-bromobutylpyrrole **2** (1.89 g, 9.35 mmol, 1 equiv.) was added to the solution which became rapidly colorless. The reaction was stirred at −10°C for 2 h and quenched by a saturated aqueous NH_4Cl solution (30 ml). THF was removed under vaccum and the resulting residue was extracted twice with dichloromethane (2 × 25 ml). The combinated organic layers were dried ($MgSO_4$), and the solvent removed under vacuum to give a residue which was purified by flash chromatography with a mixture cyclohexane/toluene (1/1) as eluent. The air- and light-sensitive product **5** was obtained as a colorless oil, which crystallized very slowly (2.03 g, 65% yield).

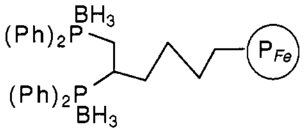
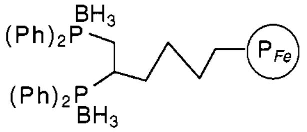
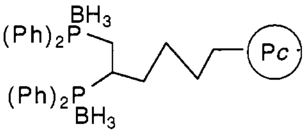
M.p. 37°C; $R_f = 0.46$ (toluene/cyclohexane 1/1); IR (KBr): $\bar{\nu}$ 3056 (w), 2932 (m), 2381 (s), 2343 (m), 2253 (w), 1722 (m), 1499 (m), 1436 (s), 1280 (m), 1062 (s), 727 (s), 701 (s) cm^{-1}; ^1H-NMR ($CDCl_3$): δ 7.68–7.60 (4H, m, $\underline{H}$ arom), 7.48–7.40 (6H, m, $\underline{H}$ arom), 6.58 (2H, t, $^3J = 2.0$ Hz, $NC\underline{H}$), 6.11 (2H, t, $^3J = 2.0$ Hz, $NCC\underline{H}$), 3.81 (2H, t, $^3J = 6.9$ Hz, $NC\underline{H}_2$), 2.15 (2H, m, $PC\underline{H}_2$), 1.73 (2H, m), 1.53 (2H, m), 1.34 (2H, m), 1.70–0.30 (3H, m, $B\underline{H}_3$); ^{13}C-NMR ($CDCl_3$): δ 132.2–128.2 ($\underline{C}$ arom), 120.4 ($N\underline{C}H$), 107.9 ($NC\underline{C}H$), 49.2 ($N\underline{C}H_2$), 31.0 ($NCH_2\underline{C}H_2$), 28.2 (d, $^1J_{PC} = 14.2$ Hz, $PC\underline{C}H_2$), 25.6 (d, $^2J_{PC} = 37.0$ Hz, $P\underline{C}H_2$), 22.6 ($N(CH_2)_2\underline{C}H_2$); ^{31}P-NMR ($CDCl_3$): δ 16.11 (q, $^1J_{PB} = 59$ Hz); HRMS (EI) calcd for $C_{21}H_{27}BNP$ $[M]^+$ 335.1974, Found 335.1953.

4.6. 1-(N-But-4-yl-pyrrol)-1,2-bis (diphenylphosphino)ethane-bis-borane 8

tert-Butyllithium (1.5 M in pentane, 0.50 ml, 0.75 mmol) was added dropwise under argon, to a solution of 1,2-bis(diphenylphosphino)ethane diborane **7** (213 mg, 0.50 mmol) in anhydrous THF (2 ml) at 0°C. The reaction was stirred at 0°C for 1.5 h, and a solution of *N*-(4-bromobutyl)pyrrole **2** (202 mg, 1.00 mmol) in anhydrous THF (2 ml) was added to the previous solution, which became rapidly clear. The reaction was stirred at 0°C for 3 h in the dark. After hydrolysis by a saturated aqueous NH_4Cl solution (5 ml) and twice extraction with dichloromethane (2 × 15 ml), the combinated extracts were dried ($MgSO_4$), and the solvent was evaporated. The residue was purified by flash chromatography with a mixture of cyclohexane/toluene (8:2) as eluent, to give the air- and light-sensitive product **8** as a colorless oil (190 mg, 69%).

$R_f = 0.26$ (toluene/cyclohexane; 1:1); IR (neat): $\bar{\nu}$ 3056 (w), 2929 (m), 2871 (w), 2382 (s), 2258 (w), 1499 (m), 1436 (s), 1051 (s), 734 (s), 694 (s) cm^{-1}; ^1H-NMR ($CDCl_3$): δ 7.66–7.59 (8H, m, $\underline{H}$ arom), 7.47–7.20 (12H, m, $\underline{H}$ arom), 6.56 (2H, t, $^3J = 2.1$ Hz, $NC\underline{H}$), 6.10 (2H, t, $^3J = 2.1$ Hz, $NCC\underline{H}$), 3.81 (2H, t, $^3J = 7.1$ Hz, $NC\underline{H}_2$), 2.23 (1H, m, $PC(H)\underline{H}$), 2.01 (2H, m, $PC\underline{H}(H)$),

Table 2
Results of allylic alkylation catalyzed by palladium complexes with phosphine boranes supported on polypyrroles **12**–**16**

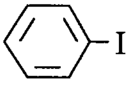
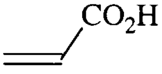
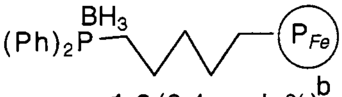
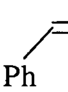
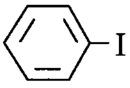
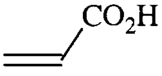
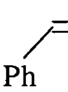
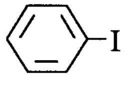
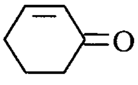
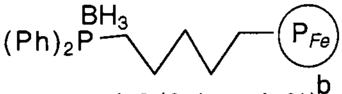
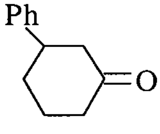
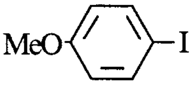
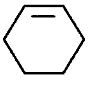
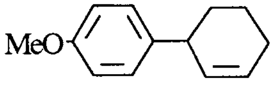
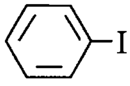
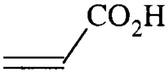
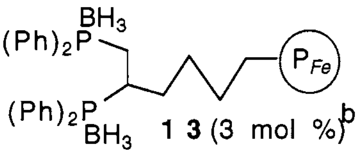
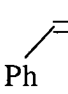
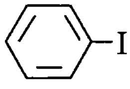
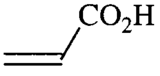
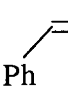
Entries	Allylic substrate	Nucleophilic reagent	Conditions	Allylic product (yield%)[a]
1	**17a**	**18**	Pd/C (3 mol %) 48h/ r.t.	**19** < 5%
2	**17a**	**18**	$Pd(dba)_2$ (3 mol %); 48h/ r.t. polypyrrole **25**[b]	**19** < 5%
3	**17a**	**18**	$Pd(OAc)_2$(3 mol %); 24h/ r.t.; **12**(6.4 mol %)[c] 	**19a** 8 5%
4	**17a**	**18**	$Pd(dba)_2$ (3 mol %); 48h/ r.t.; **12** recycled from run 3	**19a** 40%
5	**17a**	**18**	$Pd(OAc)_2$ (3 mol %); 48h/ r.t.; **13** (3 mol %)[c] 	**19a** (42 %) **19b** (17%)
6	**17a**	**18**	$Pd(dba)_2$ (3 mol %); 48h/ r.t.; **13** recycled from run 5	**19a** 35%
7	**17b** $Y= OCO_2Et$	**18**	$Pd(OAc)_2$ (3 mol %); 62h/ r.t.; **13** (3 mol %)[c] 	**19a** 70%
8	**17a**	**18**	$Pd(OAc)_2$ (3 mol %); 48h/ r.t.; **15** (3 mol %)[c] 	**19a** 55%
9	**17a**	**18**	$Pd(dba)_2$ (3 mol %); 48h/ r.t.; **15** recycled from run 8	**19a** 63%
10	**17a**	**20**	$Pd(OAc)_2$(3 mol %); 60h/ 40°C; **12**(6.4 mol %)[c] 	**21** 74%
11	**17a**	**20**	$Pd(dba)_2$ (3 mol %); 60h/ 40°C **12** recycled from run 10	**21** 69%

[a] Isolated yields of the major mono allylated product **19** [32].

[b] Reference [33].

[c] Reference [34].

Table 3
Results of coupling reaction catalyzed by palladium complexes with phosphine boranes linked on polypyrroles **12**, **13**

Entries	Aromatic iodide	Insatured compound	Conditions	product (yield%)[a]
1	 **22a**	 **23a**	Pd(OAc)$_2$ (3 mol %); 3h/ 65°C;  **1 2** (6.4 mol %)[b]	 **24a** (72 %)
2	 **22a**	 **23a**	Pd(dba)$_2$ (3 mol %); 3h/ 65°C **12** recycled from run 1	 **24a** (60%)
3	 **22a**	 **23b**	Pd(OAc)$_2$ (3 mol %); 24h/ 60°C;  **1 2** (6.4 mol %)[b]	 **24b** (50 %)
4	 **22b**	 **23c**	Pd(OAc)$_2$ (3 mol %); 60h/ 70°C;  **1 2** (6.4 mol %)[b]	 **24c** (64%)
5	 **22a**	 **23a**	Pd(OAc)$_2$ (3 mol %); 3h/ 65°C;  **1 3** (3 mol %)[b]	 **24a** (11%)
6	 **22a**	 **23a**	Pd(dba)$_2$ (3 mol %); 48h/ 65°C; **13** recycled from run 5	 **24a** (<5 %)

[a] Isolated yield.
[b] Reference [34].

1.85 (2H, m, $\mathrm{NCH_2C\underline{H}_2}$), 1.54 (4H, m, $\mathrm{(C\underline{H}_2)_2}$), 1.50–0.47 (6H, m, $\mathrm{B\underline{H}_3}$); ^{13}C-NMR ($\mathrm{CDCl_3}$): δ 132.6–128.6 ($\underline{\mathrm{C}}$ arom), 120.8 ($\mathrm{N\underline{C}H}$), 108.5 ($\mathrm{NC\underline{C}H}$), 49.4 ($\mathrm{N\underline{C}H_2}$), 33.2 ($\mathrm{NCH_2\underline{C}H_2}$), 33.00 ($\mathrm{N(CH_2)_2\underline{C}H_2}$), 25.4 (d, $^1J_{\mathrm{PC}} = 37.0$ Hz, $\mathrm{P\underline{C}H_2}$), 20.5($\mathrm{PCH\underline{C}H_2}$); ^{31}P-NMR ($\mathrm{CDCl_3}$): δ 17.02 (m, $^1J_{\mathrm{PC}} = 67$ Hz); Anal. calcd for $\mathrm{C_{34}H_{41}B_2NP_2}$ (%): C, 74.62; H, 7.55; N, 2.56. Found: C, 74.60; H, 7.68; N, 2.55.

*4.7. Chemical polymerization of N-[5-(diphenylphosphinoborane)pentyl]pyrrole **5** into supported phosphine borane **12***

A solution of anhydrous ferric(III) chloride (592 mg, 3.6 mmol, 4 equiv.) in dry diethylether (1.6 ml) was added under argon at 0°C to a solution *N*-[5-(diphenylphosphinoborane)pentyl]pyrrole **5** (305 mg, 0.91 mmol) in dry diethylether (1 ml). The previous brown solution became fastly colorless and a black precipitate appeared. This suspension was vigourously stirred at 0°C for 1 h, and then filtered to give a black powder which was washed with ether (20 ml) and dry under vacuum overnight (826 mg). This powder was insoluble in classical organic solvents.

IR (KBr): $\bar{\nu}$ 2926 (m), 2381 (m), 2345 (s), 1654 (w), 1436 (s), 1107 (s), 1063 (s), 736 (s), 692 (s) cm^{-1}; Anal. calcd for $C_{21}H_{39}NPFe_{4.2}Cl_{10}BO_6$ [M = 1032.42] (%): C, 24.43; H, 3.81; N, 1.36; P, 3.00; Fe, 22.72; Cl, 34.34. Found: C, 23.97; H, 3.78; N, 1.50; P, 3.10; Fe, 22.72; Cl, 34.34. Surface area [35]: 3.40 ± 0.05 m^2 g^{-1}.

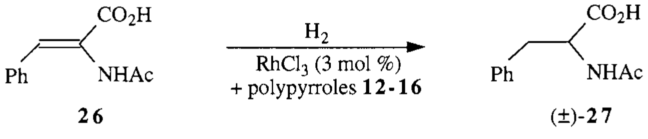
*4.8. Electrochemical polymerization of the N-[5-(diphenylphosphinoborane)pentyl] pyrrole **5** into supported phosphine borane **14***

The study was run under an argon atmosphere in a conventional three-electrode cell. The potentials were relative to the Ag/Ag^+ 10 mM reference electrode in CH_3CN. The working electrodes were macroporous carbon ($d = 12$ mm, $h = 1$ cm). The polymerization of a solution of 1-(*N*-pent-5-ylpyrrol)-diphenylphosphine borane **5** (5×10^{-3} mol l^{-1}) and tetrabutylammonium perchlorate (10^{-1} mol l^{-1}) in acetonitrile, was performed by controlled potential oxidation at 0.85 V. The polymerization was stopped when the quantity of applied electricity was 15 C, which corresponded to about 25 mg of polymer. The resulting material was kept in acetonitrile.

*4.9. Chemical polymerization of 1-(N-but-4-yl-pyrrol)-1,2-bis(diphenylphosphino)ethane diborane **8** into the supported diphosphine borane **13***

A solution of anhydrous ferric(III) chloride (700 mg, 4.3 mmol) in dry diethylether (1.6 ml), was added under argon at 0°C to a solution of 1-(*N*-but-4-yl-pyrrol)-1,2-bis(diphenylphosphino)ethane diborane **8** (500 mg, 0.91 mmol) in dry diethylether (1 ml). The previous brown solution became fastly colorless and a black precipitate appeared. This suspension was vigourously stirred at 0°C for 1 h, and then filtered. The black powder was washed with ether (20 ml) and dried under vaccum overnight (1.04 g). This powder of polypyrrole **13** was insoluble in classical organic solvents.

IR (KBr): $\bar{\nu}$ 2920 (m), 2383(w), 1642 (s), 1610 (s), 1436 (m), 1109 (m), 1024 (m), 739 (m), 691 (m), 592 (m) cm^{-1}; Anal. calcd for $C_{34}H_{55}NP_2Fe_{4.8}Cl_{13.6}B_2O_7$ [M = 1423.61](%): C, 28.69; H, 3.89; N, 0.98; P, 4.35; Fe, 18.83; Cl, 33.87, B, 1.52. Found: C, 28.73; H, 4.07; N, 1.02; P, 4.06; Fe, 18.76; Cl, 33.73, B, 1.13.



Scheme 7.

*4.10. Electrochemical polymerization of 1-(N-but-4-yl-pyrrol)-1,2-bis(diphenylphosphino) ethane diborane **8** into supported diphosphine borane **15***

Polymerization of 1-(*N*-but-4-yl-pyrrol)-1,2-bis(-diphenylphosphino) ethane diborane **8** (5×10^{-3} mol l^{-1}) was performed in acetonitrile, in the conditions previously described for polypyrrole **14** (Section 4.8).

*4.11. Decomplexation of **12** into phosphine grafted on supported phosphine **16***

Polypyrrole **12** (330 mg, 0.32 mmol) was suspended in diethylamine (3 ml) and the mixture was heated under argon overnight at 50°C. The reaction was filtered and a brown powder of **16** was obtained (428 mg).

IR (KBr): $\bar{\nu}$ 3421, 2970, 2905, 2817, 2774, 2469, 2370 (B–H), 1635, 1457, 1391, 1158, 1046 (B–N), 799, 696 cm^{-1}. Anal. calcd for $C_{66}H_{159}N_{13}PFe_{4.5}Cl_{11}BO_{13}$ [M = 2026.15] (%): C, 39.12; H, 7.91; N, 8.99; P, 1.53; Fe, 12.40; Cl, 19.25. Found: C, 39.21; H, 7.71; N, 8.83; P, 1.50; Fe, 12.48; Cl, 19.71.

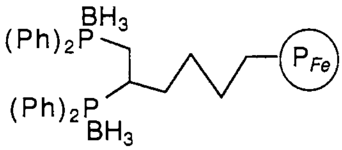
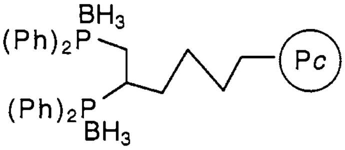
4.12. Catalysis applications

*4.12.1. Allylation of methylacetoacetate **18** catalyzed by a palladium (0) complex generated from Pd(OAc)$_2$ and supported phosphine boranes **12**–**15***

4.12.1.1. Typical procedure. A suspension of supported phosphine borane **12** (66 mg, 6.4 mol%) and $Pd(OAc)_2$ (7 mg, 3 mol%) in anhydrous THF (1 ml), was stirred at r.t. for 30 min. Then, allylacetate **17a** (108 μl, 1.0 mmol) or allylethylcarbonate **17b** (130 mg, 1.0 mmol) was added, and the mixture was stirred at r.t. for 15 min. In another flask under argon atmosphere, methylacetoacetate (108 μl, 1.0 mmol) was added to a solution of NaH (26 mg, 1.1 mmol) in anhydrous THF (2 ml), and the mixture was stirred at r.t. for 30 min. The resulting anion was added dropwise to the solution of catalyst. The new mixture was stirred at r.t. and the reaction was monitored by TLC. The ligand was removed by filtration and the solution was concentrated. The residue was purified by flash chromatography (eluent: cyclohexane/toluene; 8:2), leading to the product **19a**. The formation of a minor diallyl product **19b** is also observed.

^{1}H-NMR ($CDCl_3$): δ 5.72 (1H, m, $CH_2{=}C\underline{H}$), 5.11 (2H, m, $C\underline{H}_2{=}CH$), 3.72 (3H, s, $OC\underline{H}_3$), 3.53 (1H, t, $C\underline{H}CO_2Me$), 2.60 (1H, m, $C\underline{H}_2$), 2.27 (3H, s, $C\underline{H}_3$).

Table 4
Results of hydrogenation of **26** catalyzed by rhodium complexes with phosphine boranes grafted on polypyrrole **12**–**16**

Entries	**Catalysts**	p_{H_2} (bars)	**Reaction time** (h)	**N-acetylphenyl alanine 27** (yield%)^{a}
1	$RhCl_3$ (2.9 mol %) + **12** (9.6 mol %)^{b} 	10	72	91%
2	catalyst recycled from run 1	10	72	100
3	catalyst recycled from run 2	10	48	88
4	$RhCl_3$ (2.9 mol %) + **13** (4.5 mol %)^{b} 	10	48	94
5	catalyst recycled from run 4	10	48	100
6	$RhCl_3$ (1 mol %) + **14** (3 mol %)^{b} 	20	24	100
7	catalyst recycled from run 6	20	24	95
8	$RhCl_3$ (1 mol %) + **15** (1.5 mol %)^{b} 	20	24	84
9	catalyst recycled from run 8	20	24	93
10	$[Rh(COD)Cl]_2$ (1.5 mol %)  **16**(4.8 mol %)^{b}	10	48	75
11	catalyst recycled from run 10	10	48	100
12	catalyst recycled from run 11	10	48	100
13	$[Rh(COD)Cl]_2$ (1.5 mol %) + **25**^{c}	10	48	100
14	catalyst recycled from run 13	10	48	0

[a] Isolated yield.

[b] Reference [34].

[c] Reference [33].

Minor diallyl product **19b**: ^{1}H-NMR (CDCl$_3$): δ 5.70 (2H, m, CH$_2$=C$\underline{H}$), 5.10 (4H, m, C$\underline{H}_2$=CH), 3.72 (3H, s, OC$\underline{H}_3$), 2.60 (1H, m, C$\underline{H}_2$), 2.20 (3H, s, C$\underline{H}_3$).

4.12.1.2. Procedure using recovered polymer. To a solution of Pd(dba)$_2$ (1.5 mol%) in dry THF the removed polymer was added, and the mixture was stirred at r.t. for 30 min. Allylacetate **17a** was added, and the resulting mixture was stirred at r.t. for 15 min, generating the catalyst which was reused for another allylation as described above.

*4.12.2. Allylation of benzylamine **20** catalyzed by a palladium (0) complex generated from Pd(OAc)$_2$ and supported phosphine borane **12***

A suspension of supported phosphine borane **12** (66 mg, 6.4 mol%) and Pd(OAc)$_2$ (7 mg, 3 mol%) in anhydrous THF (2 ml), was stirred at r.t. for 30 min. Then allylacetate **17a** (216 µl, 2.0 mmol) was added and the resulting mixture was stirred at r.t. for 15 min. In another flask under argon atmosphere, benzylamine **20** (109 µl, 1.0 mmol) was added to a solution of NaH (26 mg, 1.1 mmol) in anhydrous THF (3 ml); the mixture was stirred at r.t. for 30 min and then added dropwise to the catalyst. The new mixture was heated at 40°C for 60 h. Then, the polymer was removed by filtration and the solvent was removed under vacuum. The residue is purified by flash chromatography with a (8:2) mixture of cyclohexane/ethylacetate as eluent, giving the *N*,*N*-diallylbenzylamine **21** as a colorless oil (139 mg; 74% yield).

^{1}H-NMR (CDCl$_3$) lit. ([31]b): δ 7.35–7.15 (5H, m, $\underline{H}$ arom), 5.82 (2H, dtd, $^4J = 1.3$ Hz, $^3J_{trans} = 17$ Hz, $^3J_{cis} = 10$ Hz, CH$_2$=C$\underline{H}$), 5.13 (1H, dq, $^2J = {}^4J = 1.5$ Hz, $^3J_{trans} = 17$ Hz, C($\underline{H}$)H=CH), 5.07 (1H, dq, $^2J = {}^4J = 1.5$ Hz, $^3J_{cis} = 10$ Hz, CH($\underline{H}$)=CH), 3.51 (2H, s, PhC$\underline{H}_2$), 3.01 (4H, dt, $^3J = 6.3$ Hz, $^4J = 1.2$ Hz, C$\underline{H}_2$N). ^{13}C-NMR (CDCl$_3$): δ 139.8 (C$_1$ arom), 136.3 ($\underline{C}$H arom), 129.3 ($\underline{C}$H arom), 128.6 ($\underline{C}$H arom), 127.2 ($\underline{C}$H=CH$_2$), 117.8 (CH=$\underline{C}$H$_2$), 57.9 (Ph$\underline{C}$H$_2$), 56.8 ($\underline{C}$H$_2$CH=CH$_2$).

The reuse of the recovered polymer for another preparation of catalyst was realized with Pd(dba)$_2$, as described in Section 4.12.1.

*4.12.3. Preparation of the cinnamic acid **24a** by Heck reaction catalyzed by a palladium (0) complex generated from Pd(OAc)$_2$ and supported phosphine boranes **12–15***

4.12.3.1. Typical procedure. Supported phosphine borane **12** (66 mg, 6.4 mol%) was added to a solution of Pd(OAc)$_2$ (7 mg, 3 mol%) in anhydrous THF (2 ml), and stirred at r.t. for 30 min. Then, a solution of iodobenzene **22a** (112 µl, 1.0 mmol), acrylic acid **23a** (103 µl, 1.5 mmol) and triethylamine (0.35 ml, 2.5 mmol) in dry THF (2 ml) was added to the mixture. The reaction was heated at 65°C for 3 h, and the polymer removed by filtration. The solvent was removed under reduced pressure, and the residue was poured in a 10% aqueous solution of Na$_2$CO$_3$ (5 ml) and extracted three times with dichloromethane. The aqueous layer was then acidified with HCl (0.1M) and extracted twice with dichloromethane. The organic layers were dried (MgSO$_4$) and the solvent was removed under vacuum to give the cinnamic acid **24a** (106 mg, 72% yield).

^{1}H-NMR (CDCl$_3$): δ 11.0 (1H, s, CO$_2\underline{H}$), 7.81 (1H, d, $^3J_{HH} = 16$ Hz, PhC$\underline{H}$), 7.55 (2H, m, $\underline{H}$ arom), 7.41(3H, m, $\underline{H}$ arom), 6.46 (1H, d, $^3J_{HH} = 16$ Hz, PhCH=C$\underline{H}$).

The reuse of the recovered polymer for another preparation of catalyst was achieved with Pd(dba)$_2$, as described in Section 4.12.1.

*4.12.4. Synthesis of 3-phenylcyclohexan-1-one **24b** by a Heck type reaction, catalyzed by palladium (0) complexes generated from Pd(OAc)$_2$ and supported phosphine borane **12***

Supported phosphine borane **12** (66 mg, 6.4 mol%) was added to a solution of Pd(OAc)$_2$ (7 mg, 3 mol%) in DMF (2 ml), and the mixture was stirred at r.t. for 30 min. Then, a solution of iodobenzene **22a** (112 µl, 1.0 mmol), cyclohexenone **23b** (290 µl, 3.0 mmol), formic acid (128 µl, 3.4 mmol) and triethylamine (0.41 ml, 2.9 mmol) in DMF (2 ml), was added and the mixture was heated at 60°C for 24 h. The polymer was filtered off and the filtrate was poured in an aqueous HCl solution and extracted with ether (3 × 20 ml). The combinated organic layers were dried (MgSO$_4$) and the solvent was removed under vacuum. After purification by flash chromatography with a (9:1) mixture of cyclohexane/ethyl acetate as eluent, the product **24b** was obtained as a pale yellow oil (50% yield).

3-Phenylcyclohexan-1-one **24b:** ^{1}H-NMR (CDCl$_3$): δ 7.20–6.80 (5H, m, $\underline{H}$ arom), 2.35–0.90 (9H, m, C$\underline{H}$, C$\underline{H}_2$). ^{13}C-NMR (CDCl$_3$): δ 211 ($\underline{C}$O), 144 ($\underline{C}$ arom), 128.7 ($\underline{C}$ arom), 126.7 ($\underline{C}$ arom), 126.6 ($\underline{C}$ arom), 48.9 (CO$\underline{C}$H$_2$CHPh), 44.7 ($\underline{C}$HPh), 41.2 (CH$_2\underline{C}$H$_2$CO), 32.7 (CH$_2\underline{C}$H$_2$CHPh), 25.5 ($\underline{C}$H$_2$CH$_2$CHPh).

*4.12.5. Synthesis of 3-(p-methoxyphenyl)cyclohex-1-ene **24c** by a Heck type reaction, catalyzed by palladium (0) complexes generated from Pd(OAc)$_2$ and supported phosphine borane **12***

Supported phosphine borane **12** (66 mg, 6.4 mol%) was added to a solution of Pd(OAc)$_2$ (7 mg, 3 mol%), 4-iodoanisole **22b** (234 mg, 1.0 mmol), cyclohexene **23c** (304 µl, 3.0 mmol), triethylamine (0.41 ml, 2.9 mmol), NEt$_4$Br (308 mg, 2.0 mmol) and H$_2$O (0.1 ml), in DMF (3 ml). The reaction was stirred at 70°C for 60 h, and then the polymer was filtered off. After flash chromatography of the residue on silicagel with a (9:1) mixture of cyclohexane/ethyl acetate as eluent, the product **24c** was obtained as a colorless oil (64% yield).

^{1}H-NMR ($CDCl_3$): δ 7.07 (2H, d, $^3J_{HH} = 9.5$ Hz, $\underline{H}$ arom), 6.80 (2H, d, $^3J_{HH} = 9.5$ Hz, $\underline{H}$ arom), 5.64 (2H, m, $C\underline{H}$=$C\underline{H}$), 3.70 (3H, s, $C\underline{H}_3O$), 2.60 (1H, m, $C\underline{H}$), 1.70 (6H, m, $C\underline{H}_2$). ^{13}C-NMR ($CDCl_3$): δ 157.75 (C arom), 139.51 (C arom), 127.69 ($\underline{C}$H=CH), 126.92 (C arom), 126.79 (C arom), 113.69 (CH=$\underline{C}$H), 55.19 ($\underline{C}H_3O$), 39.23 ($\underline{C}$HPh), 33.58 ($\underline{C}H_2CH$=CH), 29.96 ($\underline{C}H_2$CHPh), 25.91 ($CH_2\underline{C}H_2CH_2$).

*4.12.6. Hydrogenation of α-acetamidocinnamic acid **26** catalyzed by Rh (I) complexes generated from $RhCl_3$, and the supported phosphine boranes **12–15***

4.12.6.1. Typical procedure. The supported phosphine borane **12** (99 mg, 0.096 mmol, 9.6 mol%) was added to a solution of $RhCl_3$ (6 mg, 0.029 mmol, 2.9 mol%) in pure ethanol (1 ml), and the mixture was heated at reflux under argon for 1 h. The solution of α-acetamidocinnamic acid **26** (203 mg, 1.0 mmol) and the catalyst previously prepared in dry methanol (10 ml), was stirred at r.t. in an autoclave under hydrogen pressure (10 bars). After 24 h, the polymer bearing the catalyst was filtered off and washed with methanol. The filtrate was concentrated under vacuum and the residue was extracted with NaOH (0.5 M). The aqueous layer was filtered and acidified with HCl (1 M). The mixture was extracted with ether (3 × 25 ml). The recombinated organic phases were washed with water (5 ml), dried ($MgSO_4$) and the solvent removed. The reduction rate was deduced from the ^{1}H-NMR spectra of the crude product.

*4.12.6.2. α-Acetamidocinnamic acid **26**.* ^{1}H-NMR (DMSO D_6): δ 9.46 (1H, s, $CO_2\underline{H}$), 7.62–7.59 (2H, d, $^3J = 7$Hz, $\underline{H}$ arom), 7.50–7.21 (3H, m, $\underline{H}$ arom), 7.09 (1H, s, $C\underline{H}$=C), 2.89 (1H, sl, $N\underline{H}$), 2.50 (3H, s, $C\underline{H}_3CO$).

*4.12.6.3. N-acetyl phenyl alanine **27**.* ^{1}H-NMR (DMSO D_6): δ 7.30 (5H, s, $\underline{H}$ arom), 4.45 (1H, m, $C\underline{H}$), 3.08 (1H, dd, $^2J_{HH} = 14$ Hz, $^3J_{HH} = 4$ Hz, $PhCH(\underline{H})$), 2.86 (1H, dd, $^2J_{HH} = 14$ Hz, $^3J_{HH} = 12$ Hz), 2.50 (1H, sl, $N\underline{H}$), 1.78 (3H, s, $C\underline{H}_3CO$).

The hydrogenation of **26** catalyzed with the recovered catalyst was realized under the same conditions reported above, without addition of rhodium source.

*4.12.7. Hydrogenation of α-acetamidocinnamic acid **26** catalyzed by Rh (I) complexes generated from $[Rh(COD)Cl]_2$ and supported phosphine **16***

A solution of $[Rh(COD)Cl]_2$ (7.4 mg, 0.015 mmol, 1.5 mol%) in dry ethanol (1 ml), was stirred under argon overnight at r.t. with supported phosphine **16** (97 mg, 0.048 mmol, 4.8 mol%). Then, the catalyst was introduced following the procedure described Section 4.12.6, with a reaction time of 48 h.

The recovered catalyst was reused for an hydrogenation under the same conditions, and without addition of rhodium source.

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[32] At room temperature and under the reaction conditions, the formation of a small quantity of diallylated product was also observed (< 10% yield).

[33] The polypyrrole **25** has been prepared by chemical polymerization of freshly distilled pyrrole with $FeCl_3$, as described in the experimental part for the polymers **12**, **13**.

[34] The mol% of the phosphine grafted on polypyrrole has been calculated with respect to the phosphorus elemental analysis of **12**, **13** and **16**. In the case of **14** and **15**, the mol% has been estimated from the weight of monomers **5** or **8** which have been electropolymerized on the macroporous carbon.

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