

Syntheses, Structures and Redox Properties of New Macrocyclic Triazatriolefinic Pd⁰ Complexes and Their Polypyrrole Modified Electrodes – Application to Heterogeneous Catalytic Suzuki Cross-Coupling Reactions

Antoni Llobet,^{*[a]} Ester Masllorens,^[a] Montserrat Rodríguez,^[a] Anna Roglans,^{*[a]} and Jordi Benet-Buchholz^[b]

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New triolefinic macrocyclic ligands of the type (*E,E,E*)-1,6,11-tris(arenesulfonyl)-1,6,11-triazacyclopentadeca-3,8,13-triene (aryl: **a** = ferrocenyl, **b** = 4-pyrrol-1-ylphenyl, **c** = 4-methylphenyl) and their Pd⁰ complexes (**1aab**, **1abb** and **1bcc**) have been prepared and characterized. Further structural characterization in the solid state has also been performed by means of X-ray diffraction analysis for the complex **1bcc**. The redox properties of both the ligands and their Pd complexes have been studied using cyclic voltammetric and coulombimetric techniques. In particular, complexes and ligands containing the pyrrole group do polymerize upon exposure to

sufficiently positive potentials, on glassy carbon electrodes, generating highly stable modified electrodes. The new modified electrodes are efficient and selective heterogeneous catalysts for Suzuki cross-couplings, benefiting from simple removal of the catalyst from the reaction vessel. As an example, more than 2·10⁵ metal cycles are achieved at 65 °C in the coupling of phenylboronic acid and cinnamyl bromide. Iodoarenes and phenylboronic acid are also converted into biphenyls with relatively good conversions.

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Introduction

Homogeneous catalysis using transition metal (TM) complexes is a topic of current interest from a basic organic synthetic perspective and also from an industrial point of view.^[1] Highly efficient homogeneous catalytic systems have been described even though their potential industrial applications have been hampered by the cost and difficulty in recovering the TM catalyst and also because of the presence of trace amounts of the TM in the final product.

One of the main strategies designed to overcome the above mentioned drawbacks consists of making TM catalysts heterogeneous by incorporating them into solid materials. In this context, the development of highly efficient catalysts to compensate for TM complex cost and the fabrication of robust heterogeneous systems with negligible leaching, is essential in order to consider them as potential candidates for the scale up process at an industrial plant.

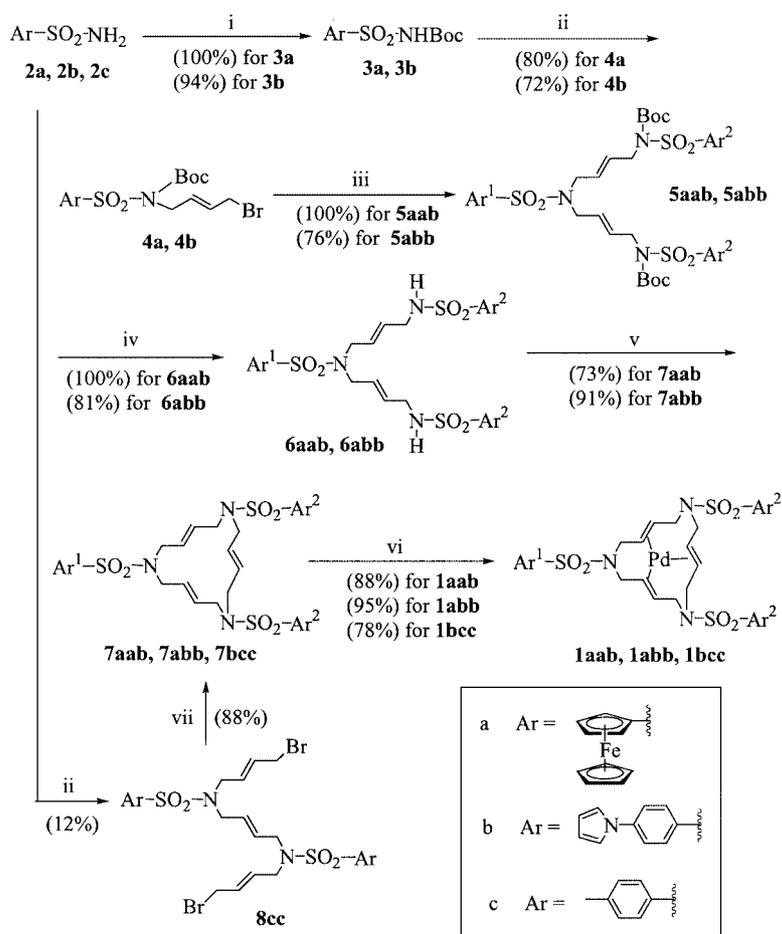
Different approaches for making TM catalysts heterogeneous have been recently reviewed.^[1b,2] Very elegant stra-

tegies based on biphasic systems (aqueous-organic^[2b,3] or fluorous-organic^[4] systems) have been developed in the last decade. Organic^[1b,5] and inorganic^[1b,6] polymer matrices have also been extensively used to immobilize TM catalysts. Among them, pyrrole electropolymerization is an attractive and convenient method given the synthetic versatility of the monomers and the stability of the resultant polypyrrole films.^[7] In general, these films attached to the electrode surface via an electropolymerization process are much more stable than those obtained by simple deposition on materials such as polystyrene,^[8] Nafion^[9] or carbon paste.^[10] The stability of the film is an important factor since it minimizes potential leaching processes from the solid surface. Furthermore the high electrical conductivity of the polypyrrole films allows the use of the conveniently designed electroactive ancillary groups, which do not participate in the catalytic transformation, but allow important aspects of the process to be monitored and thus act as built in chemical sensors.

Given the many positive aspects of the polypyrrole films just described, it is striking that they have been scarcely used with carbon-carbon bond formation catalysts in order to introduce heterogeneity. In this context it is worth mentioning the work of Jugé et al.^[11] in which they initially functionalized the polypyrrole backbone with phosphane ligands. Subsequently the catalyst was generated in situ upon adding an appropriate Pd⁰ complex.

^[a] Departament de Química, Universitat de Girona, Campus Montilivi S/N, 17071 Girona, Spain
Fax: (internat.) +34-972418150
E-mail: antoni.llobet@udg.es
anna.roglans@udg.es

^[b] BIS-SUA-SPA X-ray Laboratory, Geb. Q18; Raum 490, Bayer AG, 51368 Leverkusen, Germany



Scheme 1. Synthetic strategy; (i) $(t\text{BuOCO})_2\text{O}$, Et_3N , DMAP, CH_2Cl_2 , 3.5 h.; (ii) 4 equiv. (*E*)-1,4-dibromo-2-butene, K_2CO_3 , CH_3CN , reflux, 15 h (for **4a**), 7 h (for **4b**), 23 h (for **8cc**); (iii) to give **5aab**: 0.5 equiv. (4-pyrrol-1-ylphenyl)sulfonamide **2b**, K_2CO_3 , CH_3CN , reflux, 16 h; to give **5abb**: 0.5 equiv. ferrocenesulfonamide **2a**, K_2CO_3 , CH_3CN , reflux, 10 h; (iv) $\text{HCl}_{(\text{aq})}$, EtOAc , room temp., 2 h for **7aab**; $\text{HCl}_{(\text{g})}$, CH_2Cl_2 , room temp., 2 h for **7abb**; (v) 1 equiv. (*E*)-1,4-dibromo-2-butene, K_2CO_3 , CH_3CN , reflux, 16 h (for **7aab**) and 20 h (for **7abb**); (vi) 1.2 equiv. $\text{Pd}(\text{dba})_2$, THF, reflux, 1 h; (vii) 1 equiv. **2b**, K_2CO_3 , CH_3CN , reflux, 24 h

During the last two years, synthetic procedures for novel types of Pd^0 -triazatriolefinic macrocyclic complexes such as (*E,E,E*)-1,6,11-tris(arenesulfonyl)-1,6,11-triazacyclopentadeca-3,8,13-trienepalladium(0), **1**, (see Scheme 1) have been reported.^[12] These phosphane-free palladium(0) complexes are active and efficient catalysts for Suzuki cross-couplings,^[13] butadiene telomerization,^[14] and alkyne hydroarylation in ionic liquids.^[15] They have also been anchored in polystyrene matrices allowing the catalyst to be separated from reaction products by simple filtration for subsequent re-use.^[13]

We have recently reported^[16] the preparation of related 15-membered macrocycles functionalized with ferrocenyl units at the sulfonamide groups, and their palladium(0) complexes. We have also reported^[17] high activity and quantitative recovery of palladium(0) complexes, **1**, for the Heck reaction of diazonium salts with acrylates and styrene in a homogeneous phase.

Herein we present the synthesis, spectroscopic and electrochemical properties of new 15-membered triolefinic ligands containing pyrrole and/or ferrocene groups together with their corresponding Pd^0 complexes **1aab**, **1abb**, and

1bcc (Scheme 1). Their redox properties as well as their chemical and electrochemical polymerization processes are also described. Finally the capacity of the corresponding modified electrodes to catalyze Suzuki cross-coupling reactions has been analyzed using two different substrates.

Results and Discussion

Synthesis and Structures

The preparation of the triaza olefinic ligands and their unsaturated 16-electron Pd^0 complexes, **1aab**, **1abb** and **1bcc**, is outlined in Scheme 1, according to the general method for the synthesis of related compounds.^[12,16] Pd^0 complexes **1aab** and **1abb** were obtained in overall yields of 51% and 36%, respectively. The low yield for complex **1abb** was due to the poor solubility of several intermediates conferred by the two pyrrole groups. Complex **1bcc** was obtained in 8% overall yield by a different and more straightforward synthetic pathway (see Scheme 1). The main problem of this synthesis was that the bis(sulfonamide) **8cc** was obtained as the minor product, the major one (46% yield)

being the monosulfonamide, *N,N*-bis[(*E*)-4-bromo-2-butenyl](4-methylphenyl)sulfonamide. Optimization of this step was not successful.^[12a]

This versatile synthetic route allowed the aromatic groups to be easily changed. Thus, these aromatic groups can be used as auxiliary substituents to perform specific functions without modifying the intrinsic coordinating properties of the ligand. In the present case, ferrocene was chosen since it acts as a quantitative electrochemical sensor. On the other hand, an *N*-bonded pyrrole group was also selected since it converts the Pd complex into a monomer which can be easily polymerized. At sufficiently positive anodic potentials the pyrrole group polymerizes, ejecting its α -hydrogen atoms,^[7] while forming a relatively stable and insoluble conducting polypyrrole material. This material strongly adheres to the electrode surface to which the Pd-triolefinic complex has been covalently attached.

The crystal structure of complex **1bcc**·CH₂Cl₂ was solved by means of a single-crystal X-ray diffraction analysis. Figure 1 presents the ORTEP diagram of the molecule including selected bond lengths and angles with the corresponding labeling scheme.

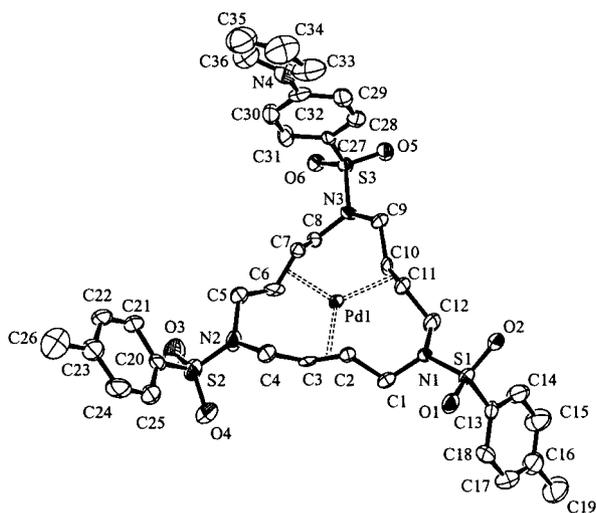


Figure 1. ORTEP plot (50 %) of complex **1bcc**, hydrogen atoms are omitted to fully appreciate the geometry of the complex; selected distances [Å] and angles [°]: Pd1–C2 2.196(6), Pd1–C3 2.216(7), Pd1–C6 2.164(17), Pd1–C7 2.214(9), Pd1–C10 2.186(7), Pd1–C11 2.187(7); C10–Pd1–C11 36.7(3), C10–Pd1–C6 115.9(4), C11–Pd1–C6 151.7(4), C10–Pd1–C2 121.9(3), C11–Pd1–C2 86.7(3), C6–Pd1–C2 121.6(4), C10–Pd1–C3 152.4(3), C11–Pd1–C3 122.5(3), C6–Pd1–C3 85.5(5), C2–Pd1–C3 37.0(2), C10–Pd1–C7 85.5(3), C11–Pd1–C7 117.9(3), C6–Pd1–C7 34.9(4), C2–Pd1–C7 151.6(3), C3–Pd1–C7 119.4(3), C3–C2–Pd1 72.3(4), C1–C2–Pd1 112.4(5), C2–C3–Pd1 70.7(4), C4–C3–Pd1 111.7(5), C5–C6–Pd1 114.4(10), C7–C6–Pd1 74.6(8), C8–C7–Pd1 111.3(7), C6–C7–Pd1 70.5(8), C11–C10–Pd1 71.7(4), C9–C10–Pd1 115.0(5), C10–C11–Pd1 71.6(4), C12–C11–Pd1 115.2(5)

The molecular structure of **1bcc** shows the macrocyclic ligand, **7bcc**, with all the olefinic *trans* double bonds coordinated to the palladium. The central point of the olefins and the palladium are all nearly situated in the same plane and

thus the coordination of the palladium is slightly distorted trigonal planar. Bond lengths and angles are within the expected ranges for this type of complex.^[12b] The three nitrogen atoms of the sulfonamides (N1, N2, N3) and the palladium center are also situated very close to a plane which will from now on be referred to as the main plane. The Pd–C bonds form a triangle with each olefinic group generating a three paddle helix centered at the palladium metal atom. It is also worth mentioning that the Pd complex suffers a slight disorder that is manifested in the chain of four carbon atoms (C5 to C8 with an occupancy factor of 80% and C5' to C8' with 20%) that links the amine atoms N2 and N3. For the molecular conformation with 80% occupancy, two of the paddles are oriented up (Pd1–C6–C7, Pd1–C10–C11) and one down (Pd1–C2–C3) if the helix is observed in a clockwise manner (following increasing values of the atom labeling scheme) with the helix parallel to the main plane, manifesting the asymmetry of the helix with regard to a hypothetical pseudo C₃ rotation axis perpendicular to the mentioned main plane. This relative orientation of the paddles is directly related to the conformation of the three six-membered rings fused to them containing N1 (Pd1, C11, C12, N1, C1, C2), N2 (Pd1, C3, C4, N2, C5, C6) and N3 (Pd1, C7, C8, N3, C9, C10), respectively. Thus when two neighboring paddles have different orientations, both a chair or a boat conformation are possible for the six member ring fused to them but when they have the same orientation then only a distorted chair or a distorted boat is possible. Indeed, two chair conformations were obtained for the six-membered rings containing the N1 and N2 atoms, respectively, whereas opposite orientations and a distorted boat was found for N3. The disordered atoms contained in the molecule with a 20% occupancy generate a paddle that has the opposite orientation with respect to that of the molecule with the 80% occupancy. The sulfonamides are oriented in such a way that the aromatic substituents are situated at 121.9° (C13–C18), 128.5° (C20–C25) and 97.3° (C27–C32) with regard to the main plane, with two of them directed over the plane, one up (S1, S3), and one down (S2). In the S3 case the *N*-pyrrolic substituent bonded to the phenyl ring is significantly rotated [C36–N4–C32–C30 torsion angle of –27.1°] to avoid steric interactions with its neighboring hydrogen atoms.

Redox Properties and Catalyst Immobilization

The redox properties of complexes **1aab**, **1abb** and **1bcc** were investigated by means of cyclic voltammetric and coulombimetric techniques. Figure 2 (A) shows the cyclic voltammograms of **1aab** in CH₂Cl₂+0.1 M *n*Bu₄NPF₆ at a glassy carbon disk electrode using Ag/10 mM Ag⁺ as the reference electrode in the dry box. By scanning anodically starting at 0.0 V a first wave was observed associated with the Fe^{III}/Fe^{II} couple at $E_{1/2} = 0.561$ V ($E_{p,a} = 0.680$ V, $E_{p,c} = 0.442$ V, $\Delta E = 232$ mV). The occurrence of a relatively high value of ΔE is a common phenomenon found in similar transition metal complex polymerization sys-

tems,^[18a] and is related to the intrinsic nature of the immobilized species as well as to the multiple processes which are taking place simultaneously.^[7]

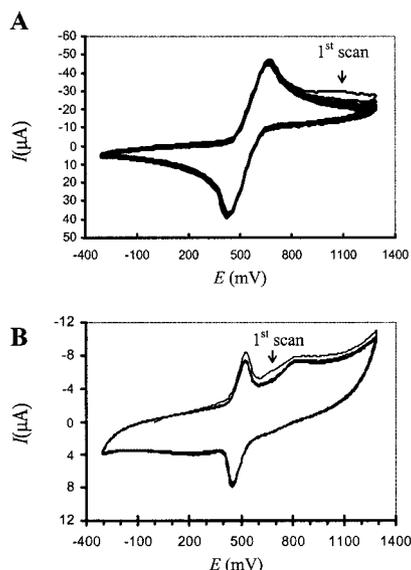


Figure 2. Top: Growth of a **C-glassy/poly-1aab** during the first 20 consecutive cyclic voltammetric scans on a glassy carbon disk electrode (3 mm diameter) in a 1 M solution of **1** in $\text{CH}_2\text{Cl}_2+0.1$ M TBAP ($\nu = 0.1$ V/s); bottom: cyclic voltammetric scan of **C-glassy/poly-1aab** ($\Gamma = 3.10 \times 10^{-10}$ mol cm^{-2}) upon transferring it to a blank electrolyte solution $\text{CH}_2\text{Cl}_2+0.1$ M TBAP ($\nu = 0.1$ V/s); first and four consecutive scans

A second small and broad wave was also observed in the first scan with $E_{p,a} = 1.05$ V which can be assigned to the irreversible oxidation of the pyrrole group with concomitant polymerization (the observation of this wave only in the first scan is typical for this kind of system and is related to the changes experienced on the electrode surface after the deposition of the first polypyrrole layer^[7b,7c]). Modified electrodes, with units of the **1aab** monomer covalently bonded to the polypyrrole chain, can be obtained by scanning the potential region repeatedly from 0.0 V up to 1.30 V. This is depicted in Figure 2 (A) where, upon scanning 20 times over the indicated potential domain, a small but consistent increase of the intensity wave for the $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ couple was observed thus indicating the growth of the **C-glassy/poly-1aab** film on the electrode surface. Figure 2 (B) shows the cyclic voltammetric response of the film when transferred to a blank electrolyte solution. As in the previous case, a first wave due to the $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ couple can be observed ($E_{1/2} = 0.490$ V, $E_{p,a} = 0.538$, $E_{p,c} = 0.442$, $\Delta E = 96$ mV), as well as a second one, with $E_{p,a} = 0.83$ V, that can be assigned to the electrochemically irreversible oxidation of palladium. The corresponding Pd^{II} reduction takes place through a broad wave found between 0 and 0.4 V. The electrochemical response of the Pd metal center can be determined from comparison of this system with the behavior shown in homogeneous phase by a family of related Pd complexes that we have described recently.^[16] Also, the

polymerization performed on the corresponding macrocyclic ligand **7aab** under equivalent conditions, does not show any significant wave around 0.8 V. This, together with the catalytic activity of the polymerized free ligands and complexes (vide infra), gives compelling evidence that the Pd metal remains coordinated to the triolefinic ligands in the generated modified electrodes containing the polypyrrolic films.

The films described here are highly stable. Upon scanning more than 40 times over the -2.0 to $+2.0$ V potential region in a fresh electrolyte solution, the decrease in charge under the $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ wave is insignificant. There is also some evidence for the preservation of the coordination environment of the Pd metal center in the complex structure, since the intensity of the anodic peak, corresponding to the $\text{Pd}^0 \rightarrow \text{Pd}^{\text{II}}$ transition, also maintains its intensity.

Similar films can also be built up by maintaining the electrode in the potential range 0.6–0.8 V with a potentiostat. As an example a film grown by maintaining $E_{\text{app}} = 0.80$ V, until a total charge of 7.22×10^{-3} C had passed, yielded a thin film with an apparent surface coverage of $\Gamma = 1.53 \times 10^{-9}$ mol/ cm^2 .

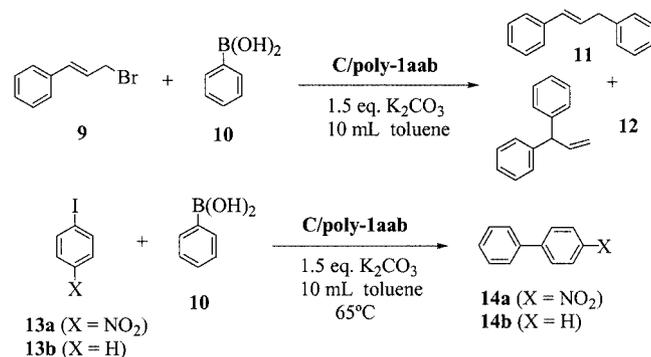
It is important to point out here that the whole process can be performed outside the dry box with carefully dried solvents under N_2 or Ar, but the Pd wave was only observed under rigorously anhydrous conditions in the dry box.

The polymerization process was also carried out for **1aab** utilizing carbon felt electrodes ($1.0 \times 0.5 \times 0.5$ cm), using the same protocols as with the glassy carbon electrodes previously described thus generating the corresponding **C-felt/poly-1aab**. Under these conditions, and using the voltamperometric methodology, different electrodes were generated with different amounts of deposited complex that, after proper cleaning, were used as catalysts. Their performance is described in the following section.

The redox properties of **1abb** parallel those of **1aab** except that the ferrocene waves have half the intensity observed in the previous case, as expected. For the complex **1bcc**, the absence of ferrocene substituents prevents the use of electrochemical monitoring since the polypyrrole backbone wave was not observed in our case, but they could also be used for catalytic purposes. The free ligands **7aab** and **7abb** can also be polymerized in the same manner as described for the Pd complex **1aab** generating very similar voltammograms except for the obvious absence of the wave due to the irreversible oxidation of Pd.

Catalytic Activity

To examine the catalytic efficiency and recovery of the **C-felt/poly-1aab** materials, two model Suzuki-type cross-coupling reactions were tested, namely the reaction of cinnamyl bromide, **9**, with phenylboronic acid, **10**, to afford *trans*-1,3-diphenylpropene, **11**,^[19] together with minor amounts of regioisomer **12**,^[20] and that of phenylboronic acid **10** with the iodoarenes **13a–b**, leading to the biphenyls **14a–b**^[21] (see Scheme 2 and Table 1)



Scheme 2. Suzuki-type cross-coupling reactions tested

Typically, the reaction was carried out by stirring a reaction mixture containing cinnamyl bromide, phenylboronic acid, potassium carbonate, and the catalyst immobilized onto the electrode surface in an anhydrous, degassed toluene solution under nitrogen. The electrode was recovered by removing it from the solution vessel, and washing with toluene before using it again in a new reaction.

Entry 1 in Table 1 shows that at 27 °C after a reaction time of 48 hours, up to 10 mL total volume of the system “C-felt/poly-1aab, 16.8·nmols/9, 15.0 mM; 10, 22.5 mM/K₂CO₃, 22.5 mM/toluene”, is capable of generating 10.50 mM *trans*-1,3-diphenylpropene, **11**, and 1.65 mM of its isomeric product 3,3-diphenylpropene, **12**. This implies a substrate conversion of 81% with a TON of 7200 cycles and a TOF of 150 cycles per hour at 48 h. When the catalytic material had been reused in a fresh system, a sharp decrease in its activity (entry 2) was observed due to partial deactivation of the supported catalyst by undesired side reactions. It is interesting to point out here that at this temperature the isomeric ratio (**11**:**12**) remains relatively constant in the range 5.0–7.0.

Entries 3–5 in Table 1 show a spectacular increase of the catalyst performance when the temperature and the Substrate/Cat ratio are increased from 27 to 65 °C and from 8930 up to 13800 respectively leaving the rest of the system parameters unchanged. In particular, entry 3 shows a substrate conversion of 96% in 24 h with an isomeric ratio of 15.0. This result clearly shows that upon increasing the temperature and the Substrate/Cat ratio, the pathways that lead

Table 1. Suzuki coupling between cinnamyl bromide, **9**, and the iodoarenes, **13a–b**, with phenylboronic acid **10**.

Entry	T, °C	Substrate, mM	Cat% ^[a] (nmols)	Substrate/Cat ^[b] (×10 ³)	Time, hours	Product, mM	Conversion, % ^[a]	TON (10 ³)
1	27	9 (15.0)	1.12·10 ⁻² (16.80)	8.93	48	11 (10.50) 12 (1.65)	81	7.2
2	27	9 (15.0)	1.12·10 ⁻² (16.80) ^[c]	8.93	48	11 (2.85) 12 (0.45)	22	1.9
3	65	9 (15.0)	7.27·10 ⁻³ (10.91)	13.8	24	11 (13.50) 12 (0.90)	96	12.5
4	65	9 (15.0)	7.27·10 ⁻³ (10.91) ^[c]	13.8	24	11 (12.90) 12 (0.45)	89	12.2
5	65	9 (15.0)	7.27·10 ⁻³ (10.91) ^[d]	13.8	24	11 (7.20) 12 (0.45)	51	7.0
6	65	9 (80.0)	9.30·10 ⁻⁴ (1.40)	107.5	24	11 (67.20) 12 (4.00)	89	95.3
7	65	9 (80.0)	9.30·10 ⁻⁴ (1.40) ^[c]	107.5	24	11 (52.80) 12 (4.00)	71	79.8
8	65	9 (80.0)	9.30·10 ⁻⁴ (1.40) ^[d]	107.5	24	11 (32.80) 12 (2.40)	44	48.0
9	65	13a (78.7)	1.51·10 ⁻³ (11.88)	66.2	24	14a (23.61)	30	19.8
10	65	13a (78.7)	1.51·10 ⁻³ (11.88) ^[c]	66.2	24	14a (25.97)	33	21.8
11	65	13a (78.7)	1.51·10 ⁻³ (11.88) ^[d]	66.2	24	14a (13.77)	17.5	11.6
12	65	13a (78.7)	1.51·10 ⁻³ (11.88) ^[e]	66.2	24	14a (3.15)	4	2.4
13	65	13b (87.4)	1.56·10 ⁻³ (13.63)	64.1	24	14b (18.35)	21	13.5
14	65	13b (87.4)	1.56·10 ⁻³ (13.63) ^[c]	64.1	24	14b (17.04)	19.5	12.5
15	65	13b (87.4)	1.56·10 ⁻³ (13.63) ^[d]	64.1	24	14b (8.74)	10	6.6
16	65	13b (87.4)	1.56·10 ⁻³ (13.63) ^[e]	64.1	24	14b (3.50)	4	2.7

^[a] Cat. is C-felt/poly-1aab. % indicates the molar percentage of the Pd complex in the C-felt/poly-1aab polymer with respect to the substrate. The total amount of the Pd complex in the C-felt/poly-1aab material in nanomoles is indicated in parentheses. ^[b] Molar ratio. ^[c] First reutilization. ^[d] Second reutilization. ^[e] Third reutilization.

to **11** are kinetically favored with regard to those that lead to **12**. Entries 4 and 5 show the effect of reusing the catalyst after cleaning and soaking in a fresh solution with a slight decrease of the activity. Several experiments were performed in which the Substrate/Cat ratio was increased but the temperature was maintained at 65 °C. A 100% conversion and 100% isomeric purity was obtained although the deactivation became more severe upon reuse. Finally in entries 6–8 the Substrate/Cat ratio was strongly increased up to 107500. This decreased conversion to 89% and isomer selectivity to 16.8 but reduced the deactivation process on reuse (entries 7, 8) and generated an impressive overall TON of 223000. This is about an order of magnitude higher than had been described previously by anchoring similar Pd complexes but using polystyrene as a solid matrix.^[13]

The results described above clearly show how, for the present system, the temperature and Substrate/Cat ratio are key parameters that strongly influence the catalytic performance. In particular the Substrate/Cat ratio can modulate: a) substrate conversion, b) isomer selectivity, c) reuse capacity and d) the TOF as well as the TON.

Iodoarene substrates were also tested for coupling reactions with phenyl boronic acid. Entries 9–16 in Table 1 show the results when **10** was treated with 4-iodonitrobenzene, **13a**, and iodobenzene, **13b**, respectively, using the similar catalytic system parameters as in the previous case i.e. at 65 °C and with a reaction time of 24 hours. In these cases conversions were lower (entries 9, 13), but the catalyst could be reused once without any significant loss of activity (entries 10, 14). In the second reuse (entries 11, 15) the catalyst activity was reduced to 50% of its initial performance and in the third (entries 12, 16) the activity was reduced dramatically until only 4% substrate conversion was observed.

To evaluate the degree of leaching during the catalytic experiments in the Suzuki cross-coupling reactions, a quantitative Pd analysis was carried out using Atomic Absorption Spectroscopy (AAS). It was shown that about 5% of the initial Pd had dissolved in the reaction solution during the first 24 h of the reaction. Nevertheless, this “leached Pd” does not significantly catalyze the Suzuki cross-coupling reaction, as verified by removing the **C-felt/poly-1aab** from a solution after a reaction time of 12 h and allowing the process to continue under the same conditions for a further 24 hours (see entry 9, Table 1). This experiment is thus evidence that the catalytic process proceeds in a true heterogeneous manner.^[22]

Control experiments were carried out in the absence of the Pd complex. Suzuki coupling between cinnamyl bromide, **9**, and phenylboronic acid, **10**, under the same conditions as in entry 3 (Table 1) but without **C-felt/poly-1aab** (“**9**, 15.0 mM; **10**, 22.5 mM/K₂CO₃, 22.5 mM/toluene” up to 10 mL total volume at 65 °C for 24 h), afforded 4.65 mM of **11** and 0.3 mM of **12** (33% of conversion). The conversion between 4-iodonitrobenzene, **13a**, and phenylboronic acid, **10**, under similar conditions as in entry 9 (“**13a**, 78.7 mM;

10, 118 mM/K₂CO₃, 118 mM/toluene” up to 10 mL total volume at 65 °C for 24 h) and without **C-felt/poly-1aab** is negligible.

Conclusion

New Pd⁰ triolefinic complexes containing ancillary pyrrole and/or ferrocene groups have been prepared and characterized. These groups have been attached with the purpose of carrying out specific functions namely, electrochemical monitoring and anchoring via anodic electropolymerization, respectively. The new polypyrrole modified electrodes prepared in this way represent the first examples reported in the literature of a successful phosphane-free system, capable of efficiently catalyzing Suzuki cross-coupling reactions. The different parameters that govern system reactivity have been established putting forward the strong appeal of these new materials with regard to their high thermal and air stability as well as excellent solvent resistance.

Experimental Section

General Remarks: ¹H NMR (¹³C NMR) spectra were recorded at 250 MHz (62.5 MHz) or at 200 MHz (50 MHz) using Me₄Si as internal standard. Chemical shifts are given in δ units. ESI mass spectra were acquired using a Navigator quadrupole instrument. The instrument was operated in the positive ion mode (ES+) at a probe tip voltage of 3 kV. HRMS and ICP analyses were obtained at “SCAI Unidad de Espectrometría de Masas de la Universidad de Córdoba”, using a Micromass VG Mass Spectrometer and a Perkin–Elmer AA spectrophotometer respectively. Elemental analyses were determined at “Servei d’Anàlisi de la Universitat de Girona”.

Cyclic voltammetric experiments and controlled-potential coulometry were carried out in a PAR 263A EG&G potentiostat using a three electrode cell. Glassy carbon disk electrodes (3 mm diameter) from BAS and carbon felt electrodes (0.5 × 0.5 × 0.5 cm) from SOFACEL were used as the working electrodes, platinum wires as auxiliary and Ag/10 mM Ag⁺ as reference electrodes. Glassy carbon disk electrodes were routinely polished with 1 μm diamond paste. Cyclic voltammograms were performed in the dry box or outside with carefully dried solvents under N₂ or Ar, and at a potential scan rate of 100 mV/s. All electrochemical experiments were conducted in CH₂Cl₂ containing 0.1 M (*n*Bu₄N)(PF₆) (TBAP) as the supporting electrolyte. All *E*_{1/2} values reported were estimated from cyclic voltammetry as the average of the oxidative and reductive peak potentials (*E*_{p,a} + *E*_{p,c})/2. Unless explicitly mentioned the concentration of the complexes was approximately 1 mM.

The protocol used for the preparation of the modified electrodes consisted of performing 20 repetitive CV scans at 100 mV/s from *E*_i = 0.0 V to *E*_{c1} = 1.3 V. Catalyst coverage for the modified electrodes was evaluated from the corresponding Fe^{III}/Fe^{II} wave charge.

Coupling product evolution was followed on a Hewlett–Packard 5890 gas chromatograph using naphthalene as an internal standard.

Palladium(0) complexes **1aab**, **1abb** and **1bcc** were prepared according to a previously reported method described for macrocycles containing different arene units.^[12a,16] Physical properties and spectroscopic data for all new compounds are described below.

(4-Pyrrol-1-ylphenyl)sulfonamide (2b): Compound was prepared by heating to reflux sulfanilamide (2.01 g, 11.4 mmol) and 2,5-dimethoxytetrahydrofuran (1.52 mL, 11.4 mmol) in glacial acetic acid according to a method for aniline derivatives^[23] (yield 1.95 g, 8.8 mmol, 75%). M.p. 246–247 °C. IR (KBr): $\tilde{\nu}$ = 3349, 3260, 1600, 1513, 1334, 1296, 1165 cm⁻¹. ¹H NMR (200 MHz, [D₆]DMSO): δ = 6.12 (t, *J* = 2.2 Hz, 2 H), 7.17 (s, 2 H), 7.29 (t, *J* = 2.2 Hz, 2 H), 7.67 (AA' part of a AA'BB' system, *J* = 8.8 Hz, 2 H), 7.58 (BB' part of a AA'BB' system, *J* = 8.8 Hz, 2 H). ¹³C NMR (50 MHz, [D₆]DMSO): δ = 111.9, 119.4, 119.6, 127.9, 140.8, 142.5.

***N*-(*tert*-Butyloxycarbonyl)ferrocenylsulfonamide (3a)**: Starting from **2a** (0.80 g, 3.0 mmol); orange solid (yield 1.10 g, 3.0 mmol, 100%). M.p. 149–151 °C.^[16] IR (KBr): $\tilde{\nu}$ = 3247, 3103, 2977, 1730, 1435, 1339, 1243, 1133 cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ = 1.42 (s, 9 H), 4.39 (s, 5 H), 4.42–4.45 (m, 2 H), 4.80–4.82 (m, 2 H), 7.05 (broad s, 1 H). ¹³C NMR (50 MHz, CDCl₃): δ = 27.9, 69.8, 70.9, 83.5, 85.8, 149.5. ESI-MS (*m/z*): 383 [M + NH₄]⁺, 365 [M]⁺. C₁₅H₁₉FeNO₄S (365.23): calcd. C 49.33, H 5.24, N 3.83; found C 49.39, H 5.28, N 3.66.

***N*-(*tert*-Butyloxycarbonyl)(4-pyrrol-1-ylphenyl)sulfonamide (3b)**: Starting from **2b** (0.50 g, 2.3 mmol); colorless solid (yield 0.68 g, 2.1 mmol, 94%). M.p. 162–163 °C. IR (KBr): $\tilde{\nu}$ = 3312, 1741, 1594, 1511, 1415, 1340, 1151 cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ = 1.42 (s, 9 H), 6.41 (t, *J* = 2.3 Hz, 2 H), 7.17 (t, *J* = 2.3 Hz, 2 H), 7.53 (AA' part of the AA'BB' system, *J* = 8.8 Hz, 2 H), 8.08 (BB' part of the AA'BB' system, *J* = 8.8 Hz, 2 H). ¹³C NMR (50 MHz, [D₆]DMSO): δ = 27.5, 82.2, 111.7, 118.8, 119.1, 129.2, 135.3, 143.2, 149.8. ESI-MS (*m/z*): 340 [M + NH₄]⁺, 323 [M + H]⁺. C₁₅H₁₈N₂O₄S (322.38): calcd. C 55.88, H 5.63, N 8.69; found C 55.52, H 5.60, N 8.49.

***N*-[(*E*)-4-Bromo-2-butenyl]-*N*-(*tert*-butyloxycarbonyl)ferrocenylsulfonamide (4a)**: Starting from **3a** (1.05 g, 2.8 mmol); orange solid (yield 1.15 g, 2.3 mmol, 80%). M.p. 122–124 °C.^[24] IR (KBr): $\tilde{\nu}$ = 2978, 2930, 1721, 1336, 1140 cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ = 1.44 (s, 9 H), 3.93 (d, *J* = 6.4 Hz, 2 H), 4.29 (d, *J* = 5.0 Hz, 2 H), 4.42 (s, 5 H), 4.40–4.43 (m, 2 H), 4.79 (apparent t, *J* = 1.9 Hz, 2 H), 5.67–5.93 (m, 2 H). ¹³C NMR (50 MHz, CDCl₃): δ = 28.0, 31.7, 47.5, 70.2, 70.6, 71.0, 84.0, 87.0, 129.1, 130.3, 150.9. ESI-MS (*m/z*): 561 [M + Na + CH₃CN]⁺, 515 [M + NH₄]⁺, 497 [M]⁺. C₁₉H₂₄BrFeNO₄S (498.21): calcd. C 45.80, H 4.86, N 2.81; found C 45.83, H 4.78, N 2.89.

***N*-[(*E*)-4-Bromo-2-butenyl]-*N*-(*tert*-butyloxycarbonyl)(4-pyrrol-1-ylphenyl)sulfonamide (4b)**: Starting from **3b** (1.33 g, 4.3 mmol); colorless solid (yield 1.36 g, 3.0 mmol, 72%). M.p. 109–110 °C. IR (KBr): $\tilde{\nu}$ = 2973, 2926, 1723, 1593, 1514, 1333, 1157 cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ = 1.39 (s, 9 H), 3.98 (d, *J* = 7.2 Hz, 2 H), 4.47 (d, *J* = 5.5 Hz, 2 H), 5.79–6.08 (m, 2 H), 6.40 (t, *J* = 2.2 Hz, 2 H), 7.17 (t, *J* = 2.2 Hz, 2 H), 7.50 (AA' part of the system AA'BB', *J* = 9.0 Hz, 2 H), 7.99 (BB' part of the system AA'BB', *J* = 9.0 Hz, 2 H). ¹³C NMR (50 MHz, CDCl₃): δ = 27.9, 31.6, 47.3, 84.8, 112.1, 119.0, 119.2, 129.9, 130.2, 130.3, 135.9, 144.2, 150.5. ESI-MS (*m/z*): 493–495 [M + K]⁺, 472–474 [M + NH₄]⁺, 455–457 [M + H]⁺. C₁₉H₂₃BrN₂O₄S (455.37): calcd. C 50.11, H 5.09, N 6.15; found C 49.68, H 5.00, N 6.00.

(*E,E*)-1,11-Bis(*tert*-butyloxycarbonyl)-1,11-bis(ferrocenylsulfonyl)-6-[(4-pyrrol-1-ylphenyl)sulfonyl]-1,6,11-triazaundeca-3,8-diene (5aab):

Starting from **4a** (1.14 g, 2.3 mmol) and **2b** (0.25 g, 1.1 mmol); orange solid (yield 1.20 g, 1.1 mmol, 100%). M.p. 98–99 °C. IR (KBr): $\tilde{\nu}$ = 2977, 2929, 1725, 1596, 1509, 1361, 1132 cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ = 1.40 (s, 18 H), 3.78 (d, *J* = 5.5 Hz, 4 H), 4.23 (d, *J* = 5.5 Hz, 4 H), 4.39–4.44 (m, 14 H), 4.75 (apparent t, *J* = 2.2 Hz, 4 H), 5.39–5.65 (m, 4 H), 6.39 (t, *J* = 2.2 Hz, 2 H), 7.19 (t, *J* = 2.2 Hz, 2 H), 7.50 (AA' part of the system AA'BB', *J* = 8.8 Hz, 2 H), 7.83 (BB' part of the AA'BB' system, *J* = 8.8 Hz, 2 H). ¹³C NMR (50 MHz, CDCl₃): δ = 28.0, 47.6, 47.7, 70.1, 70.6, 71.0, 83.8, 87.2, 111.7, 119.1, 120.0, 126.7, 128.9, 130.5, 136.9, 143.5, 151.0. ESI-MS (*m/z*): 1079 [M + Na]⁺, 1074 [M + NH₄]⁺. C₄₈H₅₆Fe₂N₄O₁₀S₃ (1056.87): calcd. C 54.55, H 5.34, N 5.30; found C 54.56, H 5.49, N 4.92.

(*E,E*)-1,11-Bis(*tert*-butyloxycarbonyl)-1,11-bis[(4-pyrrol-1-ylphenyl)sulfonyl]-6-(ferrocenylsulfonyl)-1,6,11-triazaundeca-3,8-diene (5abb): Starting from **4b** (1.30 g, 2.9 mmol) and **2a** (0.38 g, 1.4 mmol); yellow solid (yield 1.10 g, 1.1 mmol, 76%). M.p. 113–114 °C. IR (KBr): $\tilde{\nu}$ = 2979, 2930, 1729, 1596, 1510, 1356, 1335, 1168 cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ = 1.35 (s, 18 H), 3.73 (d, *J* = 5.0 Hz, 4 H), 4.37–4.39 (m, 11 H), 4.60 (apparent t, *J* = 2.0 Hz, 2 H), 5.51–5.79 (m, 4 H), 6.39 (t, *J* = 2.3 Hz, 4 H), 7.18 (t, *J* = 2.3 Hz, 4 H), 7.52 (AA' part of the system AA'BB', *J* = 8.7 Hz, 4 H), 7.95 (BB' part of the system AA'BB', *J* = 8.7 Hz, 4 H). ¹³C NMR (50 MHz, CDCl₃): δ = 27.9, 47.6, 48.1, 68.6, 70.6, 70.7, 84.5, 87.5, 112.0, 119.0, 119.2, 128.7, 129.2, 130.0, 136.1, 144.0, 150.5. ESI-MS (*m/z*): 1036 [M + Na]⁺, 1014 [M + H]⁺. C₄₈H₅₅FeN₅O₁₀S₃ (1014.02): calcd. C 56.85, H 5.47, N 6.91; found C 56.74, H 5.52, N 6.88.

(*E,E*)-1,11-Bis(ferrocenylsulfonyl)-6-[(4-pyrrol-1-ylphenyl)sulfonyl]-1,6,11-triazaundeca-3,8-diene (6aab): Starting from **5aab** (0.96 g, 0.9 mmol); orange solid (yield 0.76 g, 0.9 mmol, 100%). M.p. 95–96 °C. IR (KBr): $\tilde{\nu}$ = 3274, 2922, 1595, 1508, 1328, 1135 cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ = 3.49 (d, *J* = 4.8 Hz, 4 H), 3.68 (d, *J* = 4.8 Hz, 4 H), 4.38–4.40 (m, 14 H), 4.54–4.64 (m, 6 H), 5.39–5.60 (m, 4 H), 6.40 (t, *J* = 2.2 Hz, 2 H), 7.17 (t, *J* = 2.2 Hz, 2 H), 7.50 (AA' part of the system AA'BB', *J* = 9.0 Hz, 2 H), 7.81 (BB' part of the system AA'BB', *J* = 9.0 Hz, 2 H). ¹³C NMR (50 MHz, CDCl₃): δ = 44.3, 48.7, 68.5, 70.5, 70.7, 87.5, 111.9, 119.0, 119.8, 127.4, 128.9, 130.2, 136.2, 143.6. ESI-MS (*m/z*): 879 [M + Na]⁺, 857 [M + H]⁺. HRMS (*m/z* calcd. for [M + 1]): 857.0888; found 857.0880.

(*E,E*)-1,11-Bis[(4-pyrrol-1-ylphenyl)sulfonyl]-6-[ferrocenylsulfonyl]-1,6,11-triazaundeca-3,8-diene (6abb): Starting from **5abb** (0.53 g, 0.5 mmol); yellow solid (yield 0.34 g, 0.4 mmol, 81%). M.p. 177–178 °C. IR (KBr): $\tilde{\nu}$ = 3277, 2923, 1597, 1509, 1333, 1159 cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ = 3.52–3.54 (m, 8 H), 4.36–4.38 (m, 7 H), 4.54 (apparent t, *J* = 2.0 Hz, 2 H), 5.00 (broad s, 2 H), 5.50–5.52 (m, 4 H), 6.39 (t, *J* = 2.2 Hz, 4 H), 7.15 (t, *J* = 2.2 Hz, 4 H), 7.49 (AA' part of the system AA'BB', *J* = 9.0 Hz, 4 H), 7.90 (BB' part of the system AA'BB', *J* = 9.0 Hz, 4 H). ¹³C NMR (50 MHz, CDCl₃): δ = 44.4, 49.2, 68.6, 70.6, 70.8, 86.8, 111.9, 119.0, 119.9, 128.6, 128.9, 129.0, 136.2, 143.8. ESI-MS (*m/z*): 852 [M + K]⁺, 836 [M + Na]⁺, 814 [M + H]⁺. C₃₈H₃₉FeN₅O₆S₃ (813.79): calcd. C 56.09, H 4.83, N 8.61; found C 56.44, H 5.00, N 8.32.

(*E,E,E*)-1,6-Bis(ferrocenylsulfonyl)-11-[(4-pyrrol-1-ylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-triene (7aab): Starting from **6aab** (0.76 g, 0.9 mmol); orange solid (yield 0.60 g, 0.7 mmol, 73%). M.p. 150–151 °C. IR (KBr): $\tilde{\nu}$ = 2922, 1596, 1508, 1336, 1136 cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ = 3.55 (broad abs., 8 H), 3.70 (broad abs., 4 H), 4.38–4.40 (m, 14 H), 4.55 (apparent t,

$J = 1.9$ Hz, 4 H), 5.50–5.52 (m, 6 H), 6.40 (t, $J = 2.2$ Hz, 2 H), 7.17 (t, $J = 2.2$ Hz, 2 H), 7.51 (AA' part of the system AA'BB', $J = 8.8$ Hz, 2 H), 7.82 (BB' part of the system AA'BB', $J = 8.8$ Hz, 2 H). ^{13}C NMR (50 MHz, CDCl_3): $\delta = 50.6, 50.7, 68.6, 70.6, 70.8, 86.2, 111.9, 119.0, 120.0, 128.5, 128.9, 129.3, 130.0, 135.7, 143.7$. ESI-MS (m/z): 931 [M + Na] $^+$, 908 [M] $^+$. $\text{C}_{42}\text{H}_{44}\text{Fe}_2\text{N}_4\text{O}_6\text{S}_3\text{H}_2\text{O}$ (926.73): calcd. C 54.43, H 5.00, N 6.05; found C 54.13, H 4.98, N 5.81.

(*E,E,E*)-1,6-Bis[(4-pyrrol-1-ylphenyl)sulfonyl]-11-(ferrocenyl-sulfonyl)-1,6,11-triazacyclopentadeca-3,8,13-triene (7abb): Starting from **6abb** (0.86 g, 1.1 mmol); yellow solid (yield 0.83 g, 1.0 mmol, 91%). M.p. 139–140 °C. IR (KBr): $\tilde{\nu} = 2920, 1731, 1596, 1507, 1334, 1160, 1133$ cm^{-1} . ^1H NMR (200 MHz, CDCl_3): $\delta = 3.56$ – 3.71 (m, 12 H), 4.37–4.39 (m, 7 H), 4.54–4.56 (m, 2 H), 5.50–5.60 (m, 6 H), 6.41 (t, $J = 2.2$ Hz, 4 H), 7.16 (t, $J = 2.2$ Hz, 4 H), 7.50 (AA' part of the system AA'BB', $J = 8.8$ Hz, 4 H), 7.81 (BB' part of the system AA'BB', $J = 8.8$ Hz, 4 H). ^{13}C NMR (50 MHz, CDCl_3): $\delta = 50.1, 50.7, 68.5, 70.6, 70.7, 86.0, 111.9, 119.0, 119.8, 119.9, 128.6, 128.9, 129.3, 130.1, 135.5, 143.7$. ESI-MS (m/z): 888 [M + Na] $^+$, 883 [M + NH_4] $^+$, 866 [M + H] $^+$. HRMS (m/z calcd. for [M + 1]): 866.1804; found 866.1810.

(*E,E,E*)-1,14-Dibromo-*N,N*-bis[(4-methylphenyl)sulfonyl]-5,10-diazatetradeca-2,7,12-triene (8cc):^[22] Yield 0.58 g, 0.9 mmol, 12%, starting from **2c** (2.51 g, 10.0 mmol).

(*E,E,E*)-1,6-Bis[(4-methylphenyl)sulfonyl]-11-[(4-pyrrol-1-ylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-triene (7bcc): Starting from **8cc** (0.15 g, 0.23 mmol) and **2b** (0.05 g, 0.23 mmol); colorless solid (yield 0.14 g, 0.2 mmol, 88%). M.p. 127–128 °C. IR (KBr): $\tilde{\nu} = 2921, 1597, 1508, 1334, 1159, 1090$ cm^{-1} . ^1H NMR (200 MHz, CDCl_3): $\delta = 2.43$ (s, 6 H), 3.66–3.75 (m, 12 H), 5.51–5.60 (m, 6 H), 6.40 (t, $J = 2.1$ Hz, 2 H), 7.16 (t, $J = 2.1$ Hz, 2 H), 7.30 (AA' part of the system AA'BB', $J = 8.2$ Hz, 4 H), 7.52 (AA' part of the system AA'BB', $J = 8.6$ Hz, 2 H), 7.65 (BB' part of the system AA'BB', $J = 8.2$ Hz, 4 H), 7.83 (BB' part of the system AA'BB', $J = 8.6$ Hz, 2 H). ^{13}C NMR (50 MHz, CDCl_3): $\delta = 21.5, 50.5, 50.7, 50.8, 111.9, 119.1, 120.0, 123.9, 127.2, 128.9, 129.0, 129.6, 129.8, 135.7, 136.0, 143.6, 143.8$. ESI-MS (m/z): 738 [M + NH_4] $^+$, 721 [M + H] $^+$. $\text{C}_{36}\text{H}_{40}\text{N}_4\text{O}_6\text{S}_3$ (720.92): calcd. C 59.98, H 5.59, N 7.77; found C 59.68, H 5.69, N 7.41.

(*E,E,E*)-1,6-Bis(ferrocenylsulfonyl)-11-[(4-pyrrol-1-ylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-trienepalladium(0) (1aabb): Starting from **7aab** (0.25 g, 0.3 mmol); yellow solid (yield 0.27 g, 0.3 mmol, 88%). M.p. 211–212 °C. IR (KBr): $\tilde{\nu} = 2917, 1596, 1508, 1333, 1137, 904$ cm^{-1} . ^1H NMR (200 MHz, CDCl_3): $\delta = 1.51$ – 1.65 (m, 4 H), 2.75 (t, $J = 11.2$ Hz, 2 H), 2.85–3.15 (m, 2 H), 3.65–3.72 (m, 2 H), 3.80–4.05 (m, 2 H), 4.32–4.81 (m, 14 H), 4.40 (s, 10 H), 6.38 (t, $J = 2.4$ Hz, 2 H), 7.10 (t, $J = 2.4$ Hz, 2 H), 7.45 (AA' part of the system AA'BB', $J = 8.7$ Hz, 2 H), 7.81 (BB' part of the system AA'BB', $J = 8.7$ Hz, 2 H). ^{13}C NMR (50 MHz, CDCl_3): $\delta = 45.1, 45.2, 48.1, 48.2, 49.3, 49.4, 49.5, 68.4, 68.5, 70.6, 70.8, 77.8, 78.1, 78.4, 78.6, 78.7, 78.9, 82.2, 82.9, 83.1, 85.4, 85.5, 85.9, 112.0, 118.9, 119.9, 128.7, 128.9, 134.9, 135.4, 143.7$. ESI-MS (m/z): 1014 [M] $^+$. $\text{C}_{42}\text{H}_{44}\text{Fe}_2\text{N}_4\text{O}_6\text{PdS}_3 \cdot 1/2\text{CH}_2\text{Cl}_2$ (1057.59): calcd. C 48.27, H 4.29, N 5.30; found C 48.33, H 4.32, N 5.34.

(*E,E,E*)-1,6-Bis[(4-pyrrol-1-ylphenyl)sulfonyl]-11-(ferrocenyl-sulfonyl)-1,6,11-triazacyclopentadeca-3,8,13-trienepalladium(0) (1abb): Starting from **7abb** (0.40 g, 0.5 mmol); pale yellow solid (yield 0.43 g, 0.4 mmol, 95%). M.p. 162–163 °C. IR (KBr): $\tilde{\nu} = 2923, 1596, 1508, 1334, 1160$ cm^{-1} . ^1H NMR (200 MHz, CDCl_3): $\delta = 1.50$ – 1.66 (m, 4 H), 2.50–3.20 (m, 4 H), 3.70–3.80 (m, 2 H),

3.90–4.11 (m, 2 H), 4.23–4.77 (m, 10 H), 4.41 (s, 5 H), 6.38 (br. abs., 4 H), 7.10 (br. abs., 4 H), 7.40–7.50 (m, 4 H), 7.78–7.90 (m, 4 H). ESI-MS (m/z): 972 [M + H] $^+$. $\text{C}_{42}\text{H}_{43}\text{FeN}_5\text{O}_6\text{PdS}_3\text{C}_6\text{H}_{14}$ (1058.46): calcd. C 54.47, H 5.43, N 6.62; found C 54.33, H 5.08, N 6.67.

(*E,E,E*)-1,6-Bis[(4-methylphenyl)sulfonyl]-11-[(4-pyrrol-1-ylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-trienepalladium(0) (1bcc): Starting from **7bcc** (0.20 g, 0.3 mmol); colorless solid (yield 0.18 g, 0.2 mmol, 78%). M.p. 172–173 °C. IR (KBr): $\tilde{\nu} = 2922, 1596, 1507, 1336, 1161, 1094$ cm^{-1} . ^1H NMR (200 MHz, CDCl_3): $\delta = 1.65$ – 1.74 (m, 4 H), 2.38 (s, 6 H), 2.81 (t, $J = 12.6$ Hz, 2 H), 3.00–3.12 (m, 2 H), 3.70–3.80 (m, 2 H), 4.00–4.10 (m, 2 H), 4.60–4.70 (m, 4 H), 4.79 (d, $J = 14.4$ Hz, 2 H), 6.39 (broad abs., 2 H), 7.11 (broad abs., 2 H), 7.24–7.29 (m, 4 H), 7.45–7.54 (m, 2 H), 7.60–7.73 (m, 4 H), 7.80–7.90 (m, 2 H). ^{13}C NMR (100 MHz, CDCl_3): 21.4, 45.0, 45.2, 48.2, 49.4, 78.1, 78.3, 78.5, 78.6, 78.7, 78.8, 82.4, 82.9, 83.0, 111.9, 118.8, 118.9, 119.8, 119.9, 126.9, 127.1, 128.7, 128.9, 129.8, 129.9, 134.7, 135.0, 135.1, 135.2, 135.9, 143.4, 143.6, 143.7. ESI-MS (m/z): 827 [M + H] $^+$. $\text{C}_{36}\text{H}_{40}\text{N}_4\text{O}_6\text{PdS}_3\text{CH}_2\text{Cl}_2$ (912.28): calcd. C 48.71, H 4.64, N 6.14; found C 48.60, H 4.72, N 5.89.

Preparation of Modified Electrodes

C-felt/poly-1aabb: Electrode coating was performed through cycling the potential as described previously using a carbon felt electrode ($0.5 \times 0.5 \times 0.5$ cm) used as the working electrode in a 1 mM solution of **1aabb** in CH_2Cl_2 0.1 M TBAP. After electropolymerization, the modified electrode was transferred to a blank electrolyte solution and five more potential cycles were performed. The electrode was then soaked overnight in anhydrous toluene before using it as a heterogeneous catalyst.

Catalysis

1,3-Diphenylpropene, under Catalysis by C-felt/poly-1aabb (11): To a degassed mixture of cinnamyl bromide **9** (0.030 g, 0.150 mmol), phenylboronic acid **10** (0.028 g, 0.225 mmol), anhydrous potassium carbonate (0.031 g, 0.225 mmol), and the electrode containing the immobilized Pd^0 -catalyst, **C-felt/poly-1aabb** (see Table 1 for Pd nmols) anhydrous toluene (10 mL) was added under N_2 . The mixture was stirred at 65 °C for 24 hours. Product yield was calculated by GC using naphthalene as internal standard. 1,3-Diphenylpropene **11** has the same retention time as authentic material and the correct mass by GC/MS. ^1H NMR (200 MHz, CDCl_3): $\delta = 3.52$ (d, $J = 5.9$ Hz, 2 H), 6.32–6.50 (m, 2 H), 7.15–7.37 (m, 10 H). 3,3-Diphenyl-1-propene **12**^[24] has been identified by GC/MS analysis and by ^1H NMR spectrum. ^1H NMR (200 MHz, CDCl_3): $\delta = 4.70$ (d, $J = 7.2$ Hz, 1 H), 4.98 (b d, $J = 17.0$ Hz, 1 H), 5.20 (b d, $J = 9.2$ Hz, 1 H), 6.30 (b abs, 1 H), 7.20–7.30 (m, 10 H). The heterogeneous catalyst was removed from the reaction vessel, washed by stirring it in toluene and reused.

4-Nitrobiphenyl, under Catalysis by C-felt/poly-1aabb (14a), General Method: To a degassed mixture of 4-iodonitrobenzene **13a** (0.20 g, 0.79 mmol), phenylboronic acid **10** (0.15 g, 1.18 mmol), anhydrous potassium carbonate (0.17 g, 1.18 mmol), and the modified electrode, **C-felt/poly-1aabb** (0.0015% molar) anhydrous toluene (10 mL) was added under N_2 . The mixture was stirred at 65 °C for 24 hours. The product yield was calculated by GC using naphthalene as internal standard. 4-Nitrobiphenyl **14a** has the same retention time as authentic material and the correct mass by GC/MS. The elec-

trode with the polymeric catalyst was removed from the reaction vessel, washed by stirring in toluene and reused.

X-ray Crystallographic Study

X-ray Structure Determination of 1bcc: Very small colorless and mostly twinned crystals of **1bcc**·CH₂Cl₂ were grown by slow evaporation of a dichloromethane solution at room temperature. After different trials, a data set of moderate quality was acquired from a small crystal needle with the dimensions 44 × 14 × 6 μm. Molecular formula C₃₇H₄₂Cl₂N₄O₆Pd₁S₃, *M* = 912.23, triclinic, *a* = 11.1889(12), *b* = 14.1440(14), *c* = 14.4425(14) Å, α = 117.683(4)°, β = 100.507(4)°, γ = 90.266(3)°, *V* = 1979.5(3) Å³, space group *P* $\bar{1}$, *Z* = 2, μ = 0.812 mm⁻¹, *d*_{calcd.} = 1.530 g/cm³. The measurements were made on a Siemens P4 diffractometer equipped with a SMART-CCD-1000 area detector, a MACScience Co. rotating anode with Mo-*K*_α radiation, a graphite monochromator and a Siemens low temperature device LT2 (*T* = -120 °C). The measurements were made in the range 1.63 to 27.50°. 24003 reflections were collected of which 8939 were unique (*R*_{int} = 0.1292) and 3783 observed [*F*_o > 4σ(*F*_o)]. Full sphere data collection was carried out using ω and scans. Programs used: Data collection Smart V. 5.060 (Bruker AXS, 1999), data reduction Saint + Version 6.02 (Bruker AXS 1999) and absorption correction SADABS (max./min. transmission: 1.000000/0.709584, Bruker AXS 1999). Structure solution and refinement using SHELXTL Version 5.10 (Sheldrick, University of Göttingen, Germany, 1998). The structure was solved by direct methods and refined by full-matrix least-squares against *F*². All calculated hydrogen positions were refined and constrained. Final *R*₁ [*I* > 2σ(*I*)] = 0.0698 and *wR*(*F*²) [*I* > 2σ(*I*)] = 0.1459. The number of refined parameters was 503.

CCDC-216129 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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