Palladium(0) Complexes of a 15-Membered Macrocyclic Triolefin as a Recoverable Catalyst – Monomer- and Polystyrene-Anchored Versions

Jordi Cortés,[a] Marcial Moreno-Mañas,*[a] and Roser Pleixats[a]

Keywords: Macrocycles / Palladium / Polymer / Catalysis / Cross-coupling

Preparation of the 15-membered cycle (*E,E,E*)-1,6,11-tris[(2,4,6-triisopropylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-triene (**8**) is reported. This cyclic triolefin forms a stable Pd^0 complex **9** which catalyzes several cross-coupling reactions and can be recovered. Anchoring to a polystyrene framework affords a solid version of the catalyst, which is recovered by simple filtration and reused without loss of catalytic activity.

Introduction

Palladium has emerged as a versatile transition metal in the field of catalysis.[1][2] However, there is a gap between the enormous potential of palladium in catalysis and the industrial applications found so far.[3] One of the main problems to be addressed is the recovery of Pd-containing catalysts. In general Pd^0 requires stabilization by phosphanes, which are readily oxidized. Therefore, the development of phosphane-free Pd catalysts is a topic of enormous importance. Several reactions are catalyzed by Pd species not containing phosphanes,[4] in particular the olefin complexes $Pd(dba)_2$ and $Pd_2(dba)_3{\cdot}CHCl_3$ have found extensive use.[4] Curiously enough, very few Pd-olefin complexes were known until the recent description of Pd complexes of hepta-1,6-dienes and related structures.[5] An emerging and highly promising phosphane-free alternative is based on the coordination power of stable heterocyclic carbenes.[6]

Strategies to recover and reutilize organometallic homogeneous catalysts have been reviewed.[7−9] Anchoring the homogeneous catalyst to an organic[8][10] or inorganic[8][11] polymer (immobilization), or use of biphasic aqueous-organic[9,12−14] or fluorous-organic[15] solvent systems has been proposed for catalyst recovery, and an aqueous-organic system has become industrially significant.[9]

The use of palladium catalysts anchored to organic polymers in carbon-carbon bond forming reactions has a few precedents including Suzuki cross-couplings,[16] Grignard-based cross-couplings,[17] acetylene couplings,[17][18] Heck reactions,[17][19] allylation of nucleophiles (Tsuji-Trost reaction),[18][20] butadiene telomerization,[20e,21] and carbonylation.[20f] Only a few examples of Heck reactions[19b−19d] and Tsuji-Trost allylations[20c] are based on phosphane-free polymers.

[a] Department of Chemistry. Universitat Autònoma de Barcelona, Cerdanyola. 08193-Barcelona. Spain
Fax: (internat.) + 34-93/581-1265
E-mail: iqorb@cc.uab.es

Results and Discussion

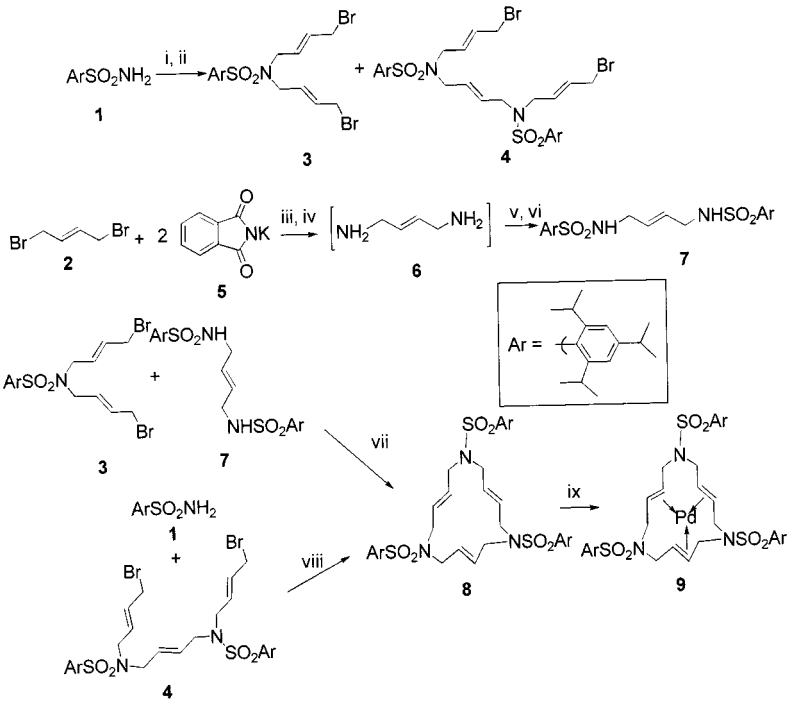
Recently we described the formation of (*E,E,E*)-1,6,11-tris[(2,4,6-triisopropylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-triene, (**8**) and its Pd^0 complex **9** where the metal is coordinated by the three ring olefinic bonds (Scheme 1).[22] Macrocycle **8** and complex **9** were formed as well as other cyclic and open-chain compounds in a non-selective reaction which required tedious separation from the complex mixture. We report in this communication an independent and selective preparation of **8** and **9**, the catalytic properties and recovery of complex **9**, and the preparation, catalytic properties and recovery of functionalized polystyrene **14** containing the 15-membered macrocycle coordinated to Pd^0 (Scheme 2).

The preparation of macrocyclic triolefin **8** is shown in Scheme 1. Alkylation of 2,4,6-triisopropylbenzenesulfonamide (**1**) with (*E*)-1,4-dibromo-2-butene (**2**) affords a mixture of the dibromo compounds **3** and **4**. These compounds can be separated by column chromatography through silica gel and each can be used for the preparation of **8**. Thus, reaction of **3** with bis-sulfonamide **7**, prepared from **2** and **5**, afforded **8** (44−56%). On the other hand alkylation of **1** with dibromobis-sulfonamide **(4)** also gave **8** in 79% yield. Introduction of Pd^0 to obtain complex **9** is achieved by treatment with either $Pd(PPh_3)_4$ in refluxing THF (95%), $Pd_2(dba)_3$ in THF (95%), or $PdCl_2$/methanol in the presence of NaCl and NaOAc (67%).

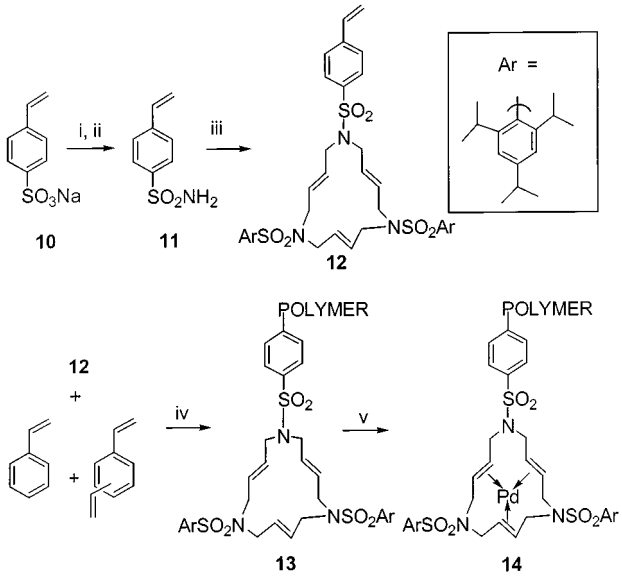
Since **9** exhibited good catalytic properties and could be recovered (vide infra) we prepared the macrocycle-containing polystyrenes **13** and **14** as indicated in Scheme 2. Thus, macrocycle **12** was prepared by alkylation of 4-vinylbenzenesulfonamide **(11)** with **4** and then copolymerized with styrene and divinylbenzene in a molar ratio 10:70:20, with initiation by AIBN, following a known general method.[23] Polymer **13** was charged with Pd^0 by treatment with $Pd(PPh_3)_4$ in dioxane at 80°C to afford **14**.[24]

The model reactions chosen to test catalytic power and recovery of catalysts are the Suzuki-type cross-coupling of cinnamyl bromide **(15)** with the arene boronic acids **16a−e**

  1434−193X/00/0102−239 $ 17.50+.50/0



Scheme 1. Preparation of macrocycles **8** and **9**; reagents and conditions:. i. NaH/DMF, then **2**, 90°C; ii. column chromatography on silica gel; iii. DMF, 80°C; iv. N_2H_4/EtOH, reflux; v. KOH/H_2O; vi. $ArSO_2Cl/Et_2O$; vii. NaH/DMF on **7**, then **3**, 80°C; viii. NaH/DMF on **1**, then **4**, 90°C; ix. $Pd(PPh_3)_4$/refluxing THF, or $Pd(dba)_2$/refluxing THF, or $PdCl_2$/MeOH/NaCl/NaOAc



Scheme 2. Preparation of polymer catalyst **14**; reagents and conditions: i. $SOCl_2$ /DMF, room temp.; ii. liquid NH_3/Et_2O, −50°C; iii. NaH/DMF on **11**, then **4**, 90°C; iv. AIBN, polyvinyl alcohol, water/THF/toluene, 0 to 75°C, N_2, 18 h; v. $Pd(PPh_3)_4$, dioxane, 80°C

leading to diarylpropenes **17a−e**,[25] and that of 4-iodonitrobenzene (**18**) with **16d** to afford 4-nitrobiphenyl **(19)** (Scheme 3).[26] First of all, the macrocyclic complex **9** was tested for the preparation of **17a−e**. The reactions were performed under the experimental conditions previously defined for other nonrecovered Pd catalysts.[25] In all cases (Table 1) complex **9** was quantitatively recovered by column chromatography on silica gel and the chemical yields of compounds **17a−e** were excellent. For polymeric catalyst **14** we performed consecutive reactions for each arene boronic acid **16** with cinnamyl bromide **(15)** (Scheme 3). Catalyst **14** was quantitatively recovered by filtration and reused for the next reaction without decrease of activity after five runs. Yields of isolated **17a−e** were in the range 82−98% (Table 2). Finally, five consecutive preparations of nitrobiphenyl **19** were performed, as above, with recovery and reuse of polymer **14**; isolated yields of **19** were 82, 91, 94, 96, and 89%. The initial amount of catalyst was 8.1 mg, and 7.9 mg was recovered after the last run.

Table 1. Preparation of **17a−e** under catalysis by macrocycle **9**[a]

17	X	time (h)	temp (°C)	yield (%)	Recovery of **9** (%)
17a	CF_3	5	80	99[b]	100[b]
17b	Br	4	80	94[b]	100[b]
17c	Cl	4	80	99[b]	100[b]
17d	H	5	Reflux[c]	75[b]	100[b]
17e	OMe	24	90	82[d]	100[d]

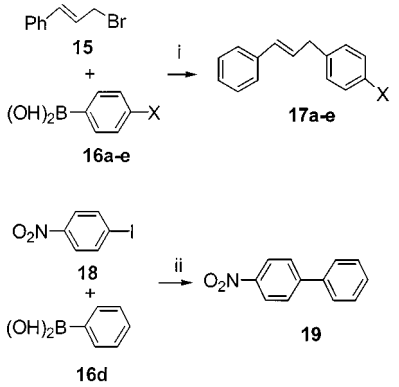
[a] Reactions in toluene unless otherwise stated and in the presence of 4−5% molar **9**. Molar ratio **15**:**16**:K_2CO_3 ca. 1:2:9, [**15**] ca. 0.4 M. − [b] Isolated by column chromatography on silica gel. − [c] In benzene. − [d] Estimated by ^1H NMR spectroscopy.

At present we can only propose a hypothesis to explain the catalytic activity of **9** and **14**. Two of the olefins in **9** appear together in the NMR spectra, but the protons and carbon atoms within each olefin do not. The third olefin is different from the other two although its protons and carbon atoms gave the same signals in the NMR spectra.[22] Thus, the complex has an averaged plane of symmetry but not a C_3 axis, and it should be considered as a PdL_2L'

Table 2. Preparation of **17a−e** under catalysis by polymer **14**[a]

17	X	Run	Yield (%)
17a	CF_3	1	96
17a	CF_3	2	98
17a	CF_3	3	87
17a	CF_3	4	87
17a	CF_3	5	85
17b	Br	1	95
17b	Br	2	87
17b	Br	3	93
17b	Br	4	89
17b	Br	5	83
17c	Cl	1	87
17c	Cl	2	92
17c	Cl	3	84
17c	Cl	4	87
17c	Cl	5	89
17d	H	1	96
17d	H	2	98
17d	H	3	87
17d	H	4	87
17d	H	5	85
17e	OMe	1	82
17e	OMe	2	89
17e	OMe	3	87
17e	OMe	4	97
17e	OMe	5	89

[a] Reactions in toluene at 80°C for 3−4 h and in the presence of 10 mg of polymer **14** (ca. 5×10^{-3} mequiv of Pd). Ratio **15**:**16**:K_2CO_3 ca. 1:1:8. [**15**] ca. 0.04 M. Polymer used in run *n* was recovered from run *n* − 1.



Scheme 3. Cross-coupling reactions; reagents and conditions: i. **9** or **14**, K_2CO_3, toluene, 80°C; ii. **14** (8 mg, ca. 4×10^{-3} mequiv of Pd), **18** (0.15 mmol), **16a** (0.16 mmol), K_2CO_3 (0.38 mmol), acetone (0.5 mL)/water (0.5 mL), 70−80°C, 1−10 h

complex. If the third olefin temporarily leaves the metal atom a situation equivalent to PdL_2 + L′ arises. Then, PdL_2 can act as the catalytic species which at the end of the cycle recovers L′ to afford the initial complex.

Conclusion

In summary, the phosphane-free macrocyclic complex **9** and its immobilized version **14** hold great promise as a recoverable catalyst for palladium(0)-catalysed organic synthesis.

Experimental Section

General: All reactions under Pd catalysis were performed under an inert atmosphere with anhydrous solvents. − Melting points were determined with a Kofler apparatus and are uncorrected. − IR spectra were recorded with a Nicolet FT-IR 510 ZDX. − NMR spectra were recorded with a Bruker AC250 or a Bruker AM400. ^{1}H NMR (250 MHz) chemical shifts are reported relative to $CHCl_3$ at δ = 7.26 and tetramethylsilane at δ = 0.00. Coupling constants are reported in Hz. ^{13}C NMR (62.5 MHz) chemical shifts are expressed relative to $CDCl_3$ at δ = 77.00 and tetramethylsilane at δ = 0.00. − Mass spectra (EIMS) were obtained with a Hewlett-Packard 5989A spectrometer and determined at an ionizing voltage of 70 eV; relevant data are listed as *m/z* (%). A MALDI-TOF spectrum of compound **12** was recorded with a BIFLEX spectrometer (Bruker-Franzen Analytik) equipped with a pulsed nitrogen laser operating in positive-ion reflector mode. − Elemental analyses were performed at "Servei d′Anàlisi Química de la Universitat Autònoma de Barcelona".

***N,N*-Bis[(*E*)-4-bromo-2-butenyl]-2,4,6-triisopropylbenzenesulfonamide (3) and (*E,E,E*)-*N,N′*-Bis[(2,4,6-triisopropylphenyl)sulfonyl]-1,14-dibromo-5,10-diazatetradeca-2,7,12-triene (4):** A mixture of 2,4,6-triisopropylbenzenesulfonamide (**1**) (3.70 g, 13.1 mmol), 60% sodium hydride in mineral oil (2.00 g, 52.2 mmol) and DMF (80 mL) was added dropwise to a stirred solution of (*E*)-1,4-dibromo-2-butene (**2**) (20.00 g, 93.5 mmol) in DMF (40 mL). The mixture was heated to 90°C for 20 h. Water was then added and distillation of volatile material at reduced pressure afforded a residue which was chromatographed through a column of silica gel with mixtures of hexanes/ethyl acetate of increasing polarity. First, compound **3** was eluted, followed by compound **4**.

3: (3.22 g, 45%), m. p. 83−86°C (hexanes). − IR (KBr): ṽ = 2960, 1600, 1462, 1427, 1363, 1315, 1153, 969, 905 cm^{-1}. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.22 (d, *J* = 6.6 Hz, 18 H), 2.88 (septet, *J* = 6.6 Hz, 1 H), 3.77 (d, *J* = 6.6 Hz, 4 H), 3.88 (d, *J* = 7.3 Hz, 4 H), 4.07 (septet, *J* = 6.6 Hz, 2 H), 5.66 (dt, *J* = 15.4, 6.6 Hz, 2 H), 5.85 (dt, *J* = 15.4, 7.3 Hz, 2 H), 7.14 (s, 2 H). − ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 23.4, 24.7, 29.2, 34.0, 46.4, 53.4, 123.9, 125.2, 129.4, 131.3, 151.3, 153.3. − $C_{23}H_{35}Br_2NO_2S$ (549.4): calcd. C 50.28, H 6.42, N 2.55, S 5.84; found C 50.42 and 50.48, H 6.48 and 6.49, N 2.67 and 2.62, S 5.56 and 5.59.

4: (1.30 g, 23%), m. p. 123−125°C. − IR (KBr): ṽ = 2958, 1602, 1457, 1429, 1364, 1315, 1261, 1153, 1125, 1068, 967, 740 cm^{-1}. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.22 (d, *J* = 6.6 Hz, 24 H), 1.23 (d, *J* = 6.6 Hz, 12 H), 2.87 (septet, *J* = 6.6 Hz, 2 H), 3.75 (m, 8 H), 3.87 (d, *J* = 7.3 Hz, 4 H), 4.07 (septet, *J* = 6.6 Hz, 4 H), 5.58−5.68 (m, 4 H), 5.82 (dt, *J* = 15.4, 7.3 Hz, 2 H), 7.13 (s, 4 H). − ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 23.5, 24.8, 29.3, 31.3, 34.2, 46.4, 46.7, 124.0, 129.4, 129.8, 130.8, 131.3, 151.5, 153.3. − $C_{42}H_{64}Br_2N_2O_4S_2$ (916.9): calcd. C 57.01, H 7.29, N 3.17, S 7.25; found C 57.32 and 57.30, H 7.06 and 7.09, N 3.39 and 3.39, S 6.96 and 7.01.

(*E*)-*N,N′*-Bis[(triisopropylphenyl)sulfonyl]-2-butene-1,4-diamine (7): The method of Feigenbaum and Lehn to prepare 2-butene-1,4-diamine was followed.[27] (*E*)-1,4-Dibromo-2-butene (**2**) (5.00 g, 23.4 mmol) was added to a mixture of potassium phthalimide (15.80 g, 85.5 mmol) and DMF (60 mL) heated to 80°C. The mixture was magnetically stirred for 2 h, then it was cooled to room temp. and poured into iced water (100 mL). The precipitate formed overnight was filtered, washed with 1% aqueous sodium hydroxide and with water and dried. The crude (*E*)-1,4-diphthalimido-2-butene (7.47 g, 92%) was used without further purification.

Hydrazine hydrate (2.17 g, 43 mmol) and water (2 mL) were added to crude (*E*)-1,4-diphthalimido-2-butene (7.00 g, 20.2 mmol) in refluxing ethanol (40 mL). The mixture was refluxed for 3 h and cooled to room temp. Then 10 N HCl was added till pH 1 and the mixture refluxed again for 30 min. The formed solid was filtered off and the solution was evaporated to dryness. The residue was dissolved in water 6 (mL) and the solution was saturated with KOH. This solution containing 2-butene-1,4-diamine (**6**) was slowly added to a vigorously stirred mixture of 2,4,6-triisopropylbenzenesulfonyl chloride (12.20 g, 40.2 mmol), water (12 mL), and diethyl ether (12 mL) kept at 5°C. Stirring was continued for 5 h and then 10% HCl was added to pH 7. The formed solid **(7)** was washed with water, dried, washed with hexanes and dried again (9.91 g, 79%), m. p. 183°C (hexanes). − IR (KBr): $\tilde{\nu}$ = 3302, 2961, 1603, 1424, 1324, 1155, 1102, 1037, 827, 657 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 1.23 (apparent d, *J* = 6.6 Hz, 24 + 12 H), 2.88 (septet, *J* = 6.6 Hz, 2 H), 3.49 (m, 4 H), 4.07 (septet, *J* = 6.6 Hz, 4 H), 4.28 (t, *J* = 5.9 Hz, 2 H), 5.56 (m, 2 H), 7.14 (s, 4 H). − ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 23.6, 24.7, 29.6, 34.1, 44.2, 123.8, 128.9, 132.0, 150.3, 153.0. − $C_{34}H_{54}N_2O_4S_2$ (618.9): calcd. C 65.98, H 8.79, N 4.53; found C 66.16 and 65.92, H 8.56 and 8.65, N 4.22 and 4.27.

(*E,E,E*)-1,6,11-Tris[(2,4,6-triisopropylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-triene (8). From 3 + 7: A solution of bromosulfonamide **3** (1.30 g, 2.4 mmol) in DMF (50 mL) was added to a mixture of bis-sulfonamide **7** (1.46 g, 2.4 mmol), 60% sodium hydride in mineral oil (0.26 g, 3.2 mmol), and DMF (60 mL) heated to 80°C and magnetically stirred. Heating at 90°C and stirring were maintained for 18 h. Ethanol was then added and volatile liquids were removed by distillation. The residue was chromatographed through silica gel with hexanes/ethyl acetate (10:1) to afford macrocycle **8** (1.03 g, 44%). All physical constants were identical to those previously described.[22]

From 4 + 1: A mixture of 2,4,6-triisopropylbenzenesulfonamide **(1)** (0.10 g, 0.34 mmol), 60% sodium hydride in mineral oil (0.06 g, 1.50 mmol) and DMF (12 mL) was added to a stirred solution of dibromobis-sulfonamide (**4**) (0.30 g, 0.34 mmol) in DMF (40 mL). The mixture was heated at 90°C for 12 h under stirring. Water was then added and volatile liquids were removed by distillation. The residue was chromatographed through silica gel with hexanes/ethyl acetate (10:1) to afford macrocycle **8** (0.270 mg, 79%). All physical constants were identical to those previously described.[22]

(*E,E,E*)-1,6,11-Tris[(2,4,6-triisopropylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-trienepalladium(0) (9): A mixture of macrocycle **8** (0.050 g, 0.05 mmol), tetrakis(triphenylphosphane)palladium(0) (0.065 g, 0.06 mmol) and THF (2 mL) was refluxed for 30 min. The solvent was evaporated and the residue was chromatographed through silica gel with mixtures of hexanes/ethyl acetate (v/v from 100:1 to 80:20) of increasing polarity to afford complex **9** (0.052 g, 95%). All physical constants were identical to those previously described.[22]

4-Vinylbenzenesulfonamide (11): Sodium 4-vinylbenzenesulfonate (10.40 g, 50.5 mmol) was added, under stirring and nitrogen atmosphere, to ice-cooled thionyl chloride (30 mL) keeping the temp. below 10°C. Then, anhydrous DMF (30 mL) was added and the mixture was stirred at room temp. for 6 h, kept one night in the refrigerator, and slowly poured into ice-water (100 mL). Extractions with diethyl ether (3 × 40 mL) were performed and the ether layer was washed with water and dried (Na_2SO_4). The ether solution of the crude 4-vinylsulfonyl chloride was reduced to a third of volume and poured into liquid ammonia (15 mL) kept at −50°C under nitrogen atmosphere. The mixture was stirred for 1 h and was then allowed to reach room temp. with simultaneous evaporation. The residue was poured into 50% sulfuric acid and was partitioned with dichloromethane (3 × 30 mL). The organic layer was dried (Na_2SO_4) and evaporated to afford **11** (5.17 g, 56%), m. p. 134−136°C (ethanol) (ref.[28] m. p. 138−139°C). − IR (KBr): $\tilde{\nu}$ = 3346, 3261, 1542, 1305, 1152, 1100, 934, 910, 842, 728 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 4.84 (s, 2 H), 5.41 (d, *J* = 11.0 Hz, 1 H), 5.85 (d, *J* = 17.5 Hz, 1 H), 6.73 (dd, *J* = 17.5, 11.0 Hz, 1 H), 7.51 (d, *J* = 8.1 Hz, 2 H), 7.85 (d, *J* = 8.1 Hz, 2 H). − ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 116.8, 126.3, 126.4, 135.2, 141.3, 141.5.

(*E,E,E*)-1,6-Bis[(2,4,6-triisopropylphenyl)sulfonyl]-11-[(4-vinylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-triene (12): A mixture of 4-vinylsulfonamide (**11**) (0.21 g, 1.1 mmol), 60% sodium hydride in mineral oil (0.20 g, 5.0 mmol), and dry DMF (50 mL) was added to a stirred solution of dibromobis-sulfonamide (4) (1.00 g, 1.1 mmol) in dry DMF (125 mL). The mixture was heated at 90°C for 20 h. After cooling to room temp. water was added and the volatile liquids distilled off at water pump pressure. The residue was chromatographed through silica gel with mixtures of hexanes/ethyl acetate to afford macrocycle **12** (0.77 g, 75%) as a glassy solid. − IR (KBr): $\tilde{\nu}$ = 2960, 2927, 2868, 1600, 1462, 1362, 1317, 1157, 1099, 974, 910, 886, 715 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 1.22 (m, 36 H), 2.87 (septet, *J* = 7.3 Hz, 2 H), 3.49 (m, 2 H), 3.65−3.79 (m, 10 H), 4.09 (septet, *J* = 7.3 Hz, 4 H), 5.40 (d, *J* = 11.0 Hz, 1 H), 5.45−5.80 (m, 6 H), 5.85 (d, *J* = 17.5 Hz, 1 H), 6.73 (dd, *J* = 17.5, 11.0 Hz, 1 H), 7.13 (s, 4 H), 7.50 (d, *J* = 8.8 Hz, 2 H), 7.73 (d, *J* = 8.8 Hz, 2 H). − ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 23.5, 24.8, 29.2, 29.7, 34.1, 48.9, 51.2, 117.4, 123.9, 126.8, 127.4, 129.7, 130.0, 130.3, 130.8, 135.5, 138.2, 141.8, 151.5, 153.2. − MALDI-TOF MS; *m/z* (%): 739.1 [M − $SO_2C_6H_4$−CH=CH_2], 638.9 [M − SO_2−$C_6H_2(C_3H_7)_3$].

Functionalized Polystyrene 13: A general method was followed.[23] A suspension of polyvinyl alcohol (0.028 g) and water (7 mL) cooled at 0°C was mechanically stirred for a few mins. Then a solution was added containing macrocycle **12** (0.50 g, 0.55 mmol), styrene (0.40 g, 0.44 mL, 3.9 mmol), divinylbenzene (0.14 g, 0.16 mL, 1.1 mmol), and azobisisobutyronitrile (0.018 g, 0.11 mmol) in toluene (2 mL) and THF (2 mL). The mixture was vigorously stirred at 0°C for 1 h and then at 75°C for 24 h. The volatile liquids were distilled off at water pump pressure. The residue was washed with water, methanol, methanol/THF and diethyl ether and finally it was dried, to afford **13** (0.44 g). − IR (KBr): $\tilde{\nu}$ = 2924, 1599, 1451, 1362, 1316, 1259, 1155, 1104, 980, 899, 799, 757, 700 cm^{-1}. − $(C_{50}H_{71}N_3O_6S_3)_{10}$ + $(C_8H_8)_{70}$ + $(C_{10}H_{10})_{20}$: calcd. C 79.83, H 7.81, N 2.20; found C 77.87 and 78.09, H 7.67 and 7.70, N 2.12 and 2.15.

Palladium-Containing Functionalized Polystyrene 14: A mixture of polymer **13** (0.200 g, 0.11 mequiv of macrocycle), tetrakis(triphenylphosphane)palladium (0.203 g, 0.18 mmol), and dioxane 8 mL) was refluxed for 2 h. The polymer was filtered, washed thoroughly with THF and with diethyl ether, and dried, to afford **14** (0.180 mg), IR (KBr): $\tilde{\nu}$ = 2958, 2924, 1599, 1450, 1360, 1317, 1154, 1097, 902, 761, 699 cm^{-1}. − $(C_{50}H_{71}N_3O_6PdS_3)_{10}$ + $(C_8H_8)_{70}$ + $(C_{10}H_{10})_{20}$: calcd. C 75.59, H 7.40, N 2.10; found C 75.66 and 75.51, H 7.12 and 7.07, N 1.97 and 1.87.

Preparation of 1,3-Diphenylpropene (17d) Under Catalysis by Macrocycle 9. General Method: Benzeneboronic acid **(16d)** (0.160 g, 1.31 mmol) in anhydrous benzene (3 mL) was added to a mixture of cinnamyl bromide **(15)** (0.12 g, 0.61 mmol), anhydrous potassium carbonate (0.75 g, 5.42 mmol), macrocycle **9** (0.028 g, 0.027 mmol), and anhydrous benzene (12 mL). The mixture was heated at 90°C

for 5 h (TLC and GC monitoring). After cooling to room temp. 30% hydrogen peroxide (13 mL) was added and the mixture stirred for 1 h. The layers were separated and the aqueous phase was extracted with ether (4 × 10 mL). The combined organic phase was dried (Na_2SO_4) and evaporated. The residue was chromatographed through silica gel with hexanes − ethyl acetate (10:1) to afford **17d** (0.090 g, 75%), oil. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.54 (d, J = 5.9 Hz, 2 H), 6.29−6.49 (m, 2 H), 7.15−7.38 (m, 10 H). − ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 39.3, 126.1, 126.2, 127.1, 128.3, 128.5, 128.7, 129.2, 131.1, 137.5, 140.2. These data were compared with those previously described.[25] Further elution gave quantitative recovery (0.028 g) of **9**.

All compounds **17** prepared exhibited the same behavior as previously described.[25]

Preparation of 1,3-Diphenylpropene (17d) Under Catalysis by Polymer 14. General Method: A mixture containing cinnamyl bromide **(15)** (30 mg, 0.15 mmol), benzeneboronic acid **(16d)** (20.4 mg, 0.17 mmol), potassium carbonate (168 mg, 1.22 mmol), polymer **14** (10.0 mg, ca. 5×10^{-3} miliequiv. Pd), and toluene (4 mL) was heated at 80°C (bath temp.) under magnetic stirring for 3 h (GC monitoring). The mixture was cooled to room temp. and water was added. The catalyst **14** was filtered off, washed with water and toluene, and dried. The organic layer of the filtrate was separated, washed with water and dried (Na_2SO_4) The solvent was evaporated, and yield and purity of **17d** in the residue were checked by weighing, GC, and ^{1}H NMR spectroscopy (see Table 2).

Preparation of 4-Nitrobiphenyl (19) Under Catalysis by Polymer 14. General Method: A stirred mixture of 4-iodonitrobenzene **(18)** (37.4 mg, 0.15 mmol), benzeneboronic acid **(16d)** (19.2 mg, 0.16 mmol), potassium carbonate (51.8 mg, 0.38 mmol), polymer **14** (8 mg, ca. 4×10^{-3} miliequiv. Pd), water (0.5 mL) and acetone (0.5 mL) was heated at 70−80°C (bath temp.) for the indicated nonoptimized time (GC monitoring). After cooling to room temp. water (3 mL) and ether (3 mL) were added and polymer **14** was filtered off, washed with water and ether, and dried. The organic layer of the filtrate was separated, washed with water, dried (Na_2SO_4) and evaporated to afford **19**, m. p. 109−111°C (ref.[26] m. p. 113−115°C, and ref.[29] m. p. 112−114°C). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.42−7.52 (m, 3 H), 7.61 (m, 2 H), 7.72 (d, J = 8.8 Hz, 2 H), 8.29 (dt, J = 8.8, 2.2 Hz, 2 H).

Acknowledgments

Financial support from DGICYT-MEC of Spain, (project PB93−0896), and from CIRIT-Generalitat de Catalunya (projects 96SGR-0030 and 98SGR0056 and a predoctoral scholarship to J. C.) are gratefully acknowledged.

[1] For reviews see: [1a] J. Tsuji, Palladium Reagents and Catalysts: Innovations in Organic Synthesis, John Wiley and Sons, Chichester, **1995**. − [1b] *Comprehensive Organometallic Chemistry II* (Eds.: E. W. Abel, F. G. A. Stone, and G. Wilkinson), Pergamon Press, New York, **1995**, vol. 12.
[2] *Transition Metals for Organic Synthesis* (Eds.: M. Beller, and C. Bolm, C.), Wiley-VCH, Weinheim, **1998**, vol. 1 and 2.
[3] J. Tsuji, *Synthesis* **1990**, 739−749.
[4] J. L. Malleron, J.-C. Fiaud, J.-Y. Legros, *Handbook of Palladium-Catalyzed Organic Reactions*, Academic Press, San Diego, **1997**.
[5] J. Krause, K.-J. Haack, G. Cestaric, R. Goddard, K.-R. Pörschke, *Chem. Commun*. **1998**, 1291−1292.
[6] W. A. Herrmann, C. Köcher, *Angew. Chem*. **1997**, *109*, 2256−2282; *Angew. Chem. Int. Ed. Engl*. **1997**, *36*, 2162−2187.
[7] W. A. Herrmann, B. Cornils, *Angew. Chem*. **1997**, *109*, 1074−1095; *Angew. Chem. Int. Ed. Engl*. **1997**, *36*, 1048−1067.
[8] *Applied Homogeneous Catalysis with Organometallic Compounds* (Eds.: B. Cornils, W. A. Herrmann), VCH, Weinheim, **1996**, vol. 1 and 2.
[9] *Aqueous-Phase Organometallic Catalysis* (Eds.: B. Cornils, W. A. Herrmann), Wiley-VCH, Weinheim, **1998**.
[10] For general reviews see: [10a] P. Panster, S. Wieland, *Immobilization*, in ref.[8] Chapter 3.1.1.3, pages 605−623. − [10b] P. Kalck, M. Dessoudeix, *Ligands or Complexes Containing Ancillary Functionalities,* in ref.[9] Chapter 3.2.3, pages 105−122.
[11] For a review on the use of immobilized metallic catalysts in inorganic solids see: J. H. Clark, D. J. Macquarrie, *Chem. Commun*. **1998**, 853−860.
[12] W. A. Herrmann, C. W. Kohlpaintner, *Angew. Chem*. **1993**, *105*, 1588; *Angew. Chem. Int. Ed. Engl*. **1993**, *32*, 1524−1544.
[13] B. Cornils, W. A. Herrmann, *Homogeneous Catalysts and Their Heterogenization or Immobilization*. In ref.[8] Chapter 3.1.1, pages 575−601.
[14] [14a] F. Joó, Á. Kathó, *J. Mol. Catal. (A)* **1997**, *116*, 3−26. − [14b] B. Cornils, W. A. Herrmann, R. W. Eckl, *J. Mol. Catal. (A)* **1997**, *116*, 27−33.
[15] For reviews see: [15a] I. T. Horváth, Heterogenization by Other Immiscible Phases. In ref. 8. Chapter 3.1.1.2, pages 601−605. − [15b] B. Cornils, *Angew. Chem*. **1997**, *109*, 2147−2149; *Angew. Chem. Int. Ed. Engl*. **1997**, *36*, 2057−2059. − [15c] I. T. Horváth, *Acc. Chem. Res*. **1998**, *31*, 641−650.
[16] [16a] S.-B. Jang, *Tetrahedron Lett*. **1997**, *38*, 1793−1796. − [16b] I. Fenger, C. Le Drian, *Tetrahedron Lett*. **1998**, *39*, 4287−4290.
[17] M. Terasawa, K. Kaneda, T. Imanaka, S. Teranishi, *J. Organometal. Chem*. **1978**, *162*, 403−414.
[18] D. E. Bergbreiter, Y.-S. Liu, *Tetrahedron Lett*. **1997**, *38*, 7843−7846.
[19] [19a] C.-M. Andersson, K. Karabelas, A. Hallberg, C. Andersson, *J. Org. Chem*. **1985**, *50*, 3891−3895. − [19b] Z. Zhuangyu, P. Yi, H. Hongwen, K. Tsi-yu, *Synth. Commun*. **1990**, *20*, 3563−3574. − [19c] Z. Zhuangyu, P. Yi, H. Honwen, K. Tsi-yu, *Synthesis* **1991**, 539−542. − [19d] L. Yi, Z. Zhuangyu, H. Hongwen, *Synth. Commun*. **1995**, *25*, 595−601. − [19e] S.-B. Jang, *Tetrahedron Lett*. **1997**, *38*, 4421−4424.
[20] [20a] B. M. Trost, E. Keinan, *J. Am. Chem. Soc*. **1978**, *100*, 7779−7781. − [20b] B. M. Trost, R. W. Warner, *J. Am. Chem. Soc*. **1982**, *104*, 6112−6114. − [20c] D. E. Bergbreiter, B. Chen, T. J. Lynch, *J. Org. Chem*. **1983**, *48*, 4179−4186. − [20d] B. M. Trost, R. W. Warner, *J. Am. Chem. Soc*. **1983**, *105*, 5940−5492. − [20e] D. E. Bergbreiter, D. A. Weatherford, *J. Org. Chem*. **1989**, *54*, 2726−2730. − [20f] D. E. Bergbreiter, B. Chen, D. Weatherford, *J. Mol. Catal*. **1992**, *74*, 409−419. − [20g] D. E. Bergbreiter, Y.-S. Liu, P. L. Osburn, *J. Am. Chem. Soc*. **1998**, *120*, 4250−4251.
[21] [21a] C. U. Pittman, Jr., Q. Ng, *J. Organometal. Chem*. **1978**, *153*, 85−97. − [21b] K. Kaneda, H. Kurosaki, M. Terasawa, T. Imanaka, S. Teranishi, *J. Org. Chem*. **1981**, *46*, 2356−2362. − [21c] F. Benvenuti, C. Carlini, A. M. Raspolli Galleti, G. Sbrana, M. Marchionna, R. Patrini, *J. Mol. Catal. (A)* **1999**, *137*, 49−63.
[22] S. Cerezo, J. Cortés, J.-M. López-Romero, M. Moreno-Mañas, T. Parella, R. Pleixats, A. Roglans, *Tetrahedron* **1998**, *54*, 14885−14904.
[23] S. Itsuno, Y. Sakurai, K. Ito, T. Maruyama, S. Nakahama, J. M. J. Fréchet, *J. Org. Chem*. **1990**, *55*, 304−310.
[24] Elemental analysis of **13** indicated full integration of all three monomers into the polymer, and elemental analysis of **14** indicated full incorporation of palladium. From this data, 0.5 miliequiv. of palladium per gram of polymer **14** has been estimated.
[25] M. Moreno-Mañas, F. Pajuelo, R. Pleixats, *J. Org. Chem*. **1995**, *60*, 2396−2397.
[26] T. I. Wallow, B. M. Novak, *J. Org. Chem*. **1994**, *59*, 5034−5037.
[27] A. Feigenbaum, J.-M. Lehn, *Bull. Soc. Chim. Fr*. **1973**, 198−202.
[28] R. H. Wiley, J. M. Schmitt, *J. Am. Chem. Soc*. **1956**, *78*, 2169−2171.
[29] E. I. Negishi, A. O. King, N. Okukado, *J. Org. Chem*. **1977**, *42*, 1821−1823.

Received August 4, 1999
[O99484]