Novel Homo- and Heterobimetallic Palladium(0) and Platinum(0) Complexes of Olefinic Mono-, Bis-, and Tris-macrocyclic Ligands

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Received January 12, 2004

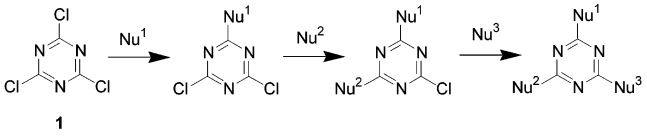
Molecular structures featuring two and three triolefinic 15-membered macrocycles of type **2** as well as their homo- and heterometallic complexes of palladium(0) and platinum(0) (**5**, **7**) have been synthesized from 2,4,6-trichloro-1,3,5-triazine, **1**. The strategy employed allows easy preparation of heterobimetallic complexes in a controlled manner. Several mass spectrometry techniques are useful to identify these complexes.

Introduction

Coordination macromolecular chemistry has grown into a major research field[1] embracing the synthesis and complexation properties of different kinds of macrocycles such as crown ethers,[2] cryptands,[2] spherands,[3] porphyrins,[4] and phthalocyanines.[5] Functionalized macrocycles coordinating metal ions hold much promise for the synthesis of molecules with a high degree of complexity such as oligo- or polymetallic complexes. Among other aspects, polynuclear metal complexes show the potential of combining the capabilities of both metallic entities, giving rise to effective homogeneous catalytic systems. However, coordination of different metal ions to identical or very similar ligand moieties present in the same molecule is a difficult process, since controlling the ordered incorporation of metals to the coordinating sites is a difficult task. Normally random mixtures are produced that require separation efforts. Hence, the development of a controlled synthesis of heterometallic complexes becomes a major goal.

2,4,6-Trichloro-1,3,5-triazine, **1** (Scheme 1), may be used for the construction of an array of novel complex derivatives and of a variety of structurally diverse macrocycles by sequential nucleophilic aromatic substitution processes.[6] Therefore, triazine **1** is an interesting building block since it shows an unusual ability of stepwise replacement of the three chlorine atoms by nucleophiles (Scheme 1). Anelli et al. were the first to synthesize bridged polyoxapolyazaheterophanes from **1**.[7] Later on, Lowe et al. adopted a stepwise approach for the synthesis of a variety of triazine-based receptors.[8] Di- and trinuclear mixed-metal complexes (Ni^{II} and Cu^{II}) of bis- and tris-azamacrocyclic ligands linked by a 1,3,5-triazine spacer group have been described by Comba et al.[9] Simanek has recently published the synthesis of dendrimers based on iterative reactions of **1** and several diamine linkers.[10]

Scheme 1. Stepwise Controlled Substitution of the Triazine Ring



In the last years we have published the synthesis and characterization of a novel type of nitrogen-containing 15-membered triolefinic macrocyclic ligands[11] as well as

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Publication on Web 04/17/2004

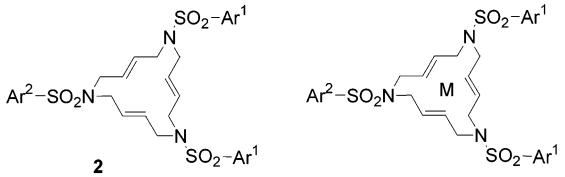

Figure 1. Structure of 15-membered triolefinic macrocyclic ligands **2** and their transition metal complexes **3**.

their palladium(0), platinum(0), and silver(I) complexes[12] (Figure 1). Especially, compounds **3** (M = Pd) are excellent recoverable catalysts in certain C−C bond formation reactions such as Suzuki cross-couplings,[11a,c] butadiene telomerization,[13] hydroarylation of alkynes in ionic liquids,[14] and Heck reactions.[15] Olefins are good ligands for palladium(0),[16] and in macrocycles **2** the three olefinic bonds are responsible for the coordination, the nitrogen atoms being devoid of any coordinating ability.

In this paper we report on polynucleating symmetrical systems (Scheme 2) that provide different polymetallic transition metal complexes (Schemes 3 and 4). Using triazine **1** as central building block, herein we describe the synthesis and characterization of new symmetric dinucleating macrocyclic ligands **4** and their homobimetallic Pd^0 complex, **5aa**, and heterobimetallic Pd^0,Pt^0 complex, **5ab**. We also present the preparation of a homotrimetallic palladium(0) complex, **7**. In addition, preliminary results based on catalytic activity of **5aa** are reported.

Results and Discussion

The triazine-based mono-, bis-, and tris-macrocyclic ligands **2c**, **4**, and **6** were synthesized as outlined in Scheme 2. Macrocycle **2a** was prepared by the method described by us for macrocycles containing two different aryl units.[11] Nucleophilic aromatic substitution was performed in **2a** by heating at 100 °C with excess ethylenediamine to afford compound **2b** in 94% yield. Macrocycle **2b** has a nucleophilic terminal amino group capable of replacing sequentially the chlorine atoms in 2,4,6-trichloro-1,3,5-triazine, **1**. Indeed, **2c**, **4**, and **6** could be obtained directly by reacting trichlorotriazine with 1, 2, or 3 equivalents of aminomacrocycle **2b** (Scheme 2). The experimental conditions for replacement of one, two, or three chlorine atoms are increasingly severe in terms of temperature and reaction time. The three final compounds were isolated in yields from reasonable to excellent. Alternatively **6** could be obtained from **4**, and **4** from **2c** by reactions with 1 equiv of **2b**, again under increasingly severe reaction conditions (Scheme 2). In summary, the triazine framework offers excellent differences in reactivity for the three C−Cl bonds, permitting efficient sequential replacement of the halogen atoms.

NMR spectra of **2c**, **4**, and **6** are similar to those of previously reported macrocycles **2**[11] (Figure 1). The ^{1}H NMR spectra of compounds **2c**, **4**, and **6** recorded in $CDCl_3$ showed two broad signals at 3.60−3.71 and 5.53−5.57 ppm for the internal methylene CH_2 and olefinic CH protons of the macrocycles, respectively. Also the spectra showed two broad signals around 3.39 and 3.60 ppm corresponding to the four methylenic protons of the ethylenediamine units. Since the three ^{1}H NMR spectra are quite similar, mass spectrometry was the best analytical technique to characterize these compounds. Electrospray ionization mass spectrometry (ESI-MS) was used for detection of compounds **2c** and **4**. Compounds **2** [**2a** (*m*/*z* 674 $[M + H]^+$), **2b** (*m*/*z* 714 $[M + H]^+$), and **2c** (*m*/*z* 861 $[M + H]^+$)] and **4** (*m*/*z* 1538 $[M + H]^+$) all showed the molecular peaks. Compound **4** also produced a doubly charged ion at *m*/*z* 770 corresponding to $[(M + 2H)/2]^{2+}$. Trimacrocycle **6** has a molecular weight greater than the mass range of the MS detector. However, its mass spectrum showed one peak corresponding to diprotonated **6** (*m*/*z* 1108 $[(M + 2H)/2]^{2+}$). Structure **6** was corroborated by matrix-assisted laser desorption ionization-time-of-flight (MALDI-TOF) mass spectrometry, which showed the molecular ion at *m*/*z* 2215 $[M + H]^+$.

Attempts to obtain X-ray quality crystals of these ligands failed.

Next we loaded macrocycles **4** and **6** with metals. The homobimetallic palladium(0) complex **5aa** was prepared in 87% yield by reaction of **4** with bis(dibenzylideneacetone)palladium(0) in refluxing THF (Scheme 3). With the same source of palladium and under the same experimental conditions, homotrimetallic palladium(0) complex **7** was obtained from **6** in 92% yield (Scheme 3).

Heterobimetallic palladium(0)−platinum(0) complex **5ab** was prepared by reaction of two units, **3c** and **3b**, each already possessing a different metal atom (Scheme 4). Thus, when macrocycle **2c** was treated with $Pd(dba)_2$ in refluxing THF, palladium(0) complex **3c**, one of the required partners, was isolated in 79% yield. The preparation of the platinum-containing **3b** required previous loading of **2a** with platinum by reaction with $Pt(PPh_3)_4$ to afford **3a**. The stable macrocyclic complex **3a** reacted with ethylenediamine to yield **3b**, a macrocyclic compound featuring a primary amine and, at the same time, a coordinated platinum atom. It is remarkable that platinum resisted the harsh experimental

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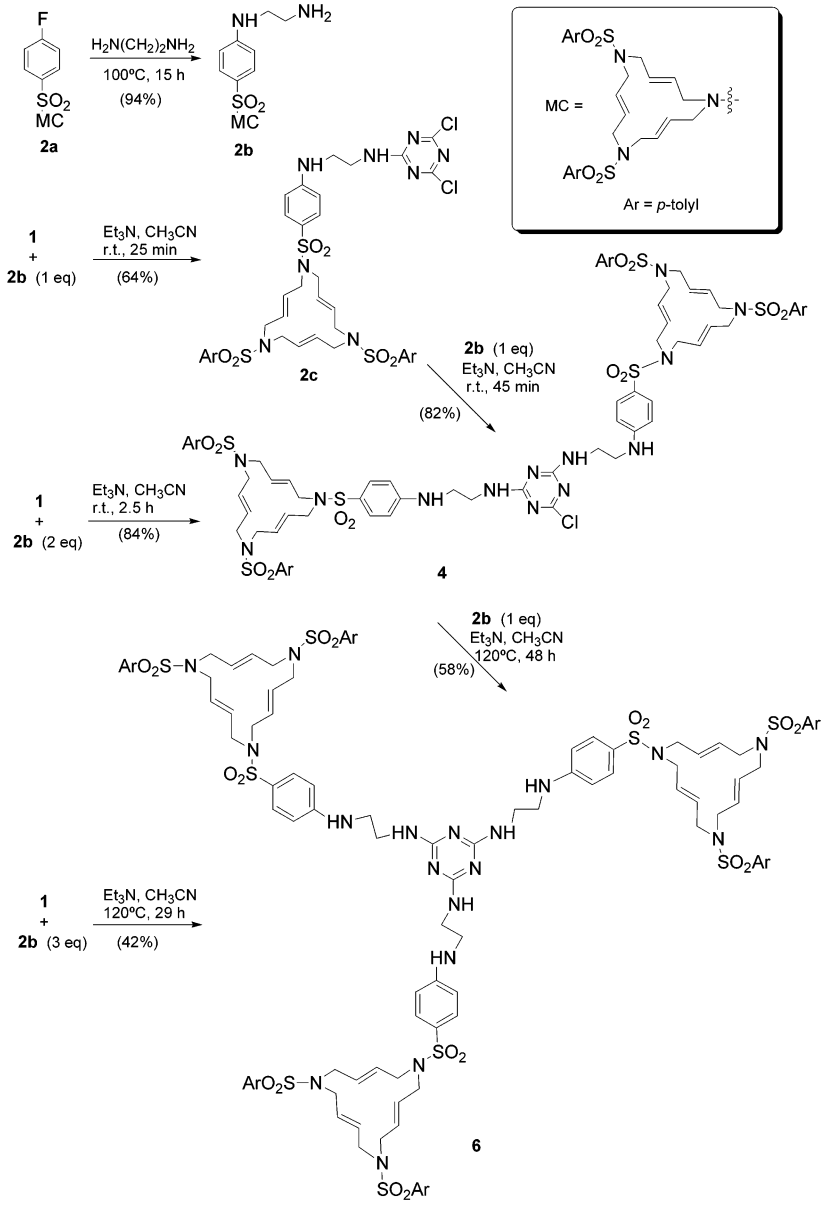
Scheme 2. Synthesis of Triazine-Spaced 15-Membered Triolefinic Macrocycles 4 and 6



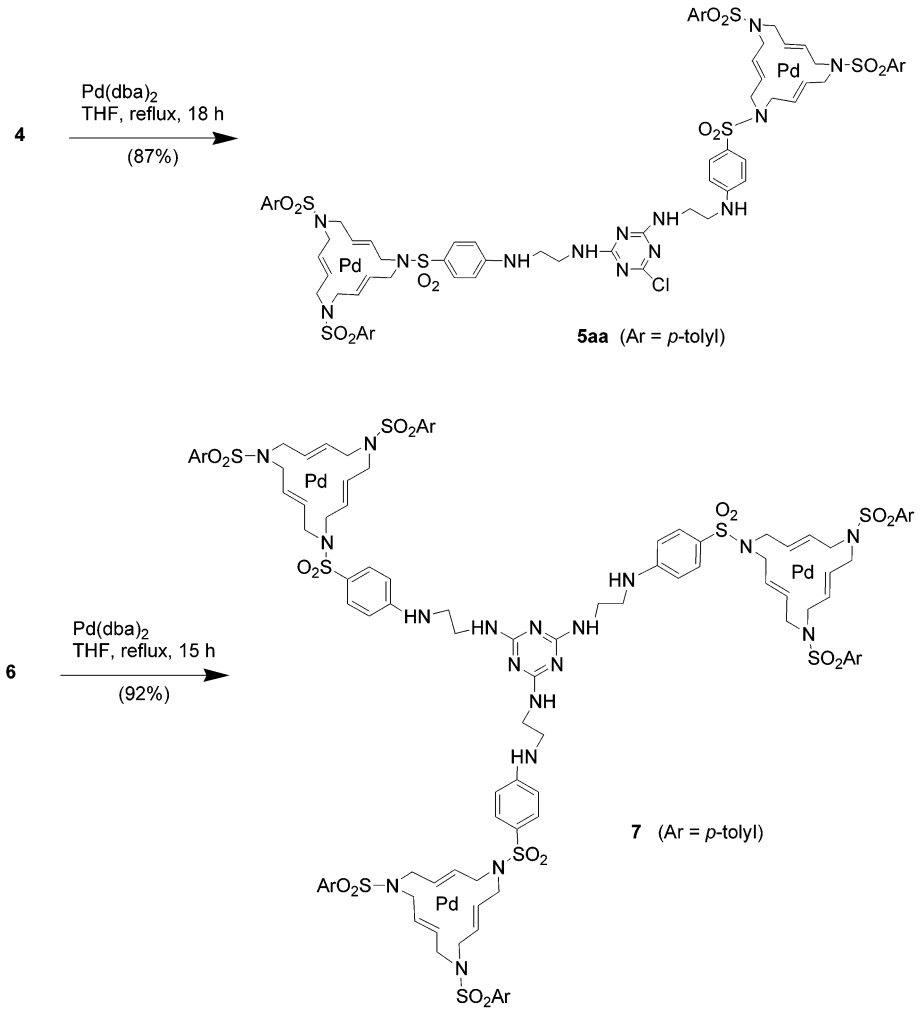
conditions without decomplexation. This is in contrast with the unsuccessful attempts to incorporate platinum to macrocyclic amine **2b**. Amines interfere with the incorporation of platinum, but platinum in the coordination site is inert toward amines even at 100 °C. Finally, reaction of palladium(0) complex **3c** and platinum(0) complex **3b** in the presence of triethylamine in refluxing acetonitrile under inert atmosphere gave heterobimetallic complex **5ab** in 72% yield (Scheme 4).

Compounds **5aa**, **5ab**, and **7** are only partially soluble in many common organic solvents, but practically insoluble in hexanes, diethyl ether, and ethanol. Their poor solubility makes difficult the registration of NMR spectra. Solubility in DMSO is high, but as time goes on, decomplexation of the metal center takes place.

As we have previously reported,[12] the introduction of a metal in the cavity of the macrocycle of type **2** (Figure 1) leads to significant changes in the ^{1}H and ^{13}C NMR spectra. The complexity of NMR data for complexes of type **3** (Figure 1) is due to the presence of different substituent-dependent stereoisomers resulting from coordination of the metal center to one of the two olefinic faces of every double bond in the macrocycle. Thus, a great number of NMR resonances appear usually overlapped in a very narrow chemical shift range for each proton or carbon atom, making very difficult their precise assignments.[12] In practice, NMR spectra for polynuclear complexes **5** and **7** are very complicated and, therefore, relatively uninformative. Moreover, apart from the broad macrocyclic signals, broad absorptions appear at ∼3.3 and 3.7 ppm in the ^{1}H NMR spectra and at ∼40 and 43 ppm in the ^{13}C NMR spectra and are assigned to the central ethylenediamine $-HNCH_2CH_2-NH-$ subunits.

Again, mass spectrometry was the best way to identify palladium(0) and platinum(0) complexes. Only monometallic complexes **3a**−**c** were successfully analyzed by positive-ion ESI-MS. Peaks due to species containing palladium and platinum were immediately identifiable by the characteristic isotope distribution of the two metals. Isotope abundance of clusters was compared with calculated values using the *Isoform* program. As

Scheme 3. Synthesis of Pd⁰ Homobimetallic Complex 5aa and Pd⁰ Homotrimetallic Complex 7



an example, Figure 2 shows the ESI-MS spectrum of compound **3b**.

The characterization of compounds **5aa**, **5ab**, and **7** by ESI-MS was unsuccessful due to their high molecular weight. Peaks for these structures consistent with loss of one metal atom from the macrocyclic cavity were detected by MALDI-TOF mass spectrometry. However, peaks for the molecular ions of **5aa**, **5ab**, and **7** were observed when LSI-MS technique was used. In addition, correct elemental analyses were achieved for the three new complexes. Unfortunately, X-ray quality crystals for these three complexes could not be obtained.

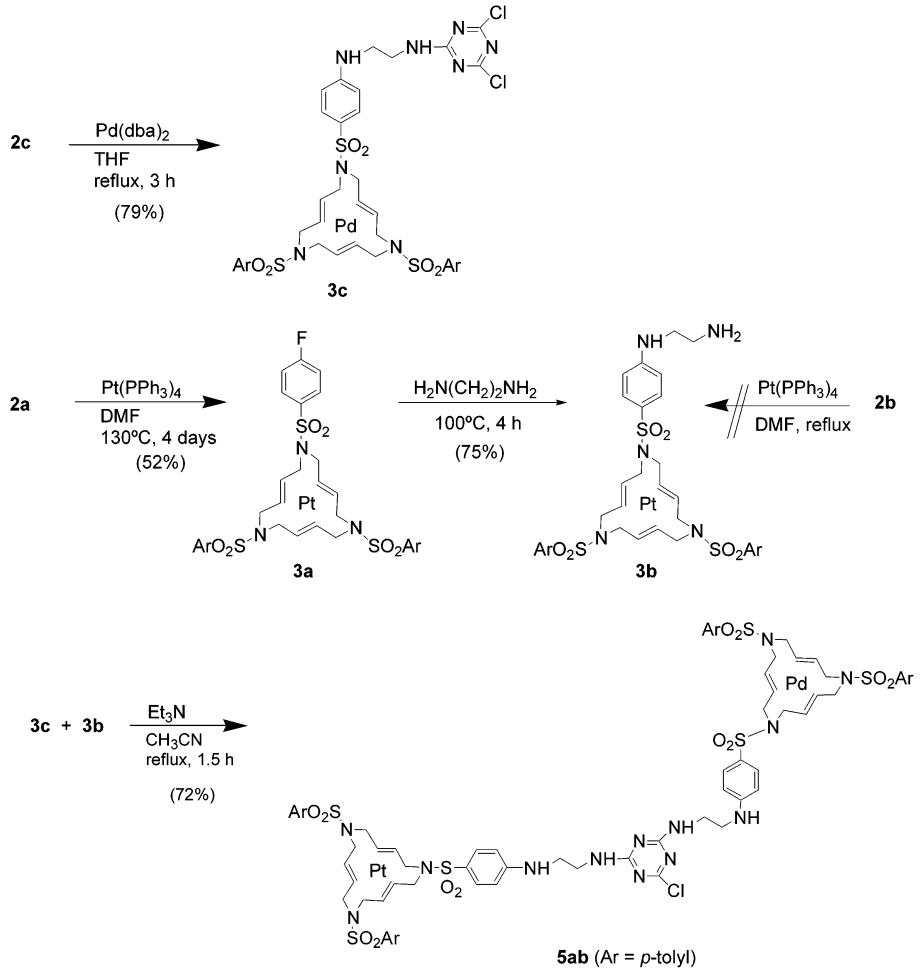
Since palladium(0) complexes of type **3** (Figure 1) are efficient and recoverable catalysts in certain C−C bond formation reactions,[11a,c,13−15] we have carried out preliminary studies on the catalytic activity of bimetallic complex **5aa** (Scheme 5). Taking advantage of the poor solubility of **5aa** in common organic solvents, precipitation of the catalyst at the end of the reaction and further recovery by simple filtration was easily achieved. Suzuki cross-coupling between phenylboronic acids **8a**,**b** and iodobenzenes **9a**,**b** in acetone−water (1:1) at 70 °C afforded the corresponding biphenyls **10a**−**c** in good yields (100% for **10a**, 92% for **10b**, and 88% for **10c**). After addition of diethyl ether to the reaction mixture, catalyst **5aa** precipitated quantitatively in all cases, and it was recovered by filtration. No decomplexation of palladium atom took place. The Mizoroki−Heck reaction between ethyl acrylate, **11**, and benzenediazonium tetrafluoroborate, **12**, in ethanol at room temperature did not afford the corresponding cinnamate in the presence of insoluble **5aa**. However, upon heating at 50 °C, catalyst **5aa** went partially into solution and ethyl cinnamate **13** was obtained in 22% yield. After cooling the reaction mixture at 0 °C, **5aa** precipitated out, and it was recovered in 95% yield without noticeable decomplexation.

Conclusion

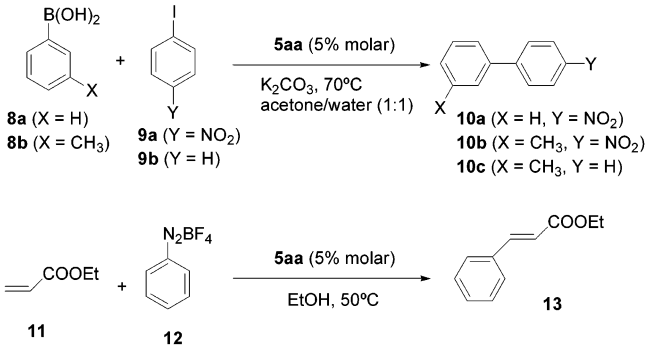
In conclusion, new symmetric polynucleating macrocyclic ligands and their homo- and heterometallic complexes of palladium(0) and platinum(0) have been prepared. The described method is versatile, permitting the preparation of heterobimetallic complexes, avoiding mixtures with homobimetallic species. Several mass spectrometry techniques are fundamental in the identification of the products.

Preliminary results proved that palladium(0) complex **5aa** is a good recoverable catalyst in certain cross-coupling reactions. The low solubility of **5aa** in common organic solvents allows its quantitative recovery at the end of the catalytic cycle by simple precipitation in the reaction mixture. Further studies about catalytic activity of these new structures are in progress.

Scheme 4. Synthesis of Pd^0,Pt^0 Heterobimetallic Complex 5ab



Scheme 5. Catalytic Reactions Tested with Pd^0 Homobimetallic Complex 5aa



Experimental Section

General Procedures. ^{1}H NMR (^{13}C NMR) spectra were recorded at 200 MHz (50 MHz), at 250 MHz (62.5 MHz), or at 500 MHz (100 MHz) using Me_4Si as internal standard. Chemical shifts are given in δ units. ESI (electrospray ionization) mass spectra were acquired using a Navigator quadrupole mass spectrometer (Finnigan AQA ThermoQuest) equipped with an electrospray ion source. The instrument was operated in the positive-ion mode (ESI+) at a probe tip voltage of 3 kV. The samples were dissolved in CH_3CN. The solution, typically of approximate concentration of 4 mM, may be further treated by the addition of 1−2 drops of a 0.1% M TFA aqueous solution. The samples were introduced into the mass spectrometer ion source directly via a Rheodyne injector with a 20 μL sample loop. The mobile phase flow (150 μL/min of 70:30 v/v CH_3CN-H_2O) was delivered by a P2000 HPLC pump (ThermoQuest) to the vaporization nozzle of the electrospray ion source (165 °C), and nitrogen was employed as both a drying and nebulizing gas. Skimmer cone voltages were varied between 10 and 100 eV. Spectra were typically an average between 10 and 20 scans. MALDI-TOF (matrix-assisted laser desorption/ionization time-of-flight) mass spectra were performed on a Ultraflex spectrometer (Bruker Daltoniks A.G.) equipped with a pulsed nitrogen laser (337 nm), operating in positive-ion reflector mode, and using a 25 kV acceleration voltage. Samples were prepared for analysis by dissolving in THF (1−5 mg/mL) and mixing with an equal volume of matrix (α-cyano-4-hydroxycinnamic acid, 5 mg/mL in THF). From this mixture, 1 mL was spotted on a stainless steel sample holder and allowed to evaporate to dryness at room temperature. Mass spectra were obtained by averaging the signals from 20−100 laser shots at 2−10 different spots within the sample. LSI (liquid secondary ion) mass spectra were recorded on a VG-Autospec EBE mass spectrometer. 3-Nitrobenzyl alcohol (3-NBA) was used as LSI MS matrix, and the standard Cs^+ gun was operated at 30 kV. Theoretical isotope patterns were calculated using the *Isoform* program and used to aid in assignment. HRMS was obtained at "S.C.A.I. Unidad de Espectrometría de Masas de la Universidad de Córdoba". Elemental analyses were determined at "Servei d'Anàlisi de la Universitat de Girona".

(*E*,*E*,*E*)-1-(4-Fluorophenylsulfonyl)-6,11-bis[(4-methylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-triene (2a). Macrocycle **2a** was prepared according to a previously reported method described for macrocycles containing different arene units.[11] Colorless solid (72% yield). Mp: 177−178 °C. IR (KBr): ν 2922, 1336, 1159 cm^{-1}. ^{1}H NMR (200

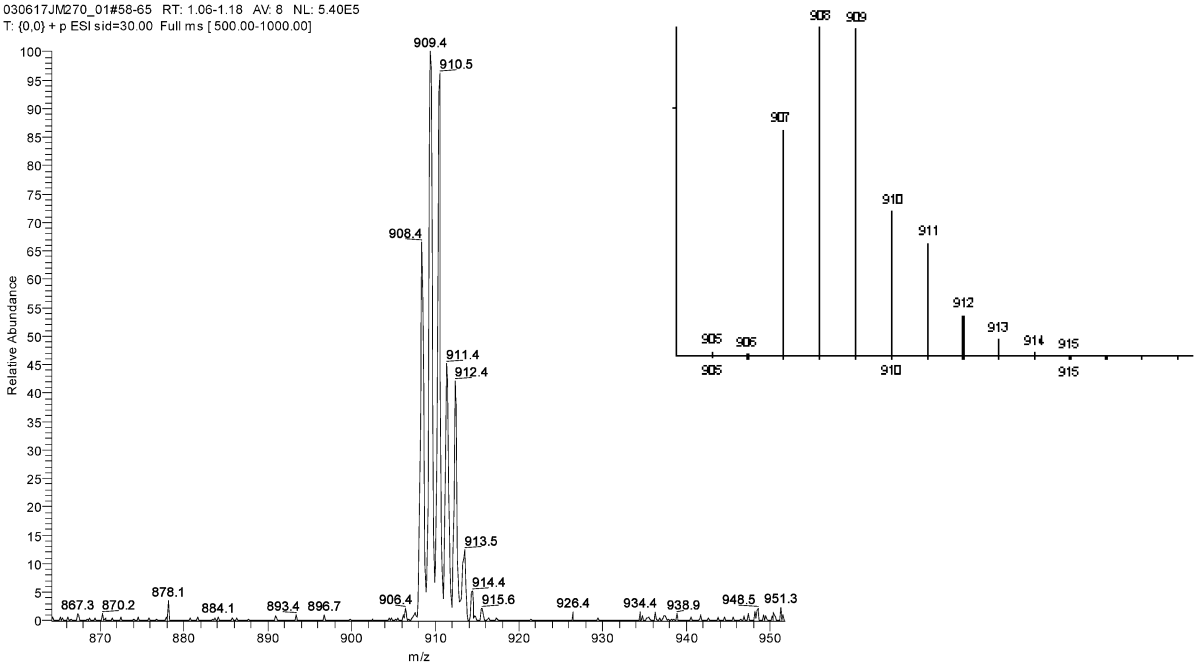


Figure 2. ESI mass spectrum of complex **3b** (bottom) compared with theoretical isotope distribution (top).

MHz, $CDCl_3$, 25 °C, TMS): δ 2.43 (s, 6H), 3.68 (br abs, 12H), 5.59 (br abs, 6H), 7.16−7.25 (m, 2H), 7.32 (d, ^3J(H,H) = 7.8 Hz, 4H), 7.66 (d, ^3J(H,H) = 8 Hz, 4H), 7.76−7.83 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C, TMS): δ 21.5, 50.5, 50.7, 50.8, 116.5 (d, ^2J(C,F) = 22.3 Hz), 127.1, 129.0, 129.5, 129.7 (d, ^3J(C,F) = 9.3 Hz), 129.8, 135.3 (d, ^4J(C,F) = 3.2 Hz), 136.0, 143.6, 165.1 (d, ^1J(C,F) = 253.2 Hz). ESI-MS (*m*/*z*): 712 [M + K]$^+$, 696 [M + Na]$^+$, 691 [M + NH_4]$^+$, 674 [M + H]$^+$. Anal. Calcd for $C_{32}H_{36}FN_3O_6S_3$: C 57.04; H 5.38; N 6.24. Found: C 56.80; H 5.30; N 6.25.

(*E*,*E*,*E*)-1-[4-(2-Aminoethylamino)phenyl]sulfonyl)-6,11-bis[(4-methylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-triene (2b). Macrocycle **2a** (0.50 g, 0.74 mmol) was stirred in ethylenediamine (6 mL) for 15 h at 100 °C. Upon addition of H_2O, product **2b** precipitated. It was washed with H_2O and digested in hexane to afford pure **2b** as a colorless solid (0.50 g, 94%). Mp: 86−88 °C. IR (neat): ν 3385, 2919, 1597, 1327, 1148 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ 1.44 (br s, 2H), 2.43 (s, 6H), 2.97 (t, ^3J(H,H) = 5.5 Hz, 2H), 3.21 (m, 2H), 3.66 (br abs, 12H), 4.81 (br s, 1H), 5.55 (br abs, 6H), 6.61 (d, ^3J(H,H) = 8.6 Hz, 2H), 7.31 (d, ^3J(H,H) = 8 Hz, 4H), 7.53 (d, ^3J(H,H) = 8.6 Hz, 2H), 7.65 (d, ^3J(H,H) = 8 Hz, 4H). ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C, TMS): δ 22.1, 41.4, 46.2, 51.3, 51.4, 112.5, 125.9, 127.8, 129.6, 129.9, 130.0, 130.5, 136.7, 144.2, 152.6. ESI-MS (*m*/*z*): 714 [M + H]$^+$. Anal. Calcd for $C_{34}H_{43}N_5O_6S_3 \cdot H_2O$: C 55.79; H 6.19; N 9.57; S 13.14. Found: C 55.45; H 5.96; N 9.48; S 13.27.

(*E*,*E*,*E*)-1-{4-[*N*′-(4,6-Dichloro-[1,3,5]triazin-2-yl)amino-ethylamino)phenyl]sulfonyl)-6,11-bis[(4-methylphenyl)-sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-triene (2c). Triethylamine (0.07 mL, 0.52 mmol) was added to a magnetically stirred solution of **2b** (0.075 g, 0.11 mmol) and 2,4,6-trichloro-1,3,5-triazine (**1**) (0.020 g, 0.11 mmol) in dry CH_3CN (10 mL) under argon atmosphere at room temperature. The solution was stirred at room temperature for 25 min (TLC monitoring). The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (*n*-hexane−EtOAc, polarity from 6:4 to 4:6) to afford **2c** (0.058 g, 64%) as a colorless solid. A sample specially purified for elemental analysis was obtained by digestion from *n*-hexane. Mp: 102−104 °C. IR (neat): ν 3386, 2922, 1591, 1322, 1149 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ 2.45 (s, 6H), 3.49 (br s, 2H), 3.65−3.68 (m, 12H), 3.74 (m, 2H), 4.82 (br s, 1H), 5.57 (s, 6H), 6.67 (d, ^3J(H,H) = 8.5 Hz, 2H), 6.84 (br abs, 1H), 7.34 (d, ^3J(H,H) = 8.05 Hz, 4H), 7.54 (dd, ^3J(H,H) = 8.5, ^4J(H,H) = 2.3 Hz, 2H), 7.67 (d, ^3J(H,H) = 8.05 Hz, 4H). ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C, TMS): δ 22.2, 41.1, 42.9, 51.4, 112.6, 126.4, 127.8, 129.7, 129.9, 130.0, 130.2, 130.5, 136.5, 144.3, 151.9, 166.8, 170.5, 171.5. ESI-MS (*m*/*z*): 899 [M + K]$^+$, 883 [M + Na]$^+$, 861 [M + H]$^+$. Anal. Calcd for $C_{37}H_{42}Cl_2N_8O_6S_3$: C 51.56; H 4.91; N 13.00. Found: C 51.40; H 4.79; N 12.51.

Bismacrocycle Monochlorotriazine Derivative (4). From reaction of 2b and 2c. Triethylamine (0.12 mL, 0.56 mmol) was added to a magnetically stirred solution of **2b** (0.062 g, 0.087 mmol) and **2c** (0.075 g, 0.087 mmol) in dry CH_3CN (10 mL) under argon atmosphere at room temperature. The solution was stirred at room temperature for 45 min (TLC monitoring). The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (*n*-hexane−EtOAc, polarity from 4:6 to 1:9) to afford **4** (0.11 g, 82%) as a colorless solid. A sample specially purified for elemental analysis was obtained by digestion from *n*-hexane. Mp: 125−127 °C. IR (neat): ν 3386, 3261, 2924, 1599, 1553, 1329, 1153 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ 2.44 (s, 12H), 3.38−3.42 (m, 4H), 3.63−3.70 (m, 24H), 3.61−3.69 (m, 4H), 4.92 (br abs, 1H), 5.21 (br abs, 1H), 5.50−5.60 (m, 12H), 5.94 (br abs, 1H), 6.27 (br abs, 1H), 6.57−6.67 (m, 4H), 7.33 (d, ^3J(H,H) = 8.0 Hz, 8H), 7.49−7.54 (m, 4H), 7.66 (d, ^3J(H,H) = 8.0 Hz, 8H). ^{13}C NMR (50 MHz, [D_6]acetone, 25 °C, TMS): δ 21.4, 40.4, 43.1, 51.2, 51.3, 112.4, 126.5, 128.0, 129.9, 130.0, 130.3, 130.7, 137.8, 144.2, 153.0, 167.3, 169.4, 169.9. ESI-MS (*m*/*z*): 1538 [M + H]$^+$, 770 [M + 2H/2]$^{2+}$. MALDI-TOF (*m*/z): 1576 [M + K]$^+$, 1560 [M + Na]$^+$, 1538 [M + H]$^+$. Anal. Calcd for $C_{71}H_{84}ClN_{13}O_{12}S_6$: C 55.40; H 5.50; N 11.83; S 12.50. Found: C 55.75; H 5.79; N 11.45; S 12.27.

From Reaction of 2b and 1. Triethylamine (0.08 mL, 0.56 mmol) was added to a magnetically stirred solution of **2b** (0.080 g, 0.11 mmol) and **1** (0.010 g, 0.060 mmol) in dry CH_3CN (10 mL) under argon atmosphere at room temperature. The solution was stirred at room temperature for 2.5 h (TLC monitoring). See preceding preparation for workup and spectral data of **4** (0.072 g, 84%).

Trismacrocycle Triazine Derivative (6). From reaction of 4 and 2b. A solution of triethylamine (0.013 mL, 0.09 mmol), **2b** (0.016 g, 0.022 mmol), and **4** (0.035 g, 0.022 mmol)

in dry CH_3CN (10 mL) was introduced in a sealed tube under argon. The stirred solution was heated at 120 °C for 48 h (TLC monitoring). The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (from *n*-hexane−EtOAc, 1:9, to EtOAc−CH_2Cl_2, 9.5:0.5) to afford **6** (0.029 g, 58%) as a colorless solid. A sample specially purified for elemental analysis was obtained by crystallization from CH_2Cl_2−*n*-hexane. Mp: 127−129 °C. IR (neat): ν 3394, 2923, 1598, 1511, 1328, 1149 cm^{-1}. ^1H NMR (500 MHz, [D_6]acetone, 25 °C, TMS): δ 2.43 (s, 18H), 3.35−3.42 (m, 6H), 3.60−3.65 (m, 6H), 3.65−3.72 (br s, 36H), 5.55 (br abs, 18H), 6.20 (br abs, 2H), 6.36 (br abs, 2H), 6.45 (br abs, 1H), 6.53 (br abs, 1H), 6.76 (br abs, 6H), 7.43 (d, ^3J(H,H) = 8.15 Hz, 12H), 7.51 (d, ^3J(H,H) = 8.4 Hz, 6H), 7.72 (d, ^3J(H,H) = 8.15 Hz, 12H). ^{13}C NMR (50 MHz, [D_6]acetone, 25 °C, TMS): δ 21.4, 40.2, 44.7 (br abs, 6C), 51.2, 112.3, 126.1, 128.0, 129.8, 130.0, 130.2, 130.7, 137.8, 144.2, 153.2, 167.4. ESI-MS (*m*/*z*): 1108 $[(M + 2H)/2]^{2+}$. MALDI-TOF (*m*/*z*): 2253 $[M + K]^+$, 2237 $[M + Na]^+$, 2215 $[M + H]^+$. Anal. Calcd for $C_{105}H_{126}N_{18}O_{18}S_9 \cdot 1/2CH_2Cl_2$: C 56.09; H 5.67; N 11.16. Found: C 55.99; H 5.78; N 10.73.

From Reaction of 2b and 1. A solution of triethylamine (0.05 mL, 0.37 mmol), **2b** (0.080 g, 0.11 mmol), and **1** (0.007 g, 0.04 mmol) in dry CH_3CN (10 mL) was introduced in a sealed tube under argon atmosphere. The stirred solution was heated at 120 °C for 29 h (TLC monitoring). See preceding preparation for workup and spectral data of **6** (0.035 g, 42%).

Homobimetallic Pd^0 Complex (5aa). A magnetically stirred solution of bismacrocycle monochlorotriazine derivative **4** (0.040 g, 0.026 mmol) and bis(dibenzylideneacetone)palladium(0) (0.039 g, 0.068 mmol) in THF (6 mL) was refluxed for 18 h (TLC monitoring). The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (*n*-hexane−EtOAc, polarity from 5:5 to 1:9) to afford **5aa** (0.039 g, 87%) as a colorless solid. A sample specially purified for elemental analysis was obtained by digestion from *n*-hexane. Mp: 216−218 °C (dec). IR (neat): ν 3386, 2923, 1598, 1574, 1331, 1152 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ 1.58−1.90 (m, 8H), 2.39 (s, 12H), 2.65−2.93 (m, 4H), 2.93−3.20 (m, 4H), 3.20−3.80 (m, 12H), 3.86−4.11 (m, 4H), 4.50−4.82 (m, 12H), 5.02 (br s, 1H), 5.43 (br s, 1H), 5.65 (br s, 1H), 5.90 (br s, 1H), 6.50−6.65 (m, 4H), 7.25−7.30 (m, 8H), 7.43−7.58 (m, 4H), 7.60−7.76 (m, 8H). ^{13}C NMR (62.5 MHz, [D_6]acetone, 25 °C, TMS): δ 21.3, 40.4 (m), 43.2 (m), 46.0, 49.1, 50.2, 78.5, 78.9, 79.1, 79.4, 83.2, 83.3, 83.9, 112.3, 127.9, 128.0, 129.9, 130.0, 130.6, 130.7, 136.8, 137.2, 144.2, 153.0, 165.5, 167.6, 168.2. LSI-MS (*m*/*z*): 1751 $[M]^+$. Anal. Calcd for $C_{71}H_{84}N_{13}O_{12}S_6ClPd_2$: C 48.67; H 4.83; N 10.39; S 10.98. Found: C 48.75; H 5.03; N 9.94; S 10.66.

Homotrimetallic Pd^0 Complex (7). A magnetically stirred solution of trismacrocycle triazine derivative **6** (0.064 g, 0.029 mmol) and bis(dibenzylideneacetone)palladium(0) (0.044 g, 0.113 mmol) in THF (10 mL) was refluxed for 15 h (TLC monitoring). The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (from *n*-hexane−EtOAc, 1:1, to EtOAc−CH_2Cl_2, 9.5:0.5) to afford **7** (0.068 g, 92%) as a colorless solid. A sample specially purified for elemental analysis was obtained by crystallization from *n*-hexane−CH_2Cl_2. Mp: 203−205 °C (dec). IR (neat): ν 3388, 2923, 1598, 1573, 1326, 1150 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ 1.51−1.76 (m, 12H), 2.35−2.40 (m, 18H), 2.78−2.90 (m, 6H), 3.15 (br abs, 6H), 3.42 (br abs, 6H), 3.59 (br abs, 12H), 3.70 (br abs, 6H), 3.95 (br abs, 6H), 4.48−4.61 (m, 12H), 4.69−4.75 (m, 6H), 6.60−6.65 (m, 6H), 7.28−7.35 (m, 12H), 7.45−7.59 (m, 6H), 7.65−7.72 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ 21.5, 39.8 (br abs), 42.5 (br abs), 45.2, 48.3, 49.4, 50.7, 78.2, 78.6, 82.5, 82.8, 83.1, 111.9, 124.3 (br abs), 125.5 (br abs), 126.9, 127.1, 129.2, 129.8, 135.2, 135.4, 136.0, 143.4, 143.5, 151.6 (br abs), 162.4, 162.9, 164.6. LSI-MS (*m*/*z*): 2537 $[M + H]^+$. Anal. Calcd for $C_{105}H_{126}N_{18}O_{18}S_9Pd_3 \cdot CH_2Cl_2$: C 48.57; H 4.92; N 9.62; S 11.01. Found: C 48.64; H 4.97; N 9.22; S 10.95.

***(E,E,E)*-1-{4-[*N'*-(4,6-Dichloro-[1,3,5]triazin-2-yl)aminoethylamino)phenyl]sulfonyl)-6,11-bis[(4-methylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-trienepalladium(0) (3c).** A magnetically stirred solution of macrocycle **2c** (0.078 g, 0.091 mmol) and bis(dibenzylideneacetone)-palladium(0) (0.068 g, 0.118 mmol) in THF (8 mL) was refluxed for 3 h (TLC monitoring). The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (*n*-hexane−EtOAc, polarity from 6:4 to 5:5) to afford **3c** (0.069 g, 79%) as a colorless solid. A sample specially purified for elemental analysis was obtained by crystallization from $CHCl_3$−*n*-hexane. Mp: 155−157 °C. IR (neat): ν 3383, 2925, 1592, 1552, 1324, 1152 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ 1.60−1.80 (m, 4H), 2.39 (s, 6H), 2.67−2.95 (m, 2H), 2.95−3.17 (m, 2H), 3.36−3.50 (m, 2H), 3.62−3.80 (m, 4H), 3.87−4.08 (m, 2H), 4.46−4.82 (m, 6H), 6.11 (br abs, 1H), 6.62 (d, ^3J(H,H) = 8.8 Hz, 2H), 7.28 (m, 4H), 7.55 (d, ^3J(H,H) = 8.8 Hz, 2H), 7.57−7.78 (m, 4H). ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C, TMS): δ 22.1, 41.0, 42.9, 45.8, 48.9, 50.1, 78.9, 79.0, 79.2, 79.4, 83.2, 83.3, 83.8, 112.5, 125.1, 127.6, 127.7, 129.6, 130.0, 130.5, 130.6, 135.7, 135.8, 136.5, 144.2, 144.3, 151.9, 166.8, 170.4, 171.4. ESI-MS (*m*/*z*): 969 $[M + H]^+$, 861 $[M - Pd + H]^+$. Anal. Calcd for $C_{37}H_{42}Cl_2N_8O_6S_3Pd \cdot CHCl_3$: C 41.96; H 3.98; N 10.30; S 8.84. Found: C 42.39; H 3.94; N 10.14; S 9.18.

***(E,E,E)*-1-(4-Fluorophenylsulfonyl)-6,11-bis[(4-methylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-trieneplatinum(0) (3a).** A solution of macrocycle **2a** (0.05 g, 0.074 mmol) and tetrakis(triphenylphosphine)platinum(0) (0.15 g, 0.111 mmol) in DMF (3 mL) was heated at 130 °C for 4 days (TLC monitoring). The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (*n*-hexane−EtOAc, polarity from 9:1 to 7:3) to afford **3a** (0.034 g, 52%) as a colorless solid. A sample specially purified for elemental analysis was obtained by crystallization from CH_2Cl_2−*n*-hexane. Mp: 175−177 °C. IR (KBr): ν 2923, 1340, 1162 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ 1.22−1.50 (m, 4H), 2.10 (t, ^3J(H,H) = 11.6 Hz, 2H), 2.39 (s, 6H), 2.99 (t, ^3J(H,H) = 12.3 Hz, 2H), 3.13−3.74 (m, 4H), 4.24−4.80 (m, 4H), 5.03 (d, ^3J(H,H) = 13.6 Hz, 2H), 7.10−7.38 (m, 6H), 7.50−7.98 (m, 6H). ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C, TMS): δ 22.1, 45.0, 47.8, 49.2, 63.0, 63.4, 63.5, 63.7, 63.9, 64.2, 69.3, 69.8, 70.0, 117.1 (d, ^2J(C,F) = 22.4 Hz), 127.7, 127.9, 130.5 (m), 135.0 (d, ^4J(C,F) = 3.3 Hz), 135.6 (m), 136.7, 144.1, 144.3, 165.8 (d, ^1J(C,F) = 253.4 Hz). ESI-MS (*m*/*z*): 869 $[M + H]^+$. Anal. Calcd for $C_{32}H_{36}FN_3O_6S_3Pt.CH_2Cl_2$: C 41.55; H 4.01; N 4.40; S 10.08. Found: C 41.67; H 4.07; N 4.28; S 10.07.

***(E,E,E)*-1-[4-(2-Aminoethylamino)phenyl]sulfonyl)-6,11-bis[(4-methylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-trieneplatinum(0) (3b).** Platinum(0) complex **3a** (0.025 g, 0.029 mmol) was stirred in ethylenediamine (3 mL) for 4 h under argon atmosphere at 100 °C (TLC monitoring). Upon addition of H_2O, product **3b** precipitated. The solid was dissolved in CH_2Cl_2 (5 mL) and was washed with H_2O (2 × 5 mL). The organic layer was dried over Na_2SO_4 and evaporated to afford pure **3b** (0.019 g, 75%) as a colorless solid. A sample specially purified for elemental analysis was obtained by digestion from *n*-hexane. Mp: 126−128 °C (dec). IR (neat): ν 3380, 2923, 1597, 1329, 1152 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ 1.34−1.46 (m, 4H), 2.00−2.22 (m, 2H), 2.38 (s, 6H), 2.86−3.12 (m, 4H), 3.13−3.30 (m, 4H), 3.32−3.55 (m, 2H), 4.37−4.80 (m, 4H), 4.80−5.21 (d, ^3J(H,H) = 12.4 Hz, 2H), 6.57 (d, ^3J(H,H) = 8 Hz, 2H), 7.26−7.33 (m, 4H), 7.52 (d, ^3J(H,H) = 8 Hz, 2H), 7.62−7.74 (m, 4H). ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C, TMS): δ 22.2, 41.3, 45.0, 46.1, 47.9, 49.2, 63.0, 63.3, 63.5, 63.8, 64.3, 69.4, 69.6, 70.2, 112.5, 112.6, 124.8, 127.7, 127.9, 129.8, 130.0, 130.5, 135.7, 135.8, 136.7, 144.1, 144.3, 152.4. ESI-MS (*m*/*z*): 909 $[M+H]^+$. Anal. Calcd for $C_{34}H_{43}N_5O_6S_3$-

Pt: C 44.92; H 4.77; N 7.70; S 10.58. Found: C 45.00; H 4.99; N 7.12; S 10.14.

Heterobimetallic Pd^0−Pt^0 Complex (5ab). A degassed solution of triethylamine (0.03 mL, 0.20 mmol) in dry CH_3CN (10 mL) was added to a magnetically stirred mixture of **3b** (0.037 g, 0.041 mmol) and **3c** (0.035 g, 0.036 mmol). The solution was refluxed under argon atmosphere for 1.5 h (TLC monitoring). The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (*n*-hexane−EtOAc, polarity from 4:6 to 1:9) to afford **5ab** (0.049 g, 72%) as a colorless solid. A sample specially purified for elemental analysis was obtained by digestion from *n*-hexane. Mp: 187−189 °C (dec). IR (neat): ν 3387, 2924, 1598, 1574, 1329, 1152 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ 1.34−1.46 (m, 4H(Pt)), 1.40−1.90 (m, 4H(Pd)), 2.00−2.22 (m, 2H(Pt)), 2.38 (s, 12H), 2.55−3.35 (m, 4H(Pd) + 4H(Pt)), 3.25−3.82 (m, 6H(Pd) + 6H(Pt)), 3.93 (m, 2H(Pd)), 4.30−4.80 (m, 4H(Pd) + 4H(Pt)), 4.75−5.22 (m, 2H(Pd) + 2H(Pt)), 5.84 (br s, 2H), 6.37 (br s, 2H), 6.57 (m, 4H), 7.20−7.30 (m, 8H), 7.40−7.55 (m, 4H), 7.60−7.75 (m, 8H). ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C, TMS): δ 22.1, 40−41 (m), 42−43 (m), 45.8, 48.2, 49.0, 50.2, 63−65 (m), 68−70 (m), 78−79 (m), 83−84 (m), 112.4 (m), 127.7, 127.8, 129.9−130.5 (m), 131.4, 135−137 (m), 144.1, 144.3, 152.2, 165−168 (m). LSI-MS (*m*/*z*): 1839 $[M + H]^+$. Anal. Calcd for $C_{71}H_{84}ClN_{13}O_{12}S_6PdPt$: C 46.32; H 4.60; N 9.89; S 10.45. Found: C 46.60; H 4.82; N 9.95; S 10.40.

Preparation of 4-Nitrobiphenyl (10a) under Catalysis by Bimetallic Pd^0 Complex 5aa. General Method. A stirred mixture of 4-iodonitrobenzene (**9a**) (0.058 g, 0.228 mmol), benzeneboronic acid (**8a**) (0.043 g, 0.342 mmol), potassium carbonate (0.079 g, 0.57 mmol), and Pd^0 complex **5aa** (0.010 g, 0.0057 mmol) in acetone−H_2O (0.5:0.5 mL) was heated at 70 °C for 1.5 h (GC monitoring). After cooling to room temperature, water (3 mL) and diethyl ether (3 mL) were added. Catalyst **5aa** precipitated in the reaction mixture, and it was filtered off. The organic layer of the filtrate was separated, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-hexane−EtOAc, 9:1) to afford **10a** as a pale yellow solid (0.046 g, 100%). Mp: 111−112 °C (lit.[11a] mp 109−111 °C). ^1H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ 7.40−7.55 (m, 3H), 7.60−7.65 (m, 2H), 7.73 (d, ^3J(H,H) = 8.8 Hz, 2H), 8.28 (d, ^3J(H,H) = 8.8 Hz, 2H). MS (*m*/*z*, %): 199 (M^+, 100), 152 (99).

The following compounds were prepared and isolated according to the general procedure.

3-Methyl-4′-nitrobiphenyl (10b): pale yellow solid (92% yield). Mp: 57−58 °C (lit.[17] mp 59−60 °C). ^1H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ 2.44 (s, 3H), 7.20−7.30 (m, 1H), 7.30−7.45 (m, 3H), 7.70 (d, ^3J(H,H) = 8.8 Hz, 2H), 8.26 (d, ^3J(H,H) = 8.8 Hz, 2H). MS (*m*/*z*, %): 213 (M^+, 100), 183 (79), 165 (84), 152 (90).

3-Methylbiphenyl (10c): colorless oil[18] (88% yield). ^1H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ 2.41 (s, 3H), 7.10−7.20 (m, 1H), 7.25−7.47 (m, 6H), 7.50−7.62 (m, 2H). MS (*m*/*z*, %): 168 (M^+, 100), 152 (77).

Preparation of Ethyl (*E*)-Cinnamate (13) under Catalysis by Bimetallic Pd^0 Complex 5aa. Ethyl acrylate **11** (0.05 mL, 0.46 mmol) was added to a suspension of benzenediazonium tetrafluoroborate **12** (0.04 g, 0.23 mmol) and Pd^0 complex **5aa** (0.010 g, 0.0057 mmol) in ethanol (4 mL) at 0 °C under magnetic stirring. The mixture was heated at 50 °C and stirred until gas evolution ceased. After cooling to 0 °C (water-ice bath), catalyst **5aa** precipitated in the reaction mixture, and it was filtered off. The filtrate was dried (Na_2SO_4), and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-hexane−EtOAc, 9:1) to afford **13** as a colorless oil[18] (0.009 g, 22%). IR (neat): ν 1708, 1635, 1309, 1169 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ 1.33 (t, ^3J(H,H) = 7.2 Hz, 3H), 4.26 (q, ^3J(H,H) = 7.2 Hz, 2H), 6.43 (d, ^3J(H,H) = 16 Hz, 1H), 7.34−7.39 (m, 3H), 7.46−7.53 (m, 2H), 7.68 (d, ^3J(H,H) = 16 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C, TMS): δ 14.2, 60.3, 118.2, 127.8, 128.7, 130.1, 134.4, 144.4, 166.8. MS (*m*/*z*, %): 176 (M^+, 42), 147 (40), 131 (70), 103 (100).

Acknowledgment. Financial support from MCYT of Spain (Project No. BQU2002-04002-C02 and predoctoral grant to J.M.) and "Generalitat de Catalunya" (Projects No. SGR2001-00291 and SGR2001-00181) is gratefully acknowledged.

OM049967S

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