Synthesis of Nitrogen-Containing 15-Membered Triacetylenic Macrocycles. Stable Complex with Palladium(0)

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Selective and efficient preparation of a new type of nitrogen-containing 15-membered triacetylenic macrocycles named 1,6,11-tris(arylsulfonyl)-1,6,11-triazacyclopentadeca-3,8,-13-triynes (**1**) ($Ar^1 = Ar^2 = Ar^3$ = 4-methylphenyl, **1aaa**; $Ar^1 = Ar^2$ = 4-methylphenyl, Ar^3 = ferrocenyl, **1aab**) has been achieved. Macrocycle **1aaa** forms a very stable complex with Pd^0, being the first palladium(0) complex with a macrocyclic triyne. The three triple bonds in **1aaa** are responsible for the complexation. The X-ray structures of both the ligand **1aaa** and its Pd^0 complex are presented. Furthermore, compound **1aaa** undergoes cycloisomerization into the corresponding 2,5,8-tris[(4-methlphenyl)sulfonyl]-2,5,8-triazatrindane, **11aaa**, when treated with $Pd(PPh_3)_4$ in refluxing toluene.

Introduction

The synthesis and properties of macrocyclic compounds are important topics in supramolecular chemistry.[1] Synthetic approaches toward these compounds usually suffer from low yields, polymer formation during the macrocyclization step, and the need of high dilution conditions and template effect. Nitrogen-containing cycloalkynes, especially with the amine functionality in the propargylic position, are uncommon.[2] Thus, compounds of type $-(N-C-C\equiv C-C-)_n$ ($n = 3$) have been isolated as side products in the preparation of 10-membered rings ($n = 2$).[3] In the past few years, we have reported a very selective and efficient preparation of nitrogen-containing 15-,[4] 20-,[5] and 30-membered[4c] polyolefinic macrocycles as well as their coordinating properties with some transition metals.[6] In particular, palladium(0) complexes of the 15-membered triolefinic macrocycles have shown excellent catalytic activity in certain C−C bond formation reactions.[7]

On the other hand, the ability of transition metals to bind to π-systems of alkynes is well-known.[8] In particular, the chemistry of alkynes with palladium complexes is extremely rich and useful. First, oxidative addition to yield Pd^{II} alkynyl hydrides seems to be the preferred pathway of Pd^0 complexes with terminal alkynes. Also, palladium alkyne complexes have received considerable attention as intermediates in a variety of alkyne oligomerizations. However, few alkyne complexes have been isolated. Among them, several stable Pd^0-alkyne complexes containing phosphanes have been reported.[9] Pörschke et al. have even published the first isolated

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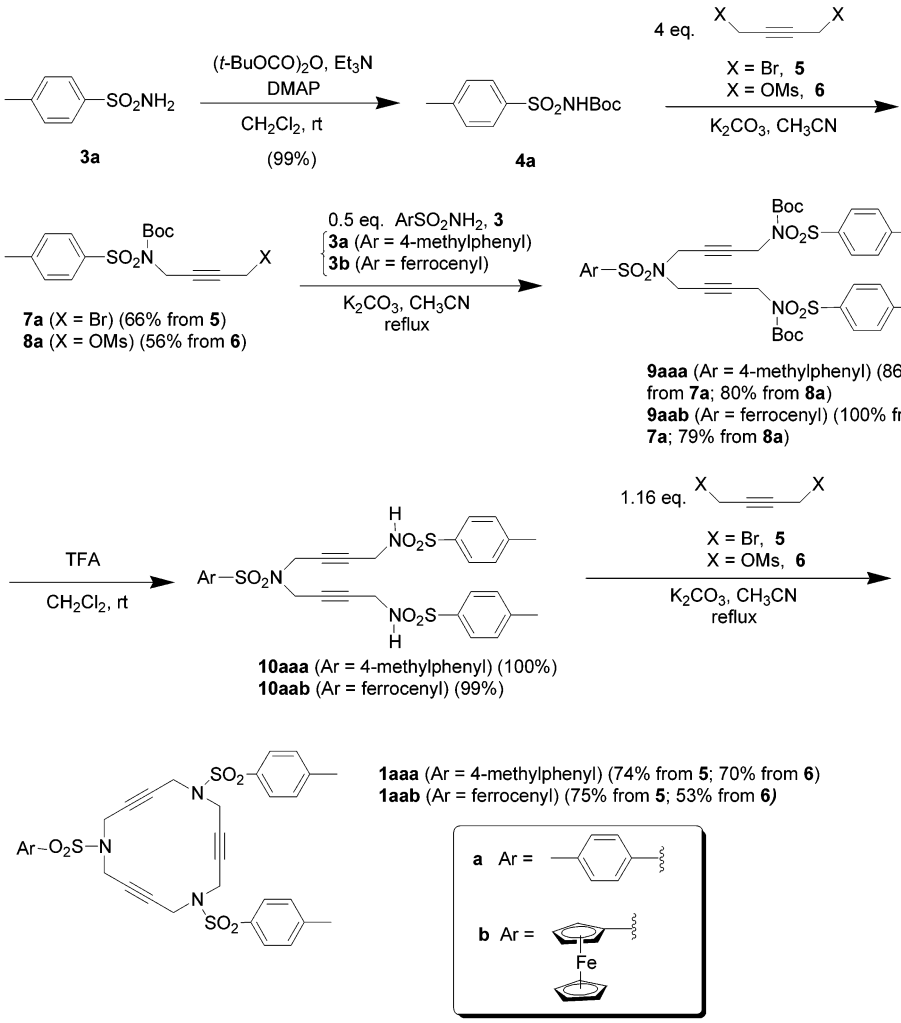
Scheme 1. Synthesis of Macrocycles 1aaa and 1aab



Pd^0-1-alkyne complex with bidentate phosphanes.[9d] Recently, Yamamoto et al. have reported the first palladium(0) trisalkyne complex, being an efficient catalyst precursor for the cyclization of the triyne ligand.[10]

We wish to describe in this paper an efficient and simple synthesis of two new 15-membered triazatriacetylenic macrocycles of type **1** (Scheme 1) as well as their coordinating capacity with palladium(0) (Scheme 2). To the best of our knowledge, we describe the first palladium(0) complex of a cyclic triyne ligand.

Results and Discussion

The preparation of macrocyclic triacetylenic derivatives **1aaa** and **1aab** is based on the retrosynthetic analysis for their homologous 15-membered triolefinic macrocycles[4a] and is shown in Scheme 1. Compound **4a** was prepared from sulfonamide **3a** according to the method described in the literature.[11] Reaction of **4a** with 4 equiv of 1,4-dibromo-2-butyne, **5**, afforded **7a** in 66% yield. In this step, we also explored 1,4-bis(methanesulfonyloxy)-2-butyne, **6**, as a 1,4-butadien-2-ylating reagent, obtaining derivative **8a** in 56% yield. Condensation of **7a** with 0.5 equiv of arylsulfonamides **3a** and **3b** led to *tert*-butyloxycarbonyl (Boc)-protected trisulfonamides **9aaa** and **9aab** in 86% and 100% yield, respectively. Compounds **9** were also obtained in good yields from methanesulfonate **8a**. Elimination of the Boc groups in compounds **9** resulted in the isolation of derivatives **10**. Final ring closure was achieved by treatment of **10** with 1.16 equiv of dibromide **5** or with bismethanesulfonate **6** to afford macrocycles **1** in good yields. From a synthetic point of view, the use of 1,4-bis(methanesulfonyloxy)-2-butyne, **6**, or 1,4-dibromo-2-butyne, **5**, did not make any difference. However, it is noteworthy that dibromo **5** is a powerful vesicant and lachrymator agent, and therefore, on a multigram scale the bismethanesulfonate protocol may be more useful.

The structure of macrocycle **1aaa** was confirmed by X-ray analysis. A perspective view of the molecule is shown in Figure 1. The molecule shows a folded struc-

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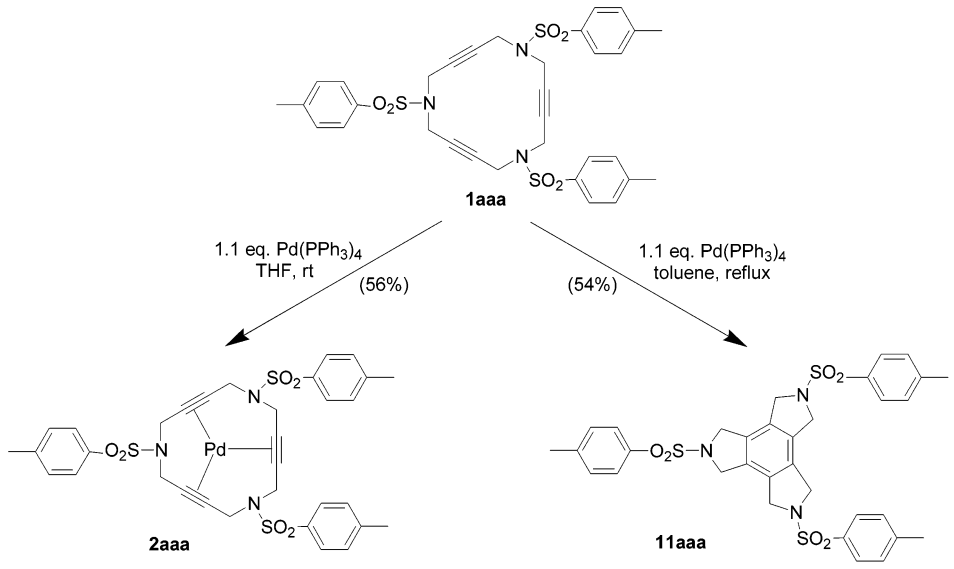
Scheme 2. Synthesis of Pd⁰ Complex 2aaa and Triazaindane 11aaa



ture with the linear substituted triple bonds ordered in different planes. Crystal data for the structure are given in Table 1.

Macrocycle **1aaa** was treated with 1 equiv of Pd(PPh$_3$)$_4$ in THF at room temperature to afford Pd^0 complex **2aaa** as an air- and moisture-stable crystalline compound (Scheme 2). Complex **2aaa** has been characterized by MS and ^{1}H and ^{13}C NMR spectra. The ESI mass spectra of **2aaa** showed a cluster centered at *m*/*z* 792 assigned to ion $[M + Na]^+$ by the characteristic isotope distribution of the palladium atom. The cluster corresponding to the molecular ion $[M + H]^+$ centered at *m*/*z* 770 was observed by MALDI-TOF mass spectrometry. In the ^{1}H NMR spectrum of **2aaa** the absorption due to the 12 methylenic protons of the ring (δ 4.38 ppm) was shifted (0.42 ppm) to lower field in comparison to that of the free macrocyclic ligand, **1aaa** (δ 3.96 ppm). In the ^{13}C NMR spectrum, the signals of the six acetylenic carbons (δ 74.1 ppm) and the six CH_2 groups (δ 36.4 ppm) in **2aaa** were displaced by 4.9 and 1.2 ppm, respectively, to upper field compared to **1aaa**. These values are in accordance to those described for a related Pd^0 trialkyne complex,[10] but differ significantly from those of mixed alkyne/phosphane-Pd^0 complexes, since the presence of other ligands such as phosphanes can change considerably the nature of the Pd−alkyne bonding.[9]

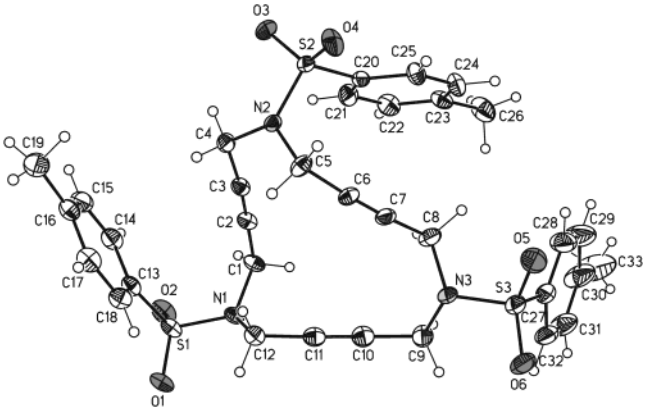


Figure 1. ORTEP plot (50%) of the structure of **1aaa**. Selected bond distances (Å) and angles (deg): C(2)−C(3): 1.1873(19); C(6)−C(7): 1.1843(19); C(10)−C(11): 1.190(2); C(1)−C(2)−C(3): 177.09(14); C(2)−C(3)−C(4): 174.39(14); C(5)−C(6)−C(7): 175.41(15); C(6)−C(7)−C(8): 176.19(15); C(9)−C(10)−C(11): 178.19(17); C(10)−C(11)−C(12): 176.84(16).

Table 1. Crystallographic Data for 1aaa and 2aaa

	1aaa	2aaa
formula	$C_{33}H_{33}N_3O_6S_3$	$C_{33}H_{33}N_3O_6Pd_1S_3$
fw	663.80	770.20
cryst size (mm^3)	0.8 × 0.8 × 0.8	0.006 × 0.06 × 0.06
cryst color	colorless	colorless
temp (K)	153(2)	153(2)
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
a (Å)	23.4132(9)	8.5644(7)
b (Å)	6.1253(2)	10.4573(9)
c (Å)	24.7974(9)	35.603(3)
β (deg)	115.5920(10)	94.302(4)
V (Å^3)	3207.4(2)	3179.6(5)
Z	4	4
ρ (g/cm^3)	1.375	1.609
μ (mm^{-1})	0.281	0.832
θ_{max} (deg)	31.55	31.52
no. of reflns measd	46 790	47 579
no. of unique reflns	10 276 [R_{int} = 0.0762]	10 194 [R_{int} = 0.1692]
absorp corr	SADABS (Bruker-AXS)	SADABS (Bruker-AXS)
transmn min./max.	0.6921/1.0000	0.7278/1.0000
no. of params	538	418
R1/wR2 [$I>2\sigma(I)$]	0.0447/0.1085	0.0554/0.0880
R1/wR2 [all data]	0.0665/0.1169	0.1649/0.1095
goodness-of-fit on F^2	1.013	0.812
largest diff peak and hole (e/Å^3)	0.431 and −0.641	0.736 and −1.244

The single-crystal X-ray structure analysis of **2aaa** confirmed the expected organometallic nature of the complex. Crystal data for the structure are given in Table 1. The obtained structure is shown in Figure 2. The triple bonds are located on the same plane bonding symmetrically to a central palladium atom. As a result of the attractive interaction with the palladium, the acetylenic atoms are shifted to the center of the molecule. They show a deviation of approximately 22° with respect to the expected linearity for a substituted triple bond. In comparison the triple bonds in the metal-free

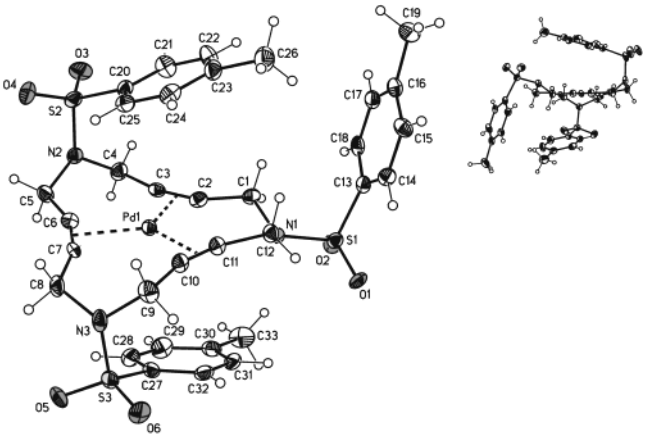


Figure 2. ORTEP plot (50%) of the structure of **2aaa**. Selected bond distances (Å) and angles (deg): Pd(1)−C(2): 2.125(4), Pd(1)−C(3): 2.149(4); Pd(1)−C(6): 2.134(5); Pd(1)−C(7): 2.141(4); Pd(1)−C(10): 2.146(4); Pd(1)−C(11): 2.138(4); C(2)−C(3): 1.249(6); C(6)−C(7): 1.235(6); C(10)−C(11): 1.231(6); C(1)−C(2)−C(3): 155.6(4); C(2)−C(3)−C(4): 160.1(5); C(5)−C(6)−(7): 157.9(5); C(6)−C(7)−C(8): 158.9(5); C(9)−C(10)−C(11): 160.7(5); C(10)−C(11)−C(12): 158.3(4).

compound **1aaa** show an asymmetrical arrangement with a bending of only approximately 4°. As a result of complexation, the triple bonds in **2aaa** are elongated 0.051 Å on average, as compared to **1aaa** (from 1.1870(15) to 1.238(5) Å). The distances of the palladium atom to the center of the acetylenic bonds are identical (2.047(3) Å) considering the standard deviations. The only previously described compound with three triple bonds complexing a palladium atom shows planar arrangements and bond distances similar to those of **2aaa**.[10]

Curiously in the crystal packing of **2aaa** two of the aromatic rings are positioned like a sandwich on the top and on the bottom of the central part of the molecule. For the aromatic ring C27−C32 there is an approximate distance from C27 to Pd1 of 3.74 Å. The aromatic ring C20−C25 is closer to the triple bond C2−C3 than to Pd1, with an approximate distance center of C20−C25 to C2 of 3.72 Å.

We also tested palladium-catalyzed cycloisomerization of cyclotriyne **1aaa** in order to obtain hexasubstituted benzene derivatives. The reaction never proceeded under catalytic conditions, but when macrocycle **1aaa** was treated with 1.1 equiv of $Pd(PPh_3)_4$ in refluxing toluene, triazatrindane **11aaa** was obtained in 54% yield (Scheme 2).[12] The ^{1}H NMR spectrum of cycloisomer **11aaa** was not very informative and served only to confirm that a new compound was formed: the absorption due to the 12 methylenic protons of **1aaa** (δ 3.96 ppm) shifted to δ 4.52 ppm in the new product. However, the ^{13}C NMR spectrum changed considerably, showing a new signal at δ 130 ppm corresponding to the six equivalent benzene carbons and the absence of the absorption at δ 79.0 ppm corresponding to the six acetylenic carbons of **1aaa**. Further studies on the stability of palladium(0) complexes of type **2** and their cycloisomerization process are now underway.

(12) The cycloisomerization process did not proceed when palladium(0) complex **2aaa** was refluxed in anhydrous toluene in the presence of 1.1 equiv of PPh_3 under argon atmosphere for 1 day. Complex **2aaa** was almost recovered (83%), and only traces of cycloisomerized compound **11aaa** were isolated.

Experimental Section

IR spectra were recorded with a FT-IR using a single-reflection ATR system as a sampling accessory. ^{1}H NMR (^{13}C NMR) were recorded at 200 MHz (50 MHz) using Me_4Si as internal standard. Chemical shifts are given in δ units. ESI mass spectra were acquired using a Navigator quadrupole instrument (Finnigan AQA ThermoQuest) equipped with an electrospray ion source. MALDI-TOF mass spectra were obtained on a BIFLEX spectrometer (Bruker-Franzen Analytik) equipped with a pulsed nitrogen laser (337 nm). Elemental analyses were determined at "Servei d'Anàlisi Química de la Universitat de Girona".

(4-Methylphenyl)sulfonamide, **3a**, is commercially available and was used without further purification. Ferrocenesulfonamide,[13] **3b**, *N*-(*tert*-butyloxycarbonyl)(4-methylphenyl)sulfonamide,[11] **4a**, 1,4-dibromo-2-butyne,[14] **5**, and 1,4-bis(methanesulfonyloxy)-2-butyne,[15] **6**, were prepared as previously reported.

***N*-(4-Bromo-2-butynyl)-*N*-(*tert*-butyloxycarbonyl)(4-methylphenyl)sulfonamide (7a).** A stirred mixture of *N*-(*tert*-butyloxycarbonyl)(4-methylphenyl)sulfonamide, **4a** (1.21 g, 4.46 mmol), 1,4-dibromo-2-butyne, **5** (3.75 g, 17.70 mmol), anhydrous potassium carbonate (3.12 g, 22.61 mmol), and acetonitrile (50 mL) was refluxed for 1.5 h (TLC monitoring). The salts were filtered off, and the filtrate was evaporated. The oily residue was chromatographed through silica gel with hexane/ethyl acetate (10:1) to afford **7a** (1.18 g, 66%) as a colorless solid; mp 116−117 °C; IR (neat) 2986, 1716, 1356, 1284, 1144, 1067 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) 1.36 (s, 9H), 2.45 (s, 3H), 3.93 (t, J = 2.0 Hz, 2H), 4.68 (t, J = 2.0 Hz, 2H), 7.33 (AA′ part of the AA′BB′ system, J = 8.4 Hz, 2H), 7.93 (BB′ part of the AA′BB′ system, J = 8.4 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) 14.8, 22.3, 28.5, 36.6, 79.4, 82.7, 85.7, 128.9, 129.9, 137.3, 145.1, 150.8; ESI-MS (*m*/*z*) 424−426 $[M + Na]^+$, 440−442 $[M + K]^+$; $C_{16}H_{20}BrNO_4S$ (402.3) calcd C, 47.77; H, 5.01; N, 3.48; found C, 47.88 and 47.94; H, 5.09 and 4.98; N, 3.38 and 3.39.

***N*-(*tert*-Butyloxycarbonyl)-*N*-(4-methanesulfonyloxy-2-butynyl)-4-methylphenyl)sulfonamide (8a)**. The experimental procedure to obtain **8a** starting from **4a** and 1,4-bis(methanesulfonyloxy)-2-butyne, **6**, is the same as described above; 24 h at room temperature; **8a**, colorless solid, 56% yield; mp 100−102 °C; IR (neat) 3023, 1716, 1353, 1149, 1072 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) 1.35 (s, 9H), 2.46 (s, 3H), 3.10 (s, 3H), 4.69 (t, J = 1.7 Hz, 2H), 4.89 (t, J = 1.7 Hz, 2H), 7.35 (AA′ part of the AA′BB′ system, J = 8.0 Hz, 2H), 7.87 (BB′ part of the AA′BB′ system, J = 8.0 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) 22.3, 28.5, 36.3, 39.9, 58.4, 76.7, 86.0, 86.1, 128.8, 130.1, 137.2, 145.5, 150.8; ESI-MS (*m*/*z*) 418 $[M + H]^+$, 435 $[M + NH_4]^+$, 440 $[M + Na]^+$; $C_{17}H_{23}NO_7S_2$ (417.5) calcd C, 48.91; H, 5.55; N, 3.35; found C, 49.38 and 49.16; H, 5.76 and 5.76; N, 3.35 and 3.24.

1,11-Bis(*tert*-butyloxycarbonyl)-1,6,11-tris[(4-methylphenyl)sulfonyl]-1,6,11-triazaundeca-3,8-diyne (9aaa). General Procedure. A stirred mixture of *N*-(4-bromo-2-butynyl)-*N*-(*tert*-butyloxycarbonyl)(4-methylphenyl)sulfonamide, **7a** (0.59 g, 1.47 mmol), (4-methylphenyl)sulfonamide, **3a** (0.13 g, 0.76 mmol), anhydrous potassium carbonate (0.63 g, 4.56 mmol), and acetonitrile (24 mL) was refluxed for 3.5 h (TLC monitoring). The salts were filtered off, and the filtrate was evaporated. The oily residue was chromatographed through silica gel with hexane/ethyl acetate (7:3) to afford **9aaa** (0.52 g, 86%; 80% yield starting from **8a**) as a colorless solid; mp 73−75 °C; IR (neat) 2982, 1728, 1351, 1255, 1149, 1089 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) 1.32 (s, 18H), 2.43 (s, 3H), 2.45 (s,

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6H), 4.15 (s, 4H), 4.47 (s, 4H), 7.31−7.37 (m, 6H), 7.74 (BB′ part of the AA′BB′ system, J = 8.0 Hz, 2H), 7.85 (BB′ part of the AA′BB′ system, J = 8.2 Hz, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) 22.2, 22.3, 28.5, 36.3, 37.2, 77.2, 81.9, 85.7, 128.4, 128.7, 130.1, 130.5, 136.0, 137.3, 144.8, 145.3, 150.8; ESI-MS (*m*/*z*) 831 [M + NH_4]$^+$, 836 [M + Na]$^+$, 852 [M + K]$^+$; $C_{39}H_{47}N_3O_{10}S_3$ (814.0) calcd C, 57.55; H, 5.82; N, 5.16; found C, 57.27 and 57.44; H, 6.07 and 5.76; N, 4.87 and 4.81.

1,11-Bis(*tert*-butyloxycarbonyl)-1,11-bis[(4-methylphenyl)sulfonyl]-6-ferrocenylsulfonyl-1,6,11-triazaundeca-3,8-diyne (9aab): orange solid (100% yield starting from **7a**; 79% yield starting from **8a**); mp 75−77 °C; IR (neat) 1728, 1351, 1139, 1089 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) 1.32 (br s, 18H), 2.45 (s, 6H), 4.03 (s, 4H), 4.40 (s, 5H), 4.42 (t, J = 1.8 Hz, 2H), 4.48 (s, 4H), 4.66 (t, J = 1.8 Hz, 2H), 7.35 (AA′ part of the AA′BB′ system, J = 9.0 Hz, 4H), 7.84 (BB′ part of the AA′BB′ system, J = 9.0 Hz, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) 22.3, 28.5, 36.4, 37.2, 70.1, 71.4, 71.6, 77.4, 81.9, 85.6, 128.7, 130.1, 137.3, 145.3, 150.8; ESI-MS (*m*/*z*) 907 [M + H]$^+$, 925 [M + NH_4]$^+$, 930 [M + Na]$^+$, 946 [M + K]$^+$; $C_{42}H_{49}FeN_3O_{10}S_3$ (907.9) calcd C, 55.56; H, 5.44; N, 4.63; found C, 55.39 and 55.58; H, 5.71 and 5.78; N, 4.39 and 4.42.

1,6,11-Tris[(4-methylphenyl)sulfonyl]-1,6,11-triazaundeca-3,8-diyne (10aaa). General Procedure. A mixture of **9aaa** (0.65 g, 0.80 mmol), trifluoroacetic acid (4 mL), and dichloromethane (4 mL) was stirred at room temperature for 4.5 h (TLC monitoring). The liquid was distilled off under vacuum, and the residue was dissolved in ethyl acetate (25 mL). The organic layer was sequentially washed with aqueous sodium bicarbonate (3 × 10 mL), with H_2O (3 × 10 mL), and with brine (15 mL), dried (Na_2SO_4), and filtered. The solvent was removed under reduced pressure to afford **10aaa** as a colorless solid (0.49 g, 100%). A pure sample of **10aaa** was obtained by column chromatography through silica gel, eluting with hexane/ethyl acetate (6:4); mp 142−144 °C; IR (neat) 3275, 1597, 1324, 1154, 1092 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) 2.43 (s, 9H), 3.62 (d, J = 5.8 Hz, 4H), 3.80 (s, 4H), 4.95 (t, J = 5.8 Hz, 2H), 7.30 (m, 6H), 7.60 (BB′ part of the AA′BB′ system, J = 8.2 Hz, 2H), 7.72 (BB′ part of the AA′BB′ system, J = 8.2 Hz, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) 22.2, 33.5, 37.2, 77.8, 80.9, 127.9, 128.6, 130.2, 130.4, 135.8, 137.1, 144.6, 144.9; ESI-MS (*m*/*z*) 614 [M + H]$^+$, 631 [M + NH_4]$^+$, 636 [M + Na]$^+$, 652 [M + K]$^+$; $C_{29}H_{31}N_3O_6S_3$ (613.7) calcd C, 56.75; H, 5.09; N, 6.85; found C, 56.87 and 56.68; H, 5.32 and 5.41; N, 6.52 and 6.59.

1,11-Bis[(4-methylphenyl)sulfonyl]-6-ferrocenylsulfonyl-1,6,11-triazaundeca-3,8-diyne (10aab): orange solid (99%); mp 72−75 °C; IR (neat) 3275, 1324, 1156, 1138 cm^{-1}; ^{1}H NMR (200 MHz, [D_6]DMSO) 2.47 (s, 6H), 3.64 (br abs, 8H), 4.43 (s, 5H), 4.52 (br abs, 2H), 4.66 (br abs, 2H), 7.47 (AA′ part of the AA′BB′ system, J = 7.8 Hz, 4H), 7.74 (BB′ part of the AA′BB′ system, J = 7.8 Hz, 4H), 8.06 (br abs, 2H); ^{13}C NMR (50 MHz, [D_6]DMSO) 20.9, 31.9, 35.8, 69.2, 70.2, 70.6, 76.3, 81.1, 84.2, 126.6, 129.4, 137.5, 142.8; ESI-MS (*m*/*z*) 708 [M + H]$^+$, 730 [M + Na]$^+$, 746 [M + K]$^+$; HRMS calcd for ($C_{32}H_{33}FeN_3O_6S_3$ + Na) 730.0773; found 730.0791.

1,6,11-Tris[(4-methylphenyl)sulfonyl]-1,6,11-triazaciclopentadeca-3,8,13-triyne (1aaa). General Procedure. A stirred mixture of **10aaa** (0.15 g, 0.24 mmol), 1,4-dibromo-2-butyne, **5** (0.06 g, 0.28 mmol), anhydrous potassium carbonate (0.17 g, 1.23 mmol), and acetonitrile (30 mL) was refluxed for 5.5 h (TLC monitoring). The salts were filtered off, and the filtrate was evaporated. The oily residue was chromatographed through silica gel with hexane/ethyl acetate (polarity from 9:1 to 6:4) to afford **1aaa** (0.12 g, 74%; 70% yield starting from 1,4-bis(methanesulfonyloxy)-2-butyne, **6**) as a colorless solid; mp 219 °C (dec); IR (KBr) 2995, 1919, 1597, 1433, 1348, 1166, 1092 cm^{-1}; ^{1}H NMR (200 MHz, [D_6]DMSO) 2.52 (s, 9H), 3.96 (s, 12H), 7.54 (AA′ part of the AA′BB′ system, J = 8.1 Hz, 6H), 7.74 (BB′ part of the AA′BB′ system, J = 8.1 Hz, 6H); ^{13}C NMR (50 MHz, [D_6]DMSO) 21.2, 37.6, 79.0, 127.7, 129.9, 134.9, 144.0; ESI-MS (*m*/*z*) 664 [M + H]$^+$, 681 [M + NH_4]$^+$, 686 [M + Na]$^+$, 702 [M + K]$^+$; $C_{33}H_{33}N_3O_6S_3$ (663.8) calcd C, 59.71; H, 5.01; N, 6.33; found C, 59.51 and 59.37; H, 4.89 and 4.98; N, 5.94 and 6.04.

6,11-Bis[(4-methylphenyl)sulfonyl]-1-ferrocenylsulfonyl-1,6,11-triazaciclopentadeca-3,8,13-triyne (1aab): orange solid (75% yield starting from 1,4-dibromo-2-butyne, **5**; 53% yield starting from 1,4-bis(methanesulfonyloxy)-2-butyne, **6**); mp 179−182 °C; IR (neat) 2923, 1332, 1157 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) 2.44 (s, 6H), 3.73 (br abs, 4H), 3.88 (br abs, 8H), 4.37−4.39 (br abs, 2H), 4.40 (s, 5H), 4.56 (t, J = 1.8 Hz, 2H), 7.29 (AA′ part of the AA′BB′ system, J = 8.2 Hz, 4H), 7.63 (BB′ part of the AA′BB′ system, J = 8.2 Hz, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) 22.2, 30.4, 38.2, 38.4, 69.9, 71.3, 71.5, 79.4, 79.5, 79.7, 85.3, 128.5, 130.2, 135.9, 144.7; ESI-MS (*m*/*z*) 758 [M + H]$^+$, 775 [M + NH_4]$^+$, 780 [M + Na]$^+$, 796 [M + K]$^+$; $C_{36}H_{35}FeN_3O_6S_3$ (757.7) calcd C, 57.07; H, 4.66; N, 5.55; found C, 57.31 and 57.47; H, 4.78 and 4.90; N, 5.50 and 5.48.

1,6,11-Tris[(4-methylphenyl)sulfonyl]-1,6,11-triazaciclopentadeca-3,8,13-triynepalladium(0) (2aaa). A mixture of **1aaa** (0.10 g, 0.15 mmol), tetrakis(triphenylphosphane)-palladium(0) (0.19 g, 0.17 mmol), and tetrahydrofuran (10 mL) was stirred at room temperature for 1 h (TLC monitoring). The liquid was distilled off under vacuum, and the residue was chromatographed through silica gel with mixtures of hexane/ethyl acetate/dichloromethane (polarity from 8:2:0 to 0:1:1) to afford **2aaa** as a colorless solid (0.065 g, 56%); mp 228 °C (dec); IR (KBr) 2981, 2013, 1349, 1162 cm^{-1}; ^{1}H NMR (200 MHz, [D_6]DMSO) 2.31 (s, 9H), 4.38 (s, 12H), 7.26 (AA′ part of the AA′BB′ system, J = 8.1 Hz, 6H), 7.54 (BB′ part of the AA′BB′ system, J = 8.1 Hz, 6H); ^{13}C NMR (50 MHz, [D_6]-DMSO) 20.8, 36.4, 74.1, 127.4, 129.1, 134.8, 143.4; ESI-MS (*m*/*z*) 792 [M + Na]$^+$; MALFI-TOF (*m*/*z*) 770 [M + H]$^+$; $C_{33}H_{33}N_3O_6S_3Pd$ (770.2) calcd C, 51.46; H, 4.32; N, 5.46; found C, 51.08; H, 4.44; N, 5.37.

2,5,8-Tris[(4-methylphenyl)sulfonyl]-2,5,8-triazatrindane (11aaa). A degassed mixture of macrocycle **1aaa** (0.05 g, 0.07 mmol) and tetrakis(triphenylphosphane)palladium(0) (0.097 g, 0.08 mmol) in anhydrous toluene was refluxed for 22 h under N_2 (TLC monitoring). The solvent was then evaporated, and the residue was chromatographed through silica gel with dichloromethane/ethyl acetate (10:1) to afford **11aaa** as a colorless solid (0.027 g, 54%); mp 258−260 °C (dec); IR (KBr) 2858, 1345, 1162, 1096 cm^{-1}; ^{1}H NMR (200 MHz, [D_6]DMSO) 2.41 (s, 9H), 4.52 (br abs, 12H), 7.42 (AA′ part of the AA′BB′ system, J = 7.8 Hz, 6H), 7.79 (BB′ part of the AA′BB′ system, J = 7.8 Hz, 6H); ^{13}C NMR (50 MHz, [D_6]-DMSO) 20.9, 51.9, 127.5, 129.8, 130.3, 132.9, 143.6; ESI-MS (*m*/*z*) 664 [M + H]$^+$, 681 [M + NH_4]$^+$, 686 [M + Na]$^+$; $C_{33}H_{33}N_3O_6S_3$·CH_2Cl_2 (748.76) calcd C, 54.54; H, 4.71; N, 5.61; S, 12.85; found C, 54.73 and 54.78; H, 4.92 and 4.89; N, 5.80 and 5.80; S, 12.77 and 12.86.

Crystal Structure Determinations. Colorless crystals of 1,6,11-tris[(4-methylphenyl)sulfonyl]-1,6,11-triazaciclopentadeca-3,8,13-triyne (**1aaa**) were obtained by slow diffusion of *n*-hexane into a dichloromethane/ethyl acetate solution of the macrocycle. Colorless crystals of 1,6,11-tris[(4-methylphenyl)-sulfonyl]-1,6,11-triazaciclopentadeca-3,8,13-triynepalladium-(0) (**2aaa**) were obtained by slow diffusion of *n*-pentane into dichloromethane, yielding in most cases twinned planar needles. After taking different data sets a carefully cut, under polarized light, nontwinned small crystal with the dimensions 6 × 60 × 60 μm^3 could be measured. Crystal structure determinations for **1aaa** and **2aaa** were carried out using a Siemens P4 diffractometer equipped with a SMART-CCD-1000 area detector, a MACScience Co rotating anode with Mo Kα radiation, a graphite monochromator, and a Siemens low-temperature device LT2 (T = −120 °C). The measurements were made in the range 1.65−31.55°/31.52° for **1aaa**/**2aaa** in theta. Full sphere data collection was done with ω and φ scans. The program used for data collection was Smart V. 5.060 (BrukerAXS 1999); for data reduction Saint + Version 6.02

(Bruker AXS 1999); and for absorption correction SADABS (Bruker AXS 1999). Crystal structure solutions for **1aaa** and **2aaa** were achieved using direct methods as implemented in SHELXTL Version 5.10 (Sheldrick, Universtität Göttingen (Germany), 1998) and visualized using the XP program. Missing atoms were subsequently located from difference Fourier synthesis and added to the atom list. Least-squares refinement on F^2 using all measured intensities was carried out using the program SHELXTL Version 5.10 (Sheldrick, Universtität Göttingen (Germany), 1998). All non hydrogen atoms were refined including anisotropic displacement parameters. Hydrogen atoms were freely refined for **1aaa** and invariably placed in geometrically optimized positions and forced to ride on the atom to which they are attached in **2aaa**.

The supplementary crystallographic data for this paper (CCDC 230219 and CCDC 230220) can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax +44 1223 336033 or e-mail deposit@ccdc.cam.ac.uk).

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Supporting Information Available: Details of the two structure determinations, including atomic coordinates, bond lengths and angles, thermal parameters, least-squares planes, and interatomic contacts of complexes **1aaa** and **2aaa**. This material is available free of charge via the Internet at http://pubs.acs.org.

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