Chiral and Stable Palladium(0) Complexes of Polyunsaturated Aza-macrocyclic Ligands: Synthesis and Structural Analysis

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A novel type of chiral and stable palladium(0) complexes of polyunsaturated aza-macrocyclic ligands were prepared and fully characterized by means of NMR spectroscopy and X-ray diffraction. Fifteen-membered alkene−alkyne type ligands as well as 20- and 25-membered polyolefinic ligands showed a preference for tricoordination with the metal. The stereochemical complexity of these complexes is related to the different isomers that can be formed by complexation of the metal to either of the two faces of each of the olefins involved. The palladacyclopropane formulation of the palladium−olefin interaction offers a clear picture of the stereogenicity of the olefin carbon atoms when they are coordinated to the metal. The preorientation of the macrocyclic ligand and the prepositioning of the olefinic bonds for complex formation facilitated by six-membered chelate rings explain the stability of the structures. The conformation of the palladacyclohexanic rings is found to be crucial in the stereoisomers formed. These structural characteristics of the complexes have been studied in solution by NMR spectroscopy and in the solid state by X-ray diffraction analysis.

Introduction

Palladium(0) complexes containing alkenes and/or alkynes as the only ligands are not as common and widespread in the literature as zerovalent palladium−phosphane complexes.[1] The explanation for this needs to be sought independently in each case. Olefin-stabilized palladium complexes,[2] which are well described by the Dewar−Chatt−Duncanson model,[3] generally suffer from low stability due to the ease with which olefins are displaced or dissociated from the metal, and this may explain their underexploitation as spectator ligands[4] (ligands coordinated to the metal during catalysis possibly influencing its catalytic properties) in palladium-catalyzed reactions. Exceptions to this are the well-known $Pd_2(dba)_3(dba)$[5] (dba = dibenzylideneacetone), which has been widely used as a catalyst and precatalyst in many palladium-catalyzed transformations, and a novel type of Pd^0 complexes with 15-membered triolefinic aza-macrocyclic ligands described by ourselves (Figure 1), which have shown unusual stability for Pd−alkene complexes and demonstrated their potential catalytic activity in Suzuki−Miyaura and Mizoroki−Heck reactions.[2h,i] A further more recent exception is the description of a chiral Pd^0 tetraolefin complex by Trauner et al., which shows catalytic activity in enyne cyclization processes.[2j]

The case for alkynes is completely different. Although alkynes act as strongly stabilizing ligands for palladium, alkyne-stabilized palladium complexes are scarce.[6] This is probably

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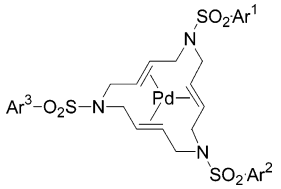


Figure 1. Structure of 15-membered triolefinic macrocyclic Pd^0 complexes.

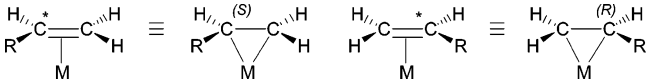


Figure 2. Stereoisomers resulting from metal coordination to monosubstituted olefins.

due to the high reactivity of these complexes to added alkynes, producing more elaborate complexes or undergoing chemical conversions.[7] Yamamoto et al. described the isolation of palladium(0) complexes of acyclic triyne derivatives as well as their catalytic cyclizations.[6a−c] We recently described the first palladium(0) complexes with a macrocyclic triyne[6d,e] and their cycloisomerization reactions.[6e]

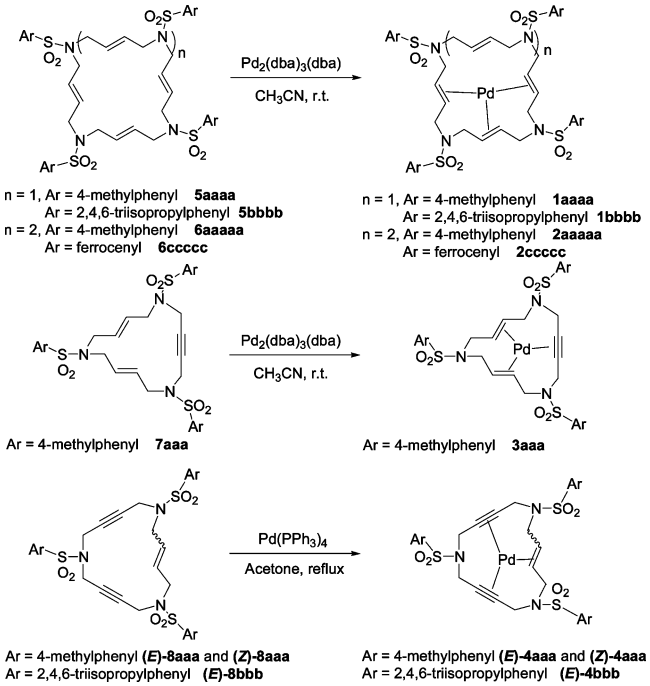
Even more scarce are palladium complexes that are simultaneously stabilized by alkenes and alkynes. As far as we know, only an enediyne palladium(0) complex isolated by Yamamoto et al.[6c] as a minor byproduct in a palladium(0)-catalyzed cyclization of an enyne ester has been described.

On the other hand, an olefinic compound without asymmetric substituents and without symmetry planes perpendicular to the plane of the double bond becomes asymmetric upon coordination to the metal (Figure 2).[8]

Based on this chirality introduced into an olefin upon coordination, several structural analyses of chiral Pd^0−olefin complexes have been reported.[2f,5e] One of these structural studies was recently made in the above-mentioned palladium complexes of the triolefinic macrocycles (*E*,*E*,*E*)-1,6,11-tris(arylsulfonyl)-1,6,11-triazacyclopentadeca-3,8,13-trienes (Figure 1).[9]

The scarcity of stable palladium complexes with π-bonded carbon ligands, together with their potential applicability in catalysis and in the design of chiral topologies, prompted us to prepare and fully characterize chiral Pd^0 complexes of 20- and 25-membered polyolefinic macrocyclic ligands, as well as structurally related complexes in which the metal is simultaneously stabilized with alkenes and alkynes. We then studied the coordination properties of those types of macrocycles with palladium(0) and compared them with those found for the triolefinic macrocycles. To the best of our knowledge, neither palladium(0) complexes of tetra- and pentaolefinic macrocycles nor cyclic complexes of palladium(0) stabilized simultaneously by alkenes and alkynes have previously been described.

Scheme 1. Synthesis and General Structure of Pd^0 Complexes of Polyunsaturated Macrocyclic Ligands[a]



[a] The nomenclature for compounds **1**−**8** is given by a number for the type of compound and a letter for each of the aryl substituents at nitrogen (**a**, Ar = 4-methylphenyl; **b**, Ar = 2,4,6-triisopropylphenyl; **c**, Ar = ferrocenyl).

Results and Discussion

Preparation of Palladium(0) Complexes. Pd^0 complexes **1**, **2**, **3**, and **4** were easily prepared by the reaction of the corresponding macrocyclic ligands with familiar sources of palladium(0) ($Pd_2(dba)_3(dba)$ or $Pd(PPh_3)_4$), as shown in Scheme 1. Macrocycles **5**,[10] **6**,[11] and **8**[6e] were prepared as previously described. Macrocycle **7aaa** was prepared by the reaction of intermediate (*E*,*E*)-1,6,11-tris(4-methylphenylsulfonyl)-1,6,11-triazaundeca-3,8-diene[12] with 1,4-bis(methanesulfonyloxy)-2-butyne.[13] Pd^0 complexes **1**, **2**, **3**, and **4** display exceptional and unprecedented stability for Pd^0 alkene or alkyne complexes. They are sufficiently stable as to allow purification by column chromatography on silica gel, and they can be handled and stored under air at room temperature.

Structural Study of 20- and 25-Membered Tetra- and Pentaolefinic Complexes. It has been seen in our previous study[9] that proton chemical shifts of the methylene groups give clear evidence of the preferred conformation of the palladacyclohexanic rings in Pd^0 complexes of Figure 1 given that they do not show fluxional behavior. The conformation of the three palladacyclohexanic rings was found to be crucial in the stereoisomers generated, with the most stable form being *chair*−*chair*−*twist*, which was the only one present in both solution and solid state.[9] In fact, proton signals belonging to *chair*-like conformers show a clear differentiation between axial (δ = 1.5−1.6 ppm) and equatorial (δ = 4.6−4.65 ppm) positions, whereas

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(8) Paiaro, G.; Panunzi, A. *J. Am. Chem. Soc.* **1964**, *86*, 5148. (b) Paiaro, G. *Organomet. Chem. Rev. Sect. A* **1970**, *6*, 319.

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in *twist*-like conformations, proton resonances for the pseudo-axial ($\delta = 3.05-3.07$ ppm) and pseudoequatorial ($\delta = 4.5-4.7$ ppm) positions are located much closer. These differences in proton chemical shift values for methylene spin systems proved to be a good indicator of the average Pd−C−C−N dihedral angle observed for this type of complexes in solution. There was also an experimental correlation in which methylenic ^{13}C signals appear downfield in the *chair* conformation ($\delta = 48-49$ ppm) with respect to the *twist* conformation ($\delta = 45$ ppm).

Macrocycles **5** and **6** have four and five binding sites, respectively, available for palladium(0) coordination. However, when mixing a palladium source, $Pd_2(dba)_3(dba)$, with each one of the ligands, only three of the available olefin centers present in the structure coordinate to the metal. Since the coordination of palladium with this kind of olefin shifts the resonances of the pseudo-olefinic proton centers upfield (from $\delta = 5.20-5.70$ to around $\delta = 2.75-4$ ppm), the number of olefins noncoordinating to the metal in complexes **1** and **2** was clearly seen by integration of the ^1H NMR signals in the olefinic region. The fact that the palladium atom prefers a stable, rigid, and nonexchangeable tricoordination over a multiplex coordination in these structures can be rationalized by the relatively long distance between the coordination sites, by the great stability of the triolefinpalladium core, and by the ideal prepositioning of the macrocyclic olefinic bonds.[14] One further concern regarding the strong palladium coordination in complexes **1** and **2** is as to whether there is a ring-whizzing[15] dynamic process involved. In this case we can rule out this possibility on the NMR time scale given the absence of a substantial chemical shift and line-shape variations, the absence of chemical exchange cross-peaks in the NOESY spectra for a wide range of temperatures, and the well-defined chemical shifts shown for the diastereotopic methylene protons.

The general structure of all possible stereoisomers for **1** and **2**, resulting from coordination of the metal center to the two olefin faces of each coordinating double bond in macrocycles **5** and **6**, is depicted in Figure 3. There are eight feasible stereoisomers, which are grouped into four pairs of enantiomers (**A1**/**A2**, **A3**/**A4**, **A5**/**A6**, and **A7**/**A8**). In the case of equivalent aryl groups, stereoisomers **A4** and **A6** become identical, and the general scheme (Figure 3) can be reduced to three enantiomeric pairs (Table 1).

In contrast to the analogous 15-membered triazatrienepalladium(0) complexes (Figure 1), there are only two palladacyclohexanic rings to be taken into account in compounds **1** and **2**. Since the *chair* conformation is energetically more favorable than the *twist* conformation, the formation of an enantiomeric pair, **A1**/**A2**, with overall *chair*−*chair* conformation was to be expected at the expense of **A3**/**A4** and **A7**/**A8**, which are more unstable stereoisomers. This is experimentally confirmed by NMR analysis. The ^{13}C NMR signal for the olefinic carbon in the free ligand appearing at $\delta = 129.7$ ppm (for **5aaaa**) and $\delta = 130.1$ ppm (for **5bbbb**) splits into four signals in the ^{13}C NMR spectra of **1aaaa** and **1bbbb**, indicating a symmetrical molecule. Therefore a signal at $\delta = 131.9$ and 131.8, for **1aaaa** and **1bbbb**, respectively, is assigned to the noncoordinating olefin, whereas the set of three signals of the same intensity at $\delta = 85.9/78.9/78.1$ ppm (for **1aaaa**) and $\delta = 86.2/78.9/78.2$ ppm (for **1bbbb**) are assigned to the pseudo-olefinic carbons (Figure 4B).[16]

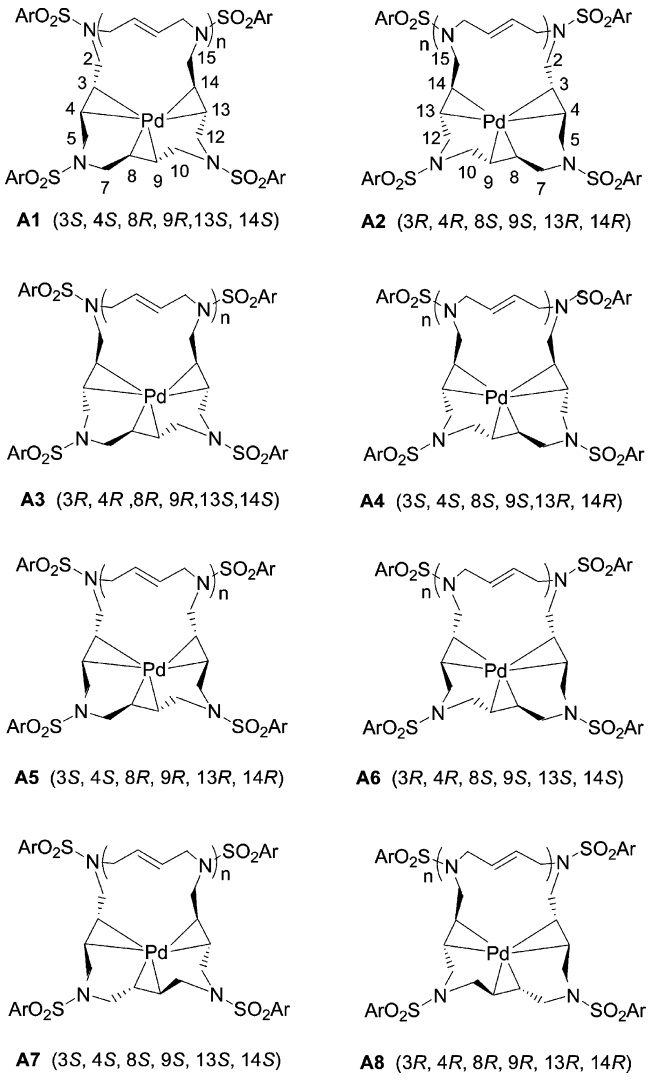

Figure 3. Stereoisomers for palladium(0) complexes **1** ($n = 1$) and **2** ($n = 2$) displayed as pairs of enantiomers.

Table 1. Symmetry Elements and Palladacyclohexanic Ring Conformation for Stereoisomers of Palladium Complexes 1 and 2

stereoisomers	palladacyclohexanic ring conformation	symmetry elements
A1/A2	*chair*−*chair*	C_2 axis
A3/A4 (A5/A6)	*chair*−*twist*	none
A7/A8	*twist*−*twist*	C_2 axis

The structure of complexes **1** can be regarded as two six-membered and one 11-membered ring alternated and fused with three-membered rings all joined by the palladium atom. The methylenic groups located in the rigid palladacyclohexanic rings clearly show differentiated chemical shifts for the diastereotopic protons since fluxional behavior is disabled by the strong palladium coordination. These proton signals appear at $\delta = 2.12/4.28$ ppm and $\delta = 2.08/4.52$ ppm (Figure 4B), indicating well-defined axial and equatorial proton positions in a minimally distorted *chair*-like conformation. This is not the case for all methylenic groups pertaining to the more flexible pallada-

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(16) Structural analysis was carried out on the 2,4,6-triisopropylphenyl analogue **1bbbb** due to the poor solubility of the 4-methylphenyl analogue **1aaaa**.

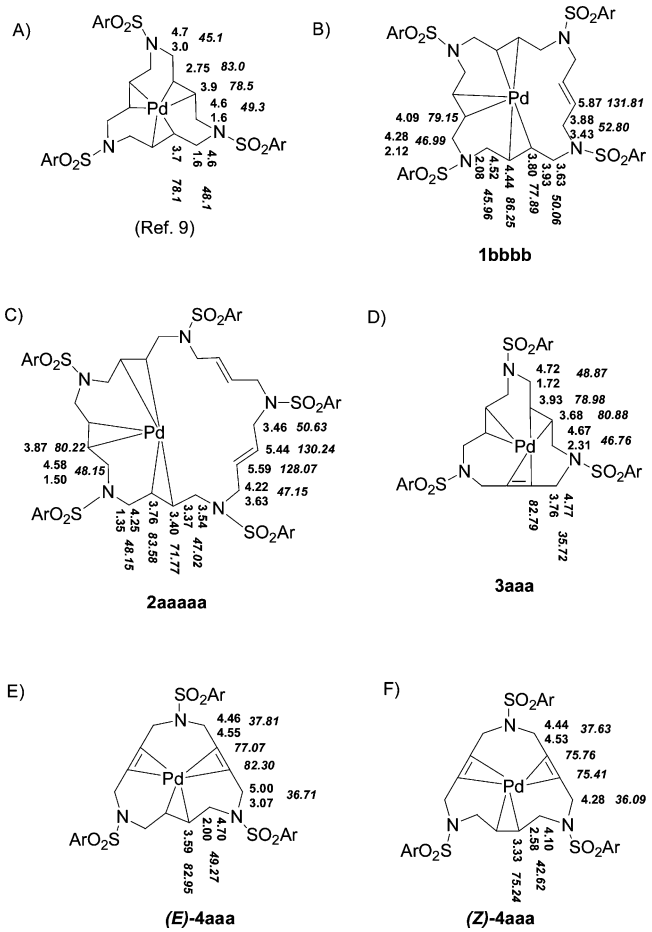

Figure 4. ^{1}H and ^{13}C NMR (in italics) chemical shift assignment for some illustrative aza-macrocyclic-Pd complexes: (A) ref 9; (B) **1bbbb**; (C) **2aaaaa**; (D) **3aaa**; (E) **(*E*)-4aaa**; (F) **(*Z*)-4aaa** (**a**, Ar = 4-methylphenyl; **b**, Ar = 2,4,6-triisopropylphenyl).

cycloundecanic ring substructure, in which diastereotopic methylenic protons appear much closer at $\delta = 3.43/3.88$ ppm and $\delta = 3.63/3.93$ ppm (Figure 4B).

An analogous NMR signal pattern is observed for the 25-membered complexes **2**. Tricoordination is again easily envisaged through olefinic chemical shift splitting from the only signal at $\delta = 129.3$ ppm (for **6aaaaa**) and $\delta = 129.1$ ppm (for **6ccccc**) into five signals for each palladium complex **2**. For instance, the ^{13}C NMR spectrum of **2aaaaa** shows two signals for the noncoordinated olefin centers at $\delta = 130.2/128.1$ ppm and three upfield resonances at $\delta = 83.6/80.2/71.8$ ppm (Figure 4C).

The methylenic groups pertaining to the rigid palladacyclohexanic rings also show great differences between the chemical shift for the axial and equatorial positions ($\Delta\delta = 3.08$ and 2.90), whereas this difference is considerably reduced in the other more flexible methylenic positions (Figure 4C). This confirms the overall *chair*−*chair* conformation of the palladacyclohexanic rings as well as the decreased rigidity of the larger 16-membered *twist*-like conformation palladium ring.

The crystal structures of complexes **1aaaa** and **2aaaaa** were determined by performing single-crystal X-ray diffraction analysis. The molecular structure and the adopted numbering scheme are presented in Figure 5. Crystal data are listed in Table 2, and selected bond lengths and angles are given in Table 3.

Complex **1aaaa** crystallizes from a chloroform−ethyl acetate−hexane solution in a centrosymmetrical space group with three disordered chloroform molecules in the crystal cell. The complex presents a local distorted C_2 symmetry with an axis perpendicular to the noncoordinated double bond in the solid-state structure, which intersects the palladium atom and interconverts the two palladacyclohexanic rings. Both palladacyclohexanic rings present *chair* conformations, which again confirms the only formation of the **A1**/**A2** enantiomeric pair (the observation of a stereoisomer in a centrosymmetrical space group implies the existence of its enantiomer in the structure).

Complex **2aaaaa** crystallizes in a centrosymmetrical space group from a dichloromethane−ethyl acetate−hexane solution. The metal complex forms a solvate with a quarter of a dichloromethane molecule in the crystal cell. The palladium atom is coordinated by three contiguous C═C bonds of the cyclopentaene, leaving the uncoordinated diene part of the ligand in a closely folded conformation. While the corrdination sphere of **2aaaaa** shows approximate C_2 symmetry (similar to that for **1aaaa**), the symmetry of the complex as a whole is C_1. The enantiomeric pair **A1**/**A2** is again the only pair present in the solid state, as shown by the *chair* conformation of both palladacyclohexanic rings.

In both structures, three of the olefinic *trans* double bonds are coordinated to the palladium(0) in a trigonal planar coordination geometry. The mean deviation from the plane defined by the center of the double bonds to the palladium atom is 0.001 Å in **1aaaa** and 0.052 Å in **2aaaaa**. In the case of compound **2aaaaa**, a slight elongation in the distance from the palladium to the C6═C7 double bond in comparison to the distance to the other double bonds can be observed ((Pd1···C2═C3: 2.082(3) Å; Pd1···C6═C7: 2.113(3) Å; Pd1···C10═C11: 2.082(3) Å)). This elongation can be explained by the high flexibility of the uncoordinated part of the molecule, which allows atoms C2 and C11 to move away from each other. As a consequence, the palladium atom shows a small shift in the direction of the double bonds C2═C3 and C10═C11. The intramolecular distance between C2 and C11 is approximately 3.05 Å, and the distances C3···C6 and C7···C10 are approximately 2.87 Å. A similar tendency, although to a lesser degree, can be observed in compound **1aaaa**. In this case the intramolecular distances show similar differences as to those in **2aaaaa** (C2···C11: 3.06 Å, C3···C6: 2.86 Å, and C7···C10: 2.83 Å), but comparing the distances from the palladium atom to the double bonds, and taking into account the standard deviation, they cannot be considered to be different.

Whereas the uncoordinated olefins show planar sp^2-hybridized carbon atoms, interaction with palladium disrupts the planarity of the coordinated olefins, causing the substituents to bend away from the palladium center. In compound **1aaaa** the olefinic substituents are bent away from the ideal plane by an average of 13.4° and in compound **2aaaaa** 15.3°. The double bonds are elongated by an average of 0.07 Å compared with similar bonds in free ligands, which corresponds to the disruption of the planarity.

Alkene- and Alkyne-Stabilized Palladium Complexes. As the complexation of a metal with an alkyne moiety does not provide chirality, but may play an important role in the stability of the complexes and introduces rigidity, we decided to study the complexation of macrocycles containing double and triple bonds in their structure (**7** and **8**, Scheme 1).

First we decided to evaluate the complexation of macrocycle **7**, which has two double and one triple bond. Upon coordination with the metal, palladium(0) complex **3** presents only four possible stereoisomers, which differ in the faces of the olefins coordinating to the palladium atom (Figure 6). However, if we consider the symmetry of these molecules, structures **B1**/**B2**

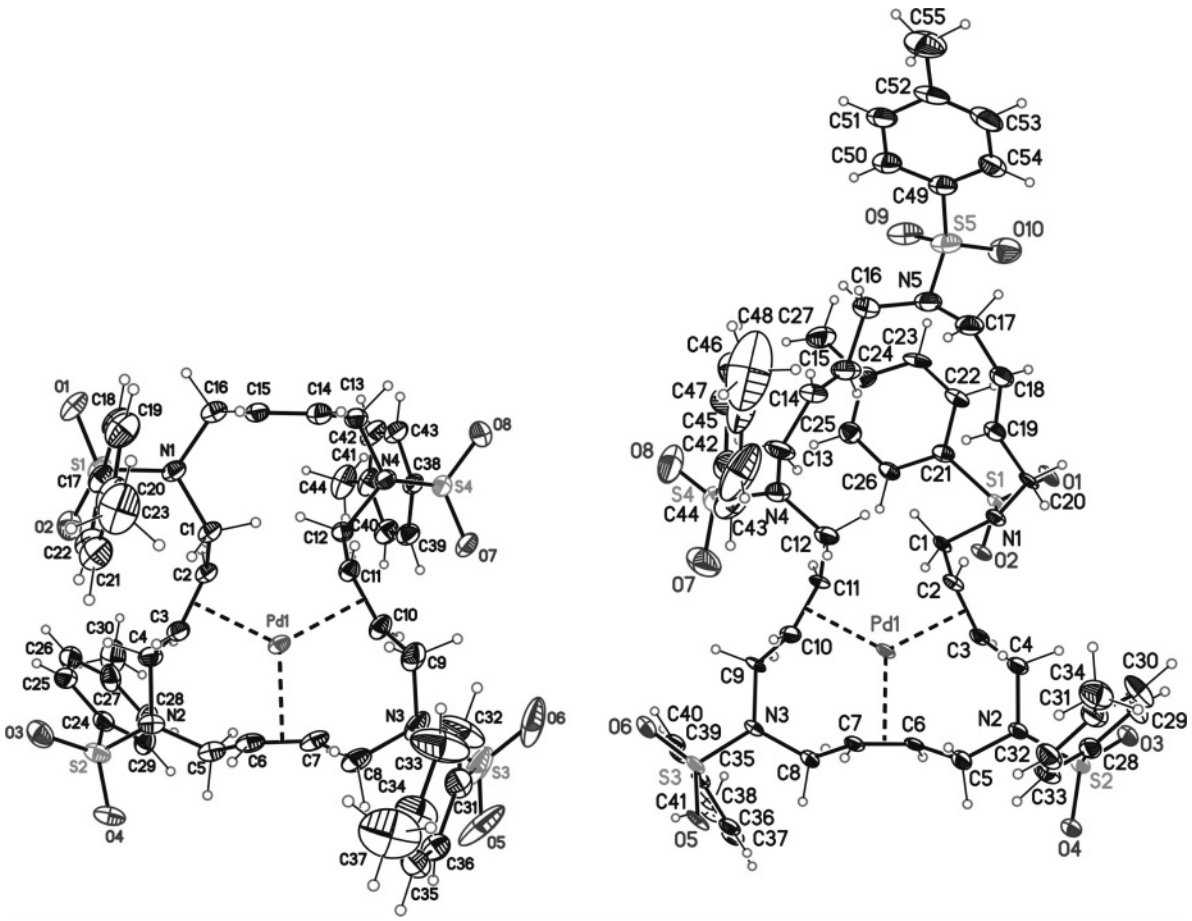

Figure 5. ORTEP plots (50%) obtained from single-crystal X-ray structure analyses of **1aaaa** and **2aaaaa**.

Table 2. Crystal Data for 1aaaa, 2aaaaa, 3aaa, and (*E*)-4aaa

	1aaaa	**2aaaaa**	**3aaa**	**(*E*)-4aaa**
formula	$C_{44}H_{52}N_4O_8S_4Pd_1 \cdot 3CHCl_3$	$C_{55}H_{65}N_5O_{10}Pd_1S_5 \cdot {}^1/_4CH_2Cl_2$	$C_{34}H_{39}N_3O_6Pd_1S_3 \cdot CH_2Cl_2$	$C_{33}H_{53}N_3O_6Pd_1S_3$
fw	1357.64	1244.05	859.16	772.22
cryst size (mm^3)	0.2 × 0.2 × 0.2	0.2 × 0.1 × 0.1	0.07 × 0.05 × 0.02	0.07 × 0.03 × 0.01
cryst color	colorless	colorless	colorless	colorless
temp (K)	100(2)	100(2)	100(2)	100(2)
cryst syst	triclinic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a (Å)	13.4499(7)	16.677(3)	11.2192(8)	16.4323(10) (2)
b (Å)	15.1587(8)	29.570(5)	11.7993(9)	11.1747(6)
c (Å)	15.6612(8)	13.074(2)	14.9326(11)	19.1546(10)
α (deg)	75.9410(10)	90	112.667(2)	90
β **(deg)**	74.7910(10)	101.293(5)	91.155(2)	113.2930(10)
γ (deg)	74.9970(10)	90	101.052(2)	90
V ($Å^3$)	2923.3(3)	6323(2)	1792.0(2)	3230.6(3)
Z	2	4	2	4
ρ (g/cm^3)	1.542	1.307	1.592	1.588
μ (mm^{-1})	0.924	0.535	0.891	0.819
θ_{max} (deg)	36.56	36.41	39.95	39.62
no. of reflns measd	51 362	73 941	35 454	65 529
no. of unique reflns	27 248 [$R_{int} = 0.0314$]	26 196 [$R_{int} = 0.1400$]	19 853 [$R_{int} = 0.0461$]	18 589 [$R_{int} = 0.0491$]
absorp correct.	SADABS (Bruker)	SADABS (Bruker)	SADABS (Bruker)	SADABS (Bruker)
transmn min./max.	0.6921/1.0000	0.7203/1.0000	0.4368/1.0000	0.6323/1.0000
no. of params	714	812	514	459
R1/wR2 [$I > 2\sigma(I)$]	0.0648/0.1800	0.0874/0.2132	0.0651/0.01706	0.0394/0.0890
R1/wR2 [all data]	0.0964/0.2066	0.2033/0.2766	0.0716/0.1742	0.0730/0.1025
goodness-of-fit (F^2)	1.043	0.990	1.130	1.082
peak/hole ($e/Å^3$)	2.650 and −1.934	3.290 and −3.048	2.157 and −2.566	1.822 and −0.934

have a symmetry plane (*σ*) perpendicular to the alkyne bond that intersects the palladium atom and the sulfonamide moiety opposite the alkyne, showing it to be a *meso* form. Enantiomers **B3**/**B4** have a C_2 axis perpendicular to the alkyne, which intersects the palladium atom and the sulfonamide moiety opposite the alkyne. Therefore, only three stereoisomers need to be considered.

Alkene and alkyne bonds have relatively different coordination geometries. Upon palladium coordination, the carbon atoms of alkene ligands show partial sp^3 rehybridization due to back-

Table 3. Selected Bond Distances for 1aaaa, 2aaaaa, 3aaa, and (*E*)-4aaa

	1aaaa	2aaaaa	3aaa	(*E*)-4aaa
C2−C3	1.386(3)	1.388(5)	1.248(4)	1.242(2)
C6−C7	1.384(5)	1.394(5)	1.380(4)	1.241(2)
C10−C11	1.388(3)	1.385(7)	1.338(8)	1.383(2)
Pd1−C2	2.190(2)	2.197(4)	2.107(4)	2.1343(15)
Pd1−C3	2.185(3)	2.192(4)	2.140(6)	2.1384(16)

bonding. Therefore the conformation of the palladacyclohexanic rings formed can be defined as *chair*-like or *twist*-like. When the ligand is an alkyne, the backbonding contribution to the metal−ligand bond rehybridizes the pseudoalkynic carbon atom into sp^2. As mentioned above, the rigid and distorted-*chair* conformation is clear from the chemical shift difference between diastereotopic methylene protons, which is a consequence of the deviation of the average Pd−C−C−N dihedral angle with respect to the theoretical 60° usually found in nondistorted *chair*-like conformations.

If the stability of the single palladacyclohexanic ring formed in complex **3** is the determining factor in stereoisomer formation, a *meso* form **B1**/**B2** with a *chair* conformation is to be expected rather than an enantiomeric pair **B3**/**B4** with a *twist* conformation. This is fully confirmed from NMR data of complex **3aaa** (Figure 4D). The nondistorted *chair* conformation of one palladacyclohexanic ring is seen by the big chemical shift difference between the diastereotopic proton signals resonating at $\delta = 1.72$ and 4.72 ppm, which is also indicative of the overall rigidity of this ring. On the other hand, alkynic carbon atoms tend to lie in the same plane as the palladium upon coordination, bringing planarity to the overall structure, which is confirmed by the smaller difference between diastereotopic protons located α with respect to the alkyne bond ($\delta = 3.76$ and 4.77). Hence, the decrease in the chemical shift difference between diastereotopic protons can be attributed to the highly strained substructure where the protons lie at very similar angles with respect to the plane defined by the alkyne−palladium plane. This overall conformation is also confirmed by NOE contacts between the methylenic proton resonating at $\delta = 2.31$ ppm and the geminal proton at $\delta = 4.67$ and the 1,3-diaxially located protons in the same palladacyclohexanic ring at $\delta = 3.76$ ppm, and also the pseudo-olefinic proton at $\delta = 3.93$.

Colorless crystals of **3aaa** were grown by the slow evaporation of a dichloromethane−ethyl acetate−hexane solution. The molecular structure and the adopted numbering scheme are presented in Figure 7. Crystal data are listed in Table 2, and selected bond lengths and angles are given in Table 3. The palladium metal in the structure is coordinated to the three multiple bonds in a trigonal planar geometry, taking the central point of the unsaturated ligands as the attaching points (the calculated mean deviation from the plane formed by the metal atom and its coordination sphere is 0.004 Å). The metal complex crystallizes in a centrosymmetrical space group as a racemate and is disordered in two orientations. The disorder observed involves the interchange of the positions of the triple bond C2≡C3 and the double bond C6═C7 with a ratio of 83:17 and the inversion of the double bond C10═C11. The molecule orientations with different ratios can be considered identical with respect to the stereochemistry of the multiple bonds and different in the orientation of the external aromatic rings attached to the sulfonamide moiety. The structures observed agree with the NMR results of the expected *meso* form **B1**/**B2**.

As a consequence of the correlation between the atoms involved in the disorder, the distances in the coordination sphere of the palladium atom are distorted. Only the orientation of the molecule with a presence of 83% will be discussed here. The distance of the triple bond to the palladium atom taking into account the distortions mentioned is shorter than the distances to the double bonds (distances from the Pd atom to the central point of the C−C bonds are 2.05 Å for the C2−C3 alkyne, 2.07 Å for the C6−C7 alkene, and 2.09 Å for the C10−C11 alkene). The palladium alkene bonds are approximately perpendicular to the plane of the olefin, and the triple bond is located on the plane defined by the central point of coordination of the two olefins and the palladium. The shift to the atoms of the multiple bonds with respect to their substituents cannot be considered due to the distortion resulting from the disorder. Nevertheless, the planarity of the multiple bonds is lost with a shift of the atoms in the direction of the metal atom. This disorder makes it difficult to examine the conformation of the palladacyclohexanic rings with precision. The ring formed by the double and triple bond shows a mixed conformation between a distorted *boat* at the side of the triple bond and a *chair* at the side of the double bond. The ring formed by both double bonds forms a *chair* conformation.

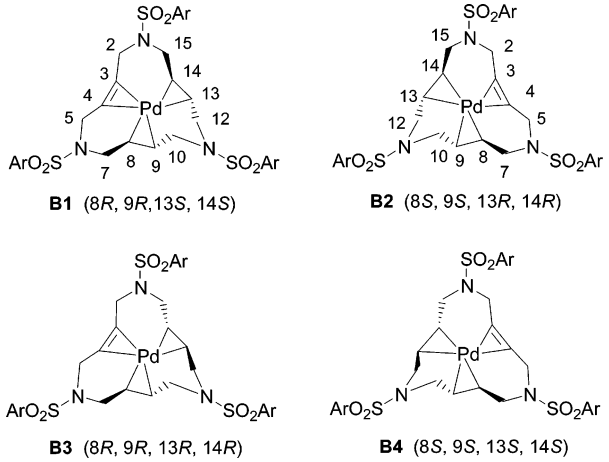

Figure 6. Stereoisomers for palladium(0) complex **3**, *meso* form **B1**/**B2**, and a pair of enantiomers **B3**/**B4**.

We next turned our attention to macrocycles **8** featuring two triple bonds and either one *E* double bond, **(*E*)-8aaa** and **(*E*)-8bbb**, or a *Z* double bond, **(*Z*)-8aaa**. Since there is just one alkene in these structures, the maximum number of stereoisomers formed upon complexation is reduced to two. The symmetry of the overall structure for complexes **4** is consistent with the local geometry of the alkene moiety. Whereas the *E* double bond complexes present a C_2 axis perpendicular to the alkene, which intersects the metal and the opposite sulfonamide moiety, leading to the enantiomeric pair **C1**/**C2** (Figure 8), the *Z* double bond complex presents a symmetry plane (σ), also perpendicular to the plane of the double bond, resulting in the *meso* form **D1**/**D2** (Figure 9). In this last example, the olefin has a symmetry plane perpendicular to the plane of the double bond, and in accordance with the definition given in the Introduction, no chirality is introduced upon coordination to the metal.

^{1}H and ^{13}C NMR analyses of complexes **4** follow the same correlation trends described for complexes **3**. Thus, compounds **(*E*)-4aaa** and **(*E*)-4bbb** show two quaternary carbon signals at $\delta = 77.1$ and 82.3 (for **(*E*)-4aaa**) and at $\delta = 78.6$ and 81.4 (for **(*E*)-4bbb**) and one pseudoalkenic carbon signal at $\delta = 82.9$ (for **(*E*)-4aaa**) and at $\delta = 82.8$ (for **(*E*)-4bbb**) (Figure 4E). Similarly, three different ^{13}C resonances resonating around 75 ppm are also observed for the achiral complex **(*Z*)-4aaa** (Figure 4F).

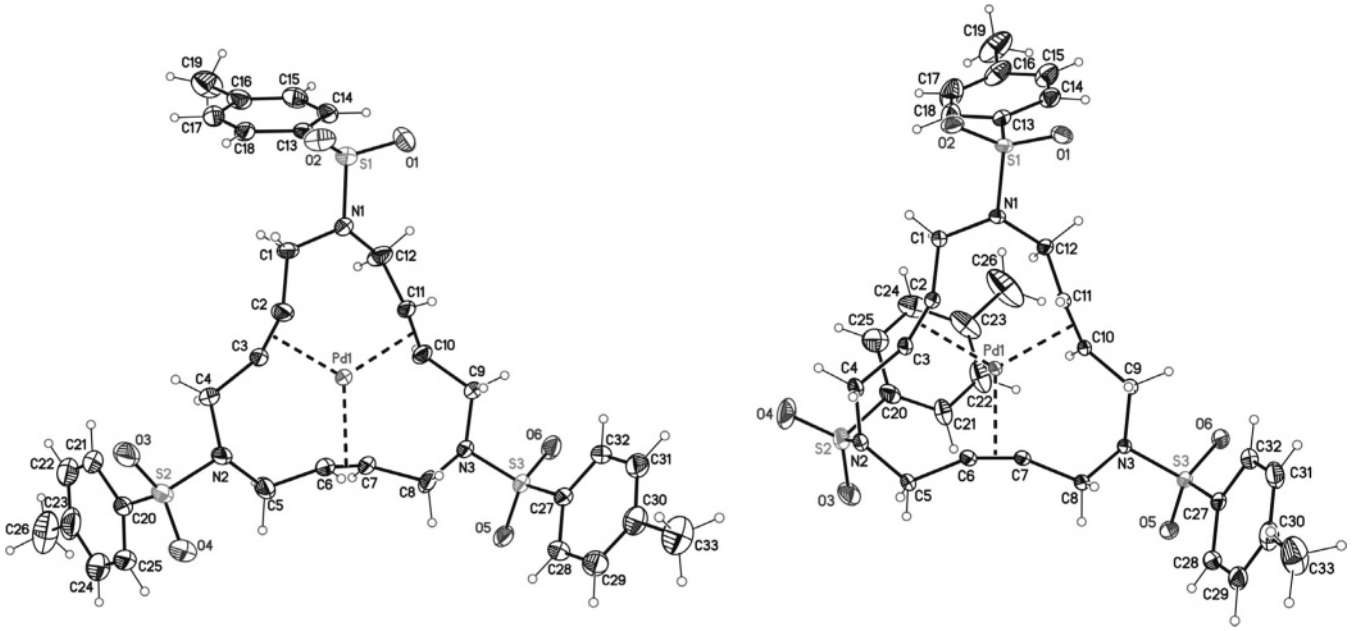

Figure 7. ORTEP plots (50%) obtained from single-crystal X-ray structure analyses of **3aaa** and **(*E*)-4aaa**.

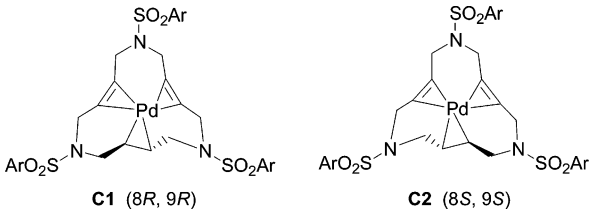

Figure 8. Stereoisomers for palladium(0) complexes **(*E*)-4**.

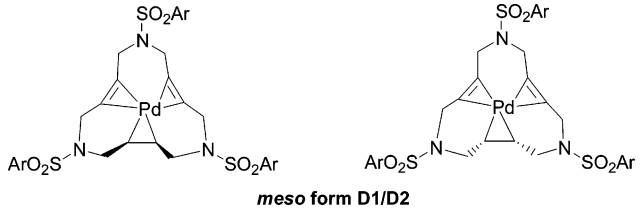

Figure 9. *meso*-Form **D1**/**D2** for palladium(0) complex **(*Z*)-4**.

On the other hand, α-nitrogen methylenic protons located next to the pseudodouble bond appear well differentiated ($\delta = 2.00/4.70$ for **(*E*)-4aaa** (Figure 4E) and $\delta = 2.58/4.10$ for **(*Z*)-4aaa** (Figure 4F)), indicating well-defined axial and equatorial positions, whereas those located next to the pseudotriple bonds appear in much closer chemical shifts, confirming their distorted position with respect to a theoretical *chair* conformation (see chemical shift assignments in Figure 4E and 4F).

The X-ray crystal structure of **(*E*)-4aaa** was obtained by single-crystal X-ray diffraction analysis of a sample obtained by slow evaporation of a chloroform−diethyl ether solution. The molecular structure and the adopted numbering scheme are presented in Figure 7. Crystal data are listed in Table 2, and selected bond lengths and angles are given in Table 3.

The molecule presents a folded structure positioning the aromatic ring C20−C25, which is attached to the sulfonamide moiety between the two alkynes, above the palladium atom and the C2≡C3 triple bond (distances: C3−C20 3.2 Å, C3−C21 3.4 Å, and Pd1−C21 3.4 Å). The coordination geometry around the palladium atom is planar trigonal, taking the central point of the C−C bonds as the attaching points (mean deviation from plane is 0.003 Å). The distances from the palladium atom to the central point of the unsaturated C−C bonds are 2.04 Å (C2, C3), 2.06 (C6, C7), and 2.11 Å (C10, C11). The distances from the palladium atom to the triple bonds are significantly shorter. The carbon atoms (C2, C3, C6, and C7) of the two triple bonds are located on the same plane formed by the palladium atom and the central points of these C−C bonds, whereas the double bond C10−C11 is located perpendicular to the coordination plane rotated through the axes of the palladium−alkene bond by approximately 61° with respect to the plane defined by the alkynes and the palladium atom. The triple bonds lose their linearity by the effect of palladium coordination and are shifted to the center of the molecule. The loss of the linearity is defined by the angles between the triple bonds and the carbon atoms attached to them (C1−C2−C3: 156.29(16)°, C2−C3−C4: 160.71(17)°; C5−C6−C7: 157.85(14)°; C6−C7−C8: 156.78(14)°). A similar effect described by the torsion angle C9−C10−C11−C12 (33.76(15°) is also observed on the double bond. This effect corresponds to a bending away of the olefinic substituents from the palladium atom of 16.9°. Both double and triple bonds are elongated upon coordination, as compared to alkene and alkyne C−C distances in analogous free ligands. Due to the centrosymmetrical nature of the crystallization space group, it was possible to confirm that both predicted enantiomers **C1**/**C2** are present in the solid state. An exact examination of the conformation of the palladacyclohexanic rings shows a *boat* conformation with the nitrogen atom out of the plane of the ring formed by the two triple bonds. The nitrogen atom N2 forms an angle of approximately 52° with the plane of the rest of the palladacyclohexanic ring. The *boat* conformation formed is slightly distorted with a *twist* corresponding to a torsion angle C4−C3−C6−C5 of approximately 8°. The palladacyclohexanic rings formed by a double and a triple bond are a mixture of the *boat* conformation at the side of the triple bond and a *chair* conformation at the side of the double bond.

Unfortunately, no crystal structure has yet been obtained for palladium(0) complex **(*Z*)-4aaa**.

Conclusions

In summary, new chiral and air- and moisture-stable palladium(0) complexes of polyunsaturated aza-macrocyclic ligands have been prepared and fully characterized by means of NMR

spectroscopy and X-ray diffraction. The stereochemical complexity of these complexes is due to the different isomers that can be formed by complexation of the metal to either of the two faces of each of the olefins involved. For the 15-membered macrocyclic ligands (**7aaa**, **(*Z*)-8aaa**, **(*E*)-8aaa**, and **(*E*)-8bbb**) the three double and triple bonds are responsible for the coordination to the palladium atom, whereas for the 20- and 25-membered ligands, only three of the four (**5aaaa**, **5bbbb**) and five (**6aaaaa**, **6ccccc**) olefins are coordinated to the metal center. The olefins in the preorganized macrocyclic ligands are correctly prepositioned for Pd^0 complex formation. This fact allows us to conclude that the palladium atom prefers a tricoordination rather than a larger coordination number due to the great stability of the triolefin palladium core in these structures. Therefore, it has been demonstrated that the incorporation of a palladium atom into the cavity of a variety of sizable aza-macrocyclic ligands forms stable tricoordinate complexes that show structural features that are characteristic of well-defined σ-type Pd−C molecular bonding. These structural characteristics of the complexes have been seen in solution by NMR spectroscopy and in the solid state by X-ray diffraction analysis.

Experimental Section

IR spectra were recorded with a FT-IR using a single-reflection ATR system as a sampling accessory. ESI mass spectra were acquired using a Navigator quadrupole instrument (Finnigan AQA ThermoQuest) equipped with an electrospray ion source. Elemental analyses were determined at "Servei d'Anàlisi Química de la Universitat de Girona".

NMR Spectroscopy. High-field ^1H and ^{13}C nuclear magnetic resonance (NMR) analyses were carried out at the Servei de Ressonancia Magnetica Nuclear, Universitat Autònoma de Barcelona, using an AVANCE 500 Bruker spectrometer for $CDCl_3$ solutions. Characterization of the described compounds was performed using typical gradient-enhanced 2D experiments, such as COSY, NOESY, HSQC, HSQC-TOCSY, and HMBC, recorded under routine conditions. In highly demanding applications, band-selective 2D HSQC and HSQC-TOCSY experiments were carried out by applying a semiselective 180° pulse, using a re-burp shape, instead of the conventional hard ^{13}C 180 pulse during the carbon evolution period. A selective pulse of 3 ms of duration was implemented in a gradient spin−echo period in order to avoid a carbon evolution period during its application, thus achieving effective refocusing over the desired bandwith. In these experiments, 256 increments with 8 scans were applied for each t_1 value, and the spectral width was reduced in both dimensions to include only the resonances of interest. Data were finally processed applying zero-filling and linear prediction to achieve full separation of all resonances.

Macrocycles **5**,[10] **6**,[11] and **8**[6e] were prepared as previously described.

1,6,11-Tris(4-methylphenylsulfonyl)-1,6,11-triazacyclopentadeca-8,13-dien-3-yne (7aaa). A mixture of 1,4-bis(methanesulfonyloxy)-2-butyne[13] (0.36 g, 1.46 mmols) and acetonitrile (10 mL) was added dropwise to a stirred solution of (*E*,*E*)-1,6,11-tris(4-methylphenylsulfonyl)-1,6,11-triazaundeca-3,8-diene[12] (0.82 g, 1.33 mmol), anhydrous potassium carbonate (0.95 g, 6.66 mmol), and acetonitrile (60 mL). The mixture was heated to reflux for 16 h (TLC monitoring). The salts were filtered off, and the filtrate was evaporated at reduced pressure. The crude residue was purified by column chromatography on silica gel (hexanes−ethyl acetate−dichloromethane, 7:2:1) to afford **7aaa** (0.26 g, 30% yield) as a colorless solid. Mp: 215−216 °C. IR (ATR): ν = 2922, 1332, 1157 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ 2.42 (s, 9H), 3.61 (d, J = 5.2 Hz, 4H), 3.68 (d, J = 6.2 Hz, 4H), 3.88 (s, 4H), 5.30−5.70 (m, 4H), 7.31 (d, J = 8.2 Hz, 6H), 7.63 (d, J = 8.2 Hz, 6H). ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C, TMS): δ 22.2, 38.4, 50.7, 51.4, 80.0, 127.8, 128.3, 130.3, 130.5, 132.1, 136.6, 136.7, 144.3, 144.5. ESI-MS: *m*/*z* 668 $[M + H]^+$, 690 $[M + Na]^+$, 706 $[M + K]^+$. Anal. Calcd (%) for $C_{33}H_{37}N_3O_6S_3$ (667.8): C 59.35, H 5.58, N 6.29, S 14.40. Found: C 59.18, H 5.85, N 6.25, S, 14.29.

(*E*,*E*,*E*,*E*,*E*)-1,6,11,16,21-Pentakis[(4-methylphenyl)-sulfonyl]-1,6,11,16,21-pentaazacyclopentacosa-3,8,13,18,23-pentaenepalladium(0) (2aaaaa). General Method for the Synthesis of Pd^0 Complexes 2ccccc, 1aaaa, 1bbbb, and 3aaa. Macrocycle **6aaaaa** (0.090 g, 0.080 mmol) was added to a solution of $Pd_2(dba)_3(dba)$ (0.055 g, 0.095 mmol of Pd) in anhydrous and degassed acetonitrile (6 mL) under nitrogen atmosphere, and the resulting mixture was stirred for 4 h at room temperature. The crude reaction mixture was filtered through Celite, and the solvent was evaporated under vacuum. The residue was purified by column chromatography on silica gel (hexane−ethyl acetate−dichloromethane, polarity from 9:1:0 to 6:2:2) to afford Pd^0 complex **2aaaaa** (0.078 g, 79%) as a colorless solid. Mp: 154−156 °C (dec). IR (ATR): ν = 2923, 1332, 1155 cm^{-1}. ESI-MS: *m*/*z* 1222 $[M + H]^+$, 1116 $[M - Pd + H]^+$. Anal. Calcd (%) for $C_{55}H_{65}N_5O_{10}PdS_5 \cdot 2H_2O$ (1258.9): C 52.48, H 5.52, N 5.56, S 12.74. Found: C 52.66, H 5.23, N 5.44, S 12.59.

(*E*,*E*,*E*,*E*,*E*)-1,6,11,16,21-Pentakis(ferrocenylsulfonyl)-1,6,11,16,21-pentaazacyclopentacosa-3,8,13,18,23-pentaenepalladium(0) (2ccccc). Mp: 183−185 °C (dec). IR (ATR): ν = 2922, 1324, 1133 cm^{-1}. Anal. Calcd (%) for $C_{70}H_{75}Fe_5N_5O_{10}PdS_5$ (1692.3): C 49.68, H 4.47, N 4.14, S 9.47. Found: C 49.48, H 4.81, N 4.00, S 9.04.

(*E*,*E*,*E*,*E*)-1,6,11,16-Tetrakis[(4-methylphenyl)sulfonyl]-1,6,11,16-tetraazacycloicosa-3,8,13,18-tetraenepalladium(0)(1aaaa). Mp: 150−152 °C (dec). IR (ATR): ν = 2849, 1332, 1160 cm^{-1}. ESI-MS: *m*/*z* 999 $[M + H]^+$. Anal. Calcd (%) for $C_{44}H_{52}N_4O_8PdS_4 \cdot 1/2H_2O$ (1008.6): C 52.40, H 5.30, N 5.55, S 12.72. Found: C 52.54, H 5.78, N 5.23.

(*E*,*E*,*E*,*E*)-1,6,11,16-Tetrakis[(2,4,6-triisopropylphenyl)sulfonyl]-1,6,11,16-tetraazacycloicosa-3,8,13,18-tetraenepalladium(0) (1bbbb). Mp: 142−143 °C (dec). IR (ATR): ν = 2958, 1313, 1148 cm^{-1}. ESI-MS: *m*/*z* 1447 $[M + H]^+$, 1469 $[M + Na]^+$. Anal. Calcd (%) for $C_{76}H_{116}N_4O_8PdS_4 \cdot C_4H_{10}O$ (1522.5): C 63.11, H 8.34, N 3.68, S 8.42. Found: C 62.69, H 8.65, N 3.83, S 8.19.

(*E*,*E*)-1,6,11-Tris[(4-methylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8-diene-13-ynepalladium(0) (3aaa). Mp: 195−198 °C (dec). IR (ATR): ν = 2923, 1341, 1156 cm^{-1}. ESI-MS: *m*/*z* 774 $[M + H]^+$. Anal. Calcd (%) for $C_{33}H_{37}N_3O_6PdS_3 \cdot C_4H_{10}O$ (848.4): C 52.38, H 5.58, N 4.95. Found: C 52.10, H 5.20, N 5.42.

(*E*)-1,6,11-Tris[(2,4,6-triisopropylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3-ene-8,13-diynepalladium(0) ((*E*)-4bbb). General method for the synthesis of Pd^0 complexes (*E*)-4aaa and (*Z*)-4aaa. A stirred mixture of macrocycle **(*E*)-8bbb** (0.05 g, 0.05 mmol) and $Pd(PPh_3)_4$ (0.063 g, 0.054 mmol) in acetone (10 mL) was refluxed for 18 h (TLC monitoring). The solvent was evaporated under vacuum. The residue was purified by column chromatography on silica gel (hexane−ethyl acetate, 10:1) to afford Pd^0 complex **(*E*)-4bbb** (0.035 g, 64%) as a colorless solid. Mp: 105−107 °C. IR (ATR): ν = 2959, 2163, 1317, 1151 cm^{-1}. ESI-MS: *m*/*z* 1108 $[M + H]^+$, 1125 $[M + NH_4]^+$. Anal. Calcd (%) for $C_{57}H_{83}N_3O_6PdS_3 \cdot C_4H_{10}O$ (1183.0): C 61.93, H 7.92, N 3.55, S 8.13. Found: C 61.78, H 8.08, N 3.73, S 8.41.

(*E*)-1,6,11-Tris[(4-methylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3-ene-8,13-diynepalladium(0) ((*E*)-4aaa). Mp: 150−152 °C (dec). IR (ATR): ν = 2991, 2163, 1338, 1157 cm^{-1}. ESI-MS: *m*/*z* 772 $[M + H]^+$, 794 $[M + Na]^+$, 810 $[M + K]^+$. Anal. Calcd (%) for $C_{33}H_{35}N_3O_6PdS_3 \cdot H_2O$ (790.3): C 50.32, H 4.72, N 5.32, S 12.17. Found: C 50.07, H 4.64, N 5.07, S 11.64.

(*Z*)-1,6,11-Tris[(4-methylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3-ene-8,13-diynepalladium(0) ((*Z*)-4aaa). Mp: 192−194 °C (dec). IR (ATR): ν = 2963, 1337, 1153 cm^{-1}. ESI MS: *m*/*z* 772 $[M + H]^+$, 794 $[M + Na]^+$, 810 $[M + K]^+$. Anal. Calcd (%) for $C_{33}H_{35}N_3O_6PdS_3 \cdot 1/2H_2O$ (781.3): C 50.73, H 4.64, N 5.38, S 12.31. Found: C 50.64, H 4.53, N 5.25, S 12.16.

X-ray Structure Determination. Colorless translucent crystals of **1aaaa**, **2aaaaa**, **3aaa**, and **(*E*)-4aaa** were grown by slow evaporation at room temperature in the solvents previously described. The measured crystals were prepared under inert conditions immersed in perfluoropolyether as protecting oil for manipulation. Data collection: Measurements were made on a Bruker-Nonius diffractometer equipped with an APPEX 2 4K CCD area detector, an FR591 rotating anode with Mo Kα radiation, Montel mirrors as monochromator, and a Kryoflex low-temperature device (T = 100 K). Full-sphere data collection was used with ω and φ scans. Programs used: data collection Apex2 V. 1.0-22 (Bruker-Nonius 2004), data reduction Saint + Version 6.22 (Bruker-Nonius 2001), and absorption correction SADABS V. 2.10 (2003). Structure solution and refinement: SHELXTL Version 6.10 (Sheldrick, 2000) was used.[17]

CCDC 609180−609183 contain the supplementary crystallographic data for this paper. The crystallographic data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Supporting Information Available: ^1H, COSY, NOESY, HSQC, HSQC-TOCSY, and HMBC NMR spectra of complexes **1bbbb**, **2aaaaa**, **3aaa**, **(*E*)-4aaa**, and **(*Z*)-4aaa**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM060667F

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