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Transition Metal-Mediated Intramolecular [2+2+2] Cycloisomerizations of Cyclic Triynes and Enediynes

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Nitrogen-containing 15-membered triacetylenic macrocycles known as 1,6,11-tris(arylsulfonyl)-1,6,11-triazacyclopentadeca-3,8,13-triynes (**1**) and enediynic macrocycles called 1,6,11-tris(arylsulfonyl)-1,6,11-triazacyclopentadeca-3-ene-8,13-diynes (**4** and **5**) were satisfactorily prepared. [2+2+2] cycloisomerization processes catalyzed by transition metals were tested in the above-mentioned macrocycles. Readily available and familiar cyclotrimerization precatalysts were examined for efficiency. Among them, the $RhCl(CO)(PPh_3)_2$ complex was found to catalyze the cycloisomerization reaction giving the desired cycloadducts in high yields.

Introduction

[2+2+2] cycloisomerization reactions of acetylenes catalyzed by transition metal complexes are an attractive and interesting tool for the synthesis of a variety of polysubstituted benzene derivatives in a very easy one-pot process.[1] Partially intramolecular approaches or fully intramolecular cycloaddition processes represent efficient entries into polycyclic compounds. Many transition metal complexes, including those of cobalt, rhodium, and palladium, have been reported to be efficient catalysts for these transformations.[1] However, the cycloisomerization of cyclotriynes into tricyclic benzene derivatives has only been reported on silicon-tethered macrocycles by Sakurai et al. in low yields and in the presence of a variety of π electron systems.[2] Recently we reported the synthesis of a novel type of nitrogen-containing 15-membered tri-

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SCHEME 1. Structure of Macrocyclic Triynes 1, Pd⁰ Complexes 2, and Triazatrindane Derivatives 3

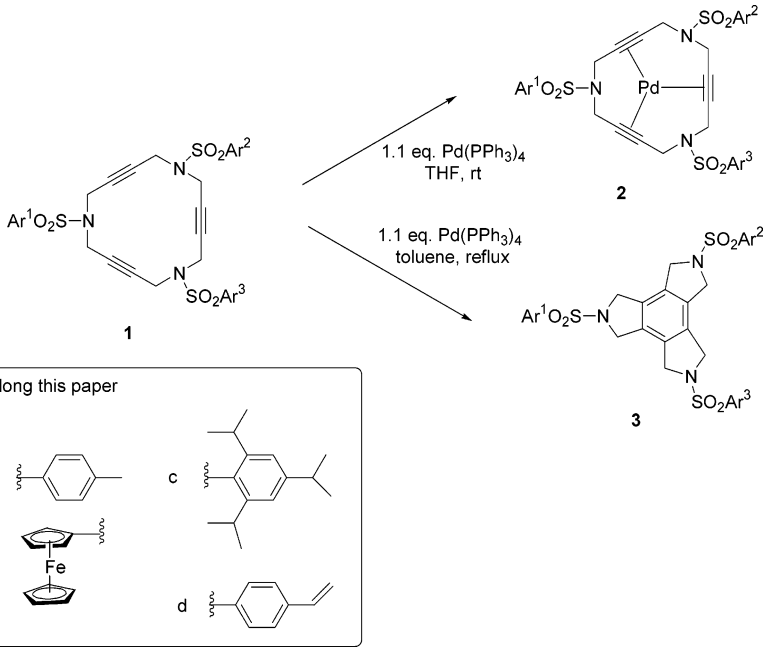

TABLE 1. Summary of 15-Membered Triacetylenic Macrocycles 1 Synthesized and Their Pd⁰ Complexes 2

entry	compd	Ar^1	Ar^2	Ar^3	ref
1	**1aaa**	4-$CH_3C_6H_4$-	4-$CH_3C_6H_4$-	4-$CH_3C_6H_4$-	3
2	**1aab**	4-$CH_3C_6H_4$-	4-$CH_3C_6H_4$-	ferrocenyl-	3
3	**1bbb**	ferrocenyl-	ferrocenyl-	ferrocenyl-	this work
4	**1ccc**	2,4,6-^{i}PrC_6H_2-	2,4,6-^{i}PrC_6H_2-	2,4,6-^{i}PrC_6H_2-	this work
5	**1abd**	4-$CH_3C_6H_4$-	ferrocenyl-	4-CH_2=CHC_6H_4-	this work
6	**2aaa**	4-$CH_3C_6H_4$-	4-$CH_3C_6H_4$-	4-$CH_3C_6H_4$-	3
7	**2aab**	4-$CH_3C_6H_4$-	4-$CH_3C_6H_4$-	ferrocenyl-	this work
8	**2bbb**	ferrocenyl-	ferrocenyl-	ferrocenyl-	this work
9	**2abd**	4-$CH_3C_6H_4$-	ferrocenyl-	4-CH_2=CHC_6H_4-	this work

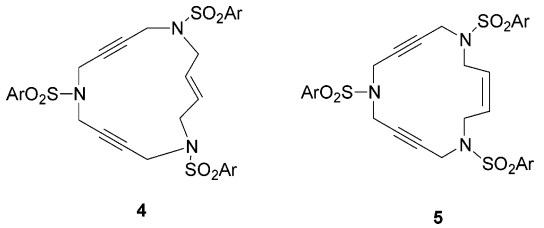

FIGURE 1. Structure of macrocyclic enediynes **4** and **5**.

acetylenic macrocycles of type **1**, and commented on their coordinating ability with palladium(0) to afford complex **2** as well as on their cycloisomerization into compound **3** promoted by palladium(0)[3] (Scheme 1).

To address this issue and to expand its synthetic scope, we have investigated the cycloisomerization reaction of several triacetylenic macrocycles of type **1** with different transition metals. Since rhodium(I) complexes are the most effective catalysts to promote the completely intramolecular cycloisomerization of compounds **1**, we use Rh^I to expand the reaction to macrocyclic trans and cis enediynes of types **4** and **5** (Figure 1).

To the best of our knowledge, this paper reports the first [2+2+2] cycloaddition reactions of macrocyclic triynes and macrocyclic enediynes.

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Results and Discussion

Preliminary results for the complexation of **1aaa** (Ar^1 = Ar^2 = Ar^3 = *p*-tolyl) with $Pd(PPh_3)_4$ in THF at room temperature gave complex **2aaa** as an air- and moisture-stable crystalline compound, the first Pd⁰ complex described with a macrocyclic triyne.[4] The cycloisomerization of **1aaa** required stoichiometric amounts of palladium metal in refluxing toluene to afford the triazatrindane derivative **3aaa** in 54% yield (Scheme 1).[3] However, the reaction never proceeded under catalytic conditions.

To extend our methodology, macrocycles of type **1** containing different aryl units in their structure were prepared and their ability to coordinate Pd⁰ was studied. The results are summarized in Table 1.

Macrocycle **1abd** containing three different aryl units, unlike other macrocycles, required a modified pathway and was prepared as outlined in Scheme 2. Compound **7a**[3] was prepared from a reaction of *N-tert*-butyloxycarbonyl (Boc)-protected sulfonamide **6a** and 4 equiv of 1,4-dibromo-2-butyne. Condensation of **7a** with 0.5 equiv of

(4) The isolation of palladium(0) complexes for an acyclic triyne or an enediyne derivative and their catalytic cyclizations has been reported: (a) Yamamoto, Y.; Nagata, A.; Arikawa, Y.; Tatsumi, K.; Itoh, K. *Organometallics* **2000**, *19*, 2403−2405. (b) Yamamoto, Y.; Nagata, A.; Nagata, H.; Ando, Y.; Arikawa, Y.; Tatsumi, K.; Itoh, K. *Chem. Eur. J.* **2003**, *9*, 2469−2483. (c) Yamamoto, Y.; Kuwabara, S.; Ando, Y.; Nagata, H.; Nishiyama, H.; Itoh, K. *J. Org. Chem.* **2004**, *69*, 6697−6705.

SCHEME 2. Synthesis of Macrocycle 1abd

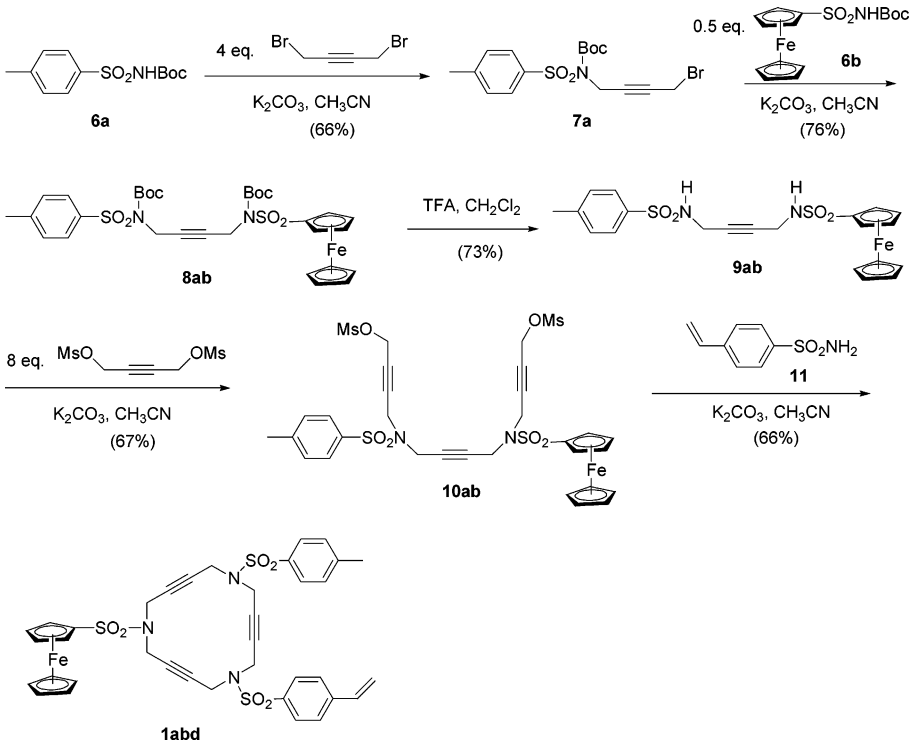

TABLE 2. Palladium(0)-Catalyzed Cycloisomerization of Macrocycles 1[a]

entry	compd	Ar^1	Ar^2	Ar^3	yield (%)
1	**3aaa**[b]	4-$CH_3C_6H_4$-	4-$CH_3C_6H_4$-	4-$CH_3C_6H_4$-	54
2	**3aab**	4-$CH_3C_6H_4$-	4-$CH_3C_6H_4$-	ferrocenyl-	54
3	**3bbb**	ferrocenyl-	ferrocenyl-	ferrocenyl-	65
4	**3ccc**	2,4,6-^{i}PrC_6H_2-	2,4,6-^{i}PrC_6H_2-	2,4,6-^{i}PrC_6H_2-	54
5	**3abd**	4-$CH_3C_6H_4$-	ferrocenyl-	4-CH_2=CHC_6H_4-	45

[a] Reactions were run with macrocycles **1** and $Pd(PPh_3)_4$ (1.1 equiv) in refluxing toluene for 24 h. [b] Reference 3.

(Boc)-protected ferrocenylsulfonamide **6b**[5] using potassium carbonate in refluxing acetonitrile led to compound **8ab** in 76% yield. The elimination of the Boc groups in compound **8ab** and subsequent treatment with an excess of 1,4-bis(methanesulfonyloxy)-2-butyne resulted in the isolation of derivative **10ab** in 67% yield. The reaction of **10ab** with 4-vinylbenzenesulfonamide **11** was straightforward and led to the formation of macrocycle **1abd** featuring three different aryl rings.

Palladium(0) complexes **2aab**, **2bbb**, and **2abd** were prepared by ligand exchange using $Pd(PPh_3)_4$ as a metal source in acetone, at room temperature and in the presence of the corresponding macrocycle. In all cases, complexes **2** were obtained in moderate yields (37%, 44%, and 41%, respectively).

Cycloisomerization reactions of macrocycles **1** using palladium always required 1.1 equiv of $Pd(PPh_3)_4$ in refluxing toluene for 1 day. Compounds **3** were obtained from moderate to good yields. The results are described in Table 2.

The structure of triazatrindane derivatives of type **3** was confirmed by X-ray analysis. A perspective view of compound **3abd** is shown in Figure 2.

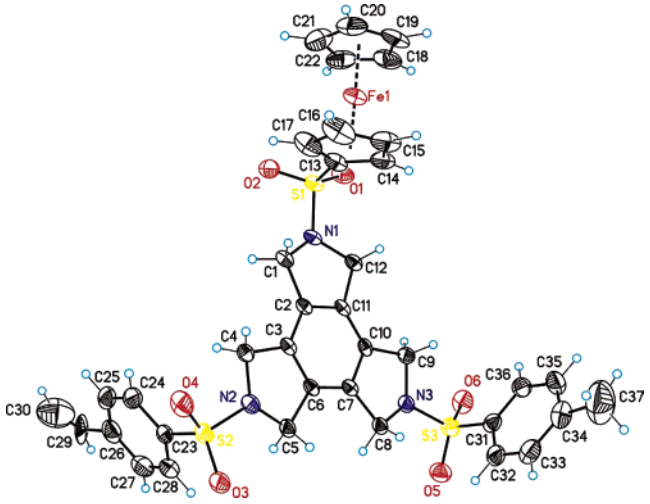

FIGURE 2. X-ray structure (Ortep-Plot with ellipsoids at the 50% probability level) of **3abd**.

The high symmetry present in compounds **3**, especially the cases with three identical aryl units, can be quickly observed in their simplified NMR spectra. Compounds **3aaa**, **3bbb**, and **3ccc** with D_3 symmetry give rise to one signal (singlet) corresponding to the 12 methylene pro-

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TABLE 3. Cycloisomerization of Macrocycles 1 Mediated by Several Transition Metals

entry	compd	catalytic system	yield (%)
1	**3ccc**	5% molar $CpCo(CO)_2$, *n*-decane, 140 °C, 3.5 h	44
2	**3ccc**	1 equiv of $CpCo(CO)_2$, *n*-decane, 140 °C, 1 h	88
3	**3aab**	7% molar Grubbs' catalyst, toluene, reflux, 22 h	42
4	**3ccc**	7% molar Grubbs' catalyst, toluene, reflux, 22 h	36
5	**3ccc**	20% molar Grubbs' catalyst, toluene, reflux, 22 h	36
6	**3aaa**	5% molar $RhCl(CO)(PPh_3)_2$, toluene, 65 °C, 24 h	88
7	**3aab**	5% molar $RhCl(CO)(PPh_3)_2$, toluene, 65 °C, 24 h	89
8	**3ccc**	5% molar $RhCl(CO)(PPh_3)_2$, toluene, 65 °C, 18 h	96
9	**3ccc**	1% molar $RhCl(CO)(PPh_3)_2$, toluene, 65 °C, 3 days	80

tons in the ring (4.52, 4.31, and 4.48 ppm for **3aaa**, **3bbb**, and **3ccc**, respectively).

To improve the yield of compounds **3** and to avoid the use of stoichiometric amounts of palladium(0), other transition metal complexes have been tested. The results are described in Table 3.

The utility of the $CpCoL_2$ system as a catalyst for this chemistry was initially revealed by Vollhardt and Bergman,[6] and nowadays the Co catalysts are the compounds of primary choice for the [2+2+2] cyclotrimerization processes.[7] Therefore, macrocycle **1ccc** was treated with a catalytic amount of cyclopentadienylcobalt dicarbonyl ($CpCo(CO)_2$) (5% molar) in *n*-decane at 140 °C for 3.5 h to give compound **3ccc** in 44% yield (entry 1, Table 3). Using a stoichiometric amount of the cobalt complex, the yield of **3ccc** was improved to 88% (entry 2, Table 3). Since stoichiometric amounts of Co^I complex were still required to obtain high yields, we turned our attention to other transition metal complexes. Ruthenium complexes such as Grubbs' catalyst, which has been widely used in the olefin metathesis reaction,[8] have been used as catalyst for the cyclotrimerization of alkynes.[9] Macrocycles **1aab** and **1ccc** were treated with a catalytic amount of bis(tricyclohexylphosphane)benzylidene ruthenium(II) dichloride in refluxing toluene to afford the corresponding triazatrindanes **3aab** and **3ccc** in moderate yield (42% and 36%, respectively) (entries 3 and 4 in Table 3). In the case of macrocycle **1ccc** 20% of Grubbs' catalyst was also tested, but the yield of **3ccc** did not improve (entry 5 in Table 3). On the other hand, rhodium complexes, such as Wilkinson's catalyst, are also known to be effective for the synthesis of polysubstituted benzenes from alkynes.[10] Since chlorocarbonylbis(triphenylphosphane)rhodium(I) was available in our laboratory, it was tested in macrocycle **1aaa.** Using catalytic amounts of $RhCl(CO)(PPh_3)_2$ (5% molar) in toluene at 65 °C, compound **3aaa** was obtained in 88% yield (entry 6, Table 3). In the same manner, the cycloisomerization of several macrocycles **1** was examined as summarized in Table 3, entries 7 and 8. In all cases the yields were very high. An attempt to reduce the catalytic amount of Rh^I complex to 1% molar did not prove to be as successful as when using 5% molar. After 3 days, the yield of **3ccc** was 80% and starting material was recovered in 17% yield (entry 9, Table 3). Therefore, 5% equiv of catalyst was chosen for all cycloadditions.

Encouraged by these results, the possibility of applying this methodology to cyclic enediynes of type **4** and **5** was evaluated (Figure 1). Cyclotrimerization of two molecules of an alkyne with an alkene is a straightforward route to substituted cyclohexadiene derivatives, which are important components for the Diels–Alder reaction. In addition, Rh^I complexes also proved to be fairly active catalysts for similar processes.[11] The synthetic versatility of such a transformation becomes more interesting if it proceeds with remarkable stereoselectivity with respect to the stereochemistry of the original double bond of the macrocyclic compound. To check that purpose, compounds **4aaa**, **4ccc**, **5aaa**, and **5ccc** were prepared from

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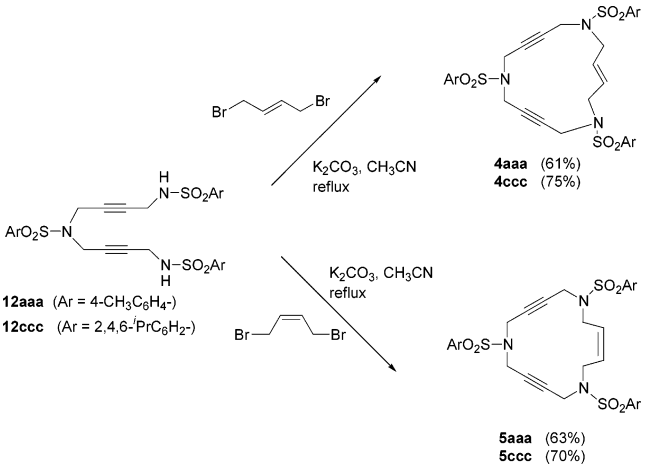
(8) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18–29 and references therein.

(9) For ruthenium-catalyzed [2+2+2] cyclotrimerizations of alkynes using Grubbs' catalyst, see: (a) Peters, J.-U.; Blechert, S. *Chem. Commun.* **1997**, 1983–1984. (b) Das, S. K.; Roy, R. *Tetrahedron Lett.* **1999**, *40*, 4015–4018. (c) Witulski, B.; Stengel, T.; Fernández-Hernández, J. M. *Chem. Commun.* **2000**, 1965–1966. Using Cp*RuCl(cod) catalyst, see: (d) Yamamoto, Y.; Arakawa, T.; Ogawa, R.; Itoh, K. *J. Am. Chem. Soc.* **2003**, *125*, 12143–12160 and references by the same authors cited therein. (e) Yamamoto, Y.; Ishii, J.; Nishiyama, H.; Itoh, K. *J. Am. Chem. Soc.* **2004**, *126*, 3712–3713. (f) Ura, Y.; Sato, Y.; Shiotsuki, M.; Kondo, T.; Mitsudo, T. *J. Mol. Catal. A*: *Chem.* **2004**, *209*, 35–39.

(10) Selected references for rhodium-catalyzed [2+2+2] alkyne cyclotrimerizations, see: (a) Collman, J. P.; Kang, J. W.; Little, W. F.; Sullivan, M. F. *Inorg. Chem.* **1968**, *7*, 1298–1303. (b) Müller, E. *Synthesis* **1974**, 761–774. (c) Grigg, R.; Scott, R.; Stevenson, P. *Tetrahedron Lett.* **1982**, *23*, 2691–2692. (d) Grigg, R.; Scott, R.; Stevenson, P. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1357–1364. (e) McDonald, F. E.; Zhu, H. Y. H.; Holmquist, C. R. *J. Am. Chem. Soc.* **1995**, *117*, 6605–6606. (f) Kotha, S.; Brahmachary, E. *Tetrahedron Lett.* **1997**, *38*, 3561–3564. (g) Ojima, I.; Vu, A. T.; McCullagh, J. V.; Kinoshita, A. *J. Am. Chem. Soc.* **1999**, *121*, 3230–3231. (h) Reference 8c. (i) Grigg, R.; Sridharan, V.; Wang, J.; Xu, J. *Tetrahedron* **2000**, *56*, 8967–8976. (j) Sun, Q.; Zhou, X.; Islam, K.; Kyle, D. J. *Tetrahedron Lett.* **2001**, *42*, 6495–6497. (k) McDonald, F. E.; Smolentsev, V. *Org. Lett.* **2002**, *4*, 745–748. (l) Witulski, B.; Zimmermann, A. *Synlett* **2002**, 1855–1859. (m) Kinoshita, H.; Shinokubo, H.; Oshima, K. *J. Am. Chem. Soc.* **2003**, *125*, 7784–7785. (n) Dufková, L.; Císarová, I.; Stepnicka, P.; Kotora, M. *Eur. J. Org. Chem.* **2003**, 2882–2887.

(11) For rhodium-catalyzed [2+2+2] cycloadditions of alkynes with olefins, see: (a) Singleton, D. M. *Tetrahedron Lett.* **1973**, *14*, 1245–1248. (b) Grigg, R.; Scott, R.; Stevenson, P. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1365–1369. (c) Oh, C. H.; Sung, H. R.; Jung, S. H.; Lim, Y. M. *Tetrahedron Lett.* **2001**, *42*, 5493–5495. For rhodium-catalyzed carbonylative cycloaddition of enediynes, see: (d) Ojima, I.; Lee, S.-Y. *J. Am. Chem. Soc.* **2000**, *122*, 2385–2386. (e) Bennacer, B.; Fujiwara, M.; Ojima, I. *Org. Lett.* **2004,** *6*, 3589–3591.

SCHEME 3. Synthesis of Macrocyclic Enediynes 4 and 5



precursors **12**[3] as outlined in Scheme 3. Ring closure was achieved by treatment of **12** with 1 equiv of either (*E*)- or (*Z*)-1,4-dibromo-2-butene,[12] respectively.

^{1}H and ^{13}C chemical shift assignments of compounds **4** and **5** have been performed by 2D homonuclear (^{1}H–^{1}H COSY) and heteronuclear (^{1}H–^{13}C HSQC) correlation spectra. In Figure 3, ^{1}H and ^{13}C NMR chemical shifts are given for ring signals of isopropylphenyl derivatives **4ccc** and **5ccc**. Using conventional NMR experiments, it is not possible to differentiate between the diastereoisomers **4** and **5**. However, characterization of the trans/cis double bond configuration in enediynes **4** and **5** has been confirmed by measuring the proton–proton coupling constants between the chemically equivalent olefinic protons. This coupling value is not visible from the conventional proton spectra due to the symmetry properties of both isomeric products, one having a C_2 axis and the other a symmetry plane. To measure these coupling constants, we have developed a new NMR method called IFSERF (Isotope-Filtered SElective ReFocusing), which allows the precise measurement of the proton–proton coupling constants between chemically equivalent protons from the indirect dimension of a 2D *J*-resolved NMR spectrum. A detailed description of this experiment will be presented elsewhere.[13] To distinguish between these isomers we have taken into consideration the general trend that trans isomers exhibit a larger *J*(HH) coupling value than the cis isomer. In compound **4ccc**, the magnitude of *J*(HH) is 15.2 Hz whereas in **5ccc** it is about 11 Hz. The downfield effect on the olefinic chemical shift of compounds **4ccc** also confirms such a prediction.

Next, macrocycles **4** and **5** were treated under the optimized reaction conditions that had been used for triacetylenic macrocycles: 5% molar of $RhCl(CO)(PPh_3)_2$ in toluene at 65 °C. However, the cyclization process was slow and heating to 90 °C was necessary to speed the process up. The results are shown in Scheme 4. In all cases, yields of cycloisomerized compounds **13** and **14** were high. No side reactions of the cyclohexadiene system, such as aromatization or further cycloadditions, took place. The reaction proceeded with total stereoselectivity and initial stereochemistry of the macrocyclic double bond was maintained during the cycloaddition process. This experimental fact is consistent with the common mechanism proposed for these kinds of cycloadditions in which two alkyne groups undergo initial coupling and subsequent incorporation of the olefin may then occur by either an insertion process or a Diels–Alder reaction.[1,6c] However, as a main difference with compounds **4** and **5**, NOE data obtained from selective NOESY experiments when possible or from 2D NOESY spectra were enough to determine the relative syn/anti stereochemistry of the symmetrical center in the highly rigid **13** and **14** derivatives. The syn disposition structure for compounds **14** was confirmed by the single NOE enhancement between the H_c and H_a protons, while no NOE signal was observed between H_c and H_b/$H_{b'}$ protons. On the other hand, the methine H_c proton (δ 2.85) in compound **13ccc** showed a substantial NOE effect on both closely placed H_a (δ 3.02) and $H_{b'}$ (δ 3.67) protons, confirming its anti stereochemistry (Figure 3).

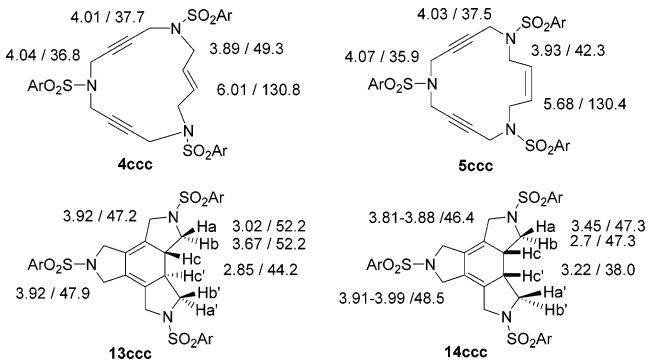


FIGURE 3. Experimental ^{1}H and ^{13}C NMR chemical shifts of the ring part of **4ccc**, **5ccc**, **13ccc**, and **14ccc**.

Figure 3 shows the ^{1}H and ^{13}C NMR chemical shifts of the fused rings of **13ccc** and **14ccc**. All CH_2 groups adjacent to the cyclohexadiene ring provide diastereotopic protons for both compounds, although in compound **13ccc** some of them are only partially resolved. As a general correlation trend, a remarkable upfield ^{13}C chemical shift effect of about 5–6 ppm can be observed for both central CH and CH_2 carbon resonances in compounds **14** when compared to the related anti isomers **13**, whereas a +0.3 ppm downfield effect is always observed for the ^{1}H chemical shift of the central CH proton.

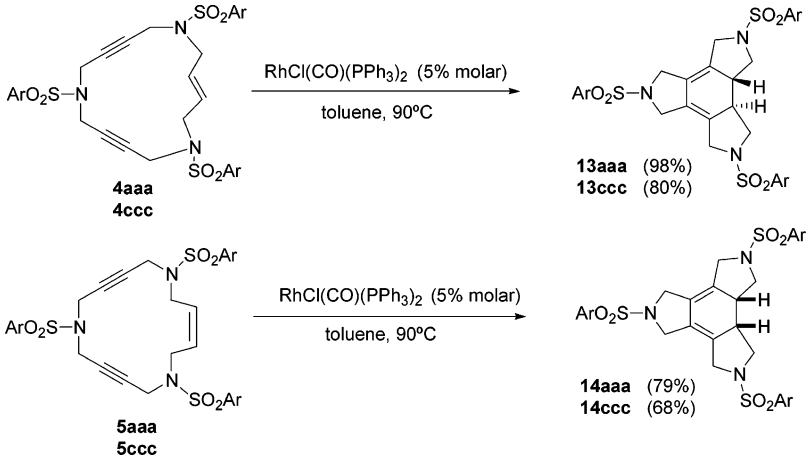
To see if Wilkinson's catalyst also promotes the cycloisomerization process, macrocycle **4ccc** was treated with 5% molar of $RhCl(PPh_3)_3$ in toluene at 90 °C. Compound **13ccc** was obtained in 80% yield, demonstrating that Wilkinson's catalyst exhibits a similar efficiency with respect to $RhCl(CO)(PPh_3)_2$.

In conclusion, we have prepared new types of nitrogen-containing 15-membered macrocycles with triple and double bonds and with different aryl units in their structure. Triacetylenic macrocycles of type **1** have an excellent ability to coordinate palladium(0). Furthermore, we have developed an efficient and stereoselective rhodium(I)-catalyzed [2+2+2] cycloisomerization of macrocyclic triynes **1** and enediynes **4** and **5**. These reactions offer a very convenient and mild method for the synthesis of various multiple ring compounds in good yields.

(12) (*E*)-1,4-Dibromo-2-butene is commercially available. (*Z*)-1,4-Dibromo-2-butene was prepared following a procedure described in the literature: Feigenbaum, A.; Lehn, J.-M. *Bull. Soc. Chim. Fr.* **1973**, *1* (part *2*), 198–202.

(13) Nolis, P.; Roglans, A.; Parella, T. *J. Magn. Reson.* In press.

SCHEME 4. Cycloisomerization Reactions of Macrocyclic Enediynes 4 and 5



Experimental Section

Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. All reactions requiring anhydrous conditions were conducted in oven-dried glassware under a dry nitrogen atmosphere. All solvents were distilled under nitrogen over appropriate drying reagents (sodium or calcium hydride). Solvents were removed under reduced pressure with a rotary evaporator. Residues were chromatographed on a silica gel column (230−400 mesh) using a gradient solvent system (hexane/ethyl acetate or hexane/dichloromethane) as the eluant.

^{1}H and ^{13}C NMR spectra were measured on a 500 or 200 MHz NMR spectrometer. Chemical shifts (δ) for ^{1}H and ^{13}C were referenced to internal solvent resonances and reported relative to $SiMe_4$.

1,6,11-Tris[(4-methylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-triyne, **1aaa**, 6,11-bis[(4-methylphenyl)sulfonyl]-1-ferrocenylsulfonyl-1,6,11-triazacyclopentadeca-3,8,13-triyne, **1aab**, 1,6,11-tris[(4-methylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-triynepalladium(0), **2aaa**, and 2,5,8-tris[(4-methylphenyl)sulfonyl]-2,5,8-triazatrindane, **3aaa**, were prepared as previously reported by us.[3]

1,6,11-Tris(ferrocenylsulfonyl)-1,6,11-triazacyclopentadeca-3,8,13-triyne (1bbb): 1bbb was prepared according to the method previously reported by us.[3] Orange solid (57% yield); mp 203−205 °C dec; IR (ATR) 2922, 1346, 1135 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.78 (s, 12H), 4.35−4.45 (br abs, 21H), 4.56 (br abs, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 38.3, 70.0, 71.2, 71.5, 79.7, 85.5; ESI-MS (*m/z*) 946 $[M + H]^+$. Anal. Calcd for $C_{42}H_{39}Fe_3N_3O_6S_3$ (945.51): C, 53.35; H, 4.16; N, 4.44. Found: C, 53.06; H, 4.18; N, 4.32.

1,6,11-Tris[(2,4,6-triisopropylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-triyne (1ccc): 1ccc was prepared according to the method previously reported by us.[3] Colorless solid (88% yield); mp 197−199 °C dec; IR (ATR) 2958, 1316, 1149 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.10−1.30 (m, 54H), 2.89 (sept, J = 7 Hz, 3H), 4.05 (br abs, 18H), 7.15 (br s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 24.2, 25.4, 30.0, 34.9, 37.1, 80.0, 124.7, 130.4, 152.5, 154.4; ESI-MS (*m/z*) 1000 $[M + H]^+$, 1017 $[M + NH_4]^+$. Anal. Calcd for $C_{57}H_{81}N_3O_6S_3$·EtOAc (1088.57): C, 67.30; H, 8.24; N, 3.86. Found: C, 67.59; H, 8.32; N, 4.23.

***N,N′*-Bis(*tert*-butyloxycarbonyl)-*N*-ferrocenylsulfonyl-*N′*-(4-methylphenyl)sulfonyl-2-butyn-1,4-diamine (8ab):** A stirred mixture of *N*-(4-bromo-2-butynyl)-*N*-(*tert*-butyloxycarbonyl)(4-methylphenyl)sulfonamide (**7a**,[3] 1.07 g, 2.66 mmol), *N*-(*tert*-butyloxycarbonyl)ferrocenylsulfonamide (**6b**,[5] 0.97 g, 2.65 mmol), anhydrous potassium carbonate (1.87 g, 13.53 mmol), and acetonitrile (70 mL) was refluxed for 21 h (TLC monitoring). The salts were filtered off and the filtrate was evaporated. The oily residue was purified by column chromatography on silica gel with hexane/ethyl acetate (10:1) to afford **8ab** (1.37 g, 76%) as an orange solid; mp 79−81 °C; IR (ATR) 2981, 1726, 1355, 1134 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.31 (s, 9H), 1.39 (s, 9H), 2.44 (s, 3H), 4.35 (s, 5H), 4.41 (t, J = 2 Hz, 2H), 4.54 (br abs, 2H), 4.63 (br abs, 2H), 4.89 (t, J = 2 Hz, 2H), 7.37 (AA′ part of the AA′BB′ system, J = 8.2 Hz, 2H), 7.95 (BB′ part of the AA′BB′ system, J = 8.2 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 22.3, 28.5, 28.7, 36.4, 36.7, 71.2, 71.5, 71.6, 79.2, 80.1, 85.1, 85.5, 87.3, 128.9, 130.1, 137.3, 144.9, 150.9, 151.3; ESI-MS (*m/z*) 686 $[M]^+$, 704 $[M + NH_4]^+$, 709 $[M + Na]^+$. Anal. Calcd for $C_{31}H_{38}FeN_2O_8S_2$ (686.62): C, 54.23; H, 5.58; N, 4.08. Found: C, 54.19; H, 5.71; N, 3.90.

***N*-Ferrocenylsulfonyl-*N′*-(4-methylphenyl)sulfonyl-2-butyn-1,4-diamine (9ab):** A mixture of **8ab** (2.61 g, 3.80 mmol), trifluoroacetic acid (14 mL), and dichloromethane (14 mL) was stirred at room temperature for 8 h (TLC monitoring). The liquid was distilled off under vacuum and the residue was dissolved in ethyl acetate (25 mL). The organic layer was subsequently washed with aqueous sodium bicarbonate (3 × 25 mL), H_2O (3 × 15 mL), and brine (20 mL), dried (Na_2SO_4), and filtered. The solvent was evaporated and the oily residue was purified by column chromatography on silica gel with hexane/ethyl acetate (polarity from 6:4 to 3:7) to afford **9ab** as an orange solid (1.35 g, 73%); mp 104−106 °C; IR (ATR) 3273, 1313, 1134 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.45 (s, 3H), 3.56 (dt, J = 6.1 and 2.0 Hz, 2H), 3.63 (dt, J = 6.1 and 2.0 Hz, 2H), 4.10 (t, J = 6.1 Hz, 1H), 4.39 (s, 5H), 4.41 (m, 2H), 4.45 (br abs, 1H), 4.63 (t, J = 2 Hz, 2H), 7.32 (AA′ part of the AA′BB′ system, J = 8.0 Hz, 2H), 7.72 (BB′ part of the AA′BB′ system, J = 8.0 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 22.2, 33.5, 33.6, 69.7, 71.2, 71.5, 79.7, 80.3, 87.6, 128.1, 130.3, 137.3, 144.6; ESI-MS (*m/z*) 487 $[M + H]^+$. Anal. Calcd for $C_{21}H_{22}FeN_2O_4S_2$ (486.39): C, 51.86; H, 4.56; N, 5.76. Found: C, 52.01; H, 4.75; N, 5.71.

1,14-Bis(methanesulfonyloxy)-*N*-ferrocenylsulfonyl-*N′*-(4-methylphenyl)sulfonyl-5,10-diazatetradeca-2,7,12-triyne (10ab): A mixture of **9ab** (1.26 g, 2.60 mmol), 1,4-bis(methanesulfonyloxy)-2-butyne[14] (3.79 g, 15.64 mmol), anhydrous potassium carbonate (2.57 g, 18.59 mmol), and acetonitrile (80 mL) was stirred at room temperature for 3 h (TLC monitoring). The salts were filtered off and the filtrate was evaporated. The oily residue was purified by column chromatography on silica gel with hexane/ethyl acetate/dichloromethane (polarity from 8:2:1 to 6:4:2) to afford **10ab** (1.35 g, 67%) as an orange solid; mp 63−65 °C; IR (ATR) 2938, 1345, 1160, 1139 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.45 (s, 3H), 3.05 (s, 6H), 3.89 (br abs, 2H), 3.96 (br abs, 2H), 4.01 (br abs, 2H), 4.10 (br abs, 2H), 4.40 (s, 5H), 4.43 (t, J = 1.8 Hz, 2H), 4.60 (t, J = 1.8 Hz, 2H), 4.66 (t, J = 1.6 Hz, 2H), 4.68 (t,

(14) Alcaide, B.; Almendros, P.; Rodríguez-Acebes, R. *J. Org. Chem.* **2002**, *67*, 1925−1928.

J = 1.6 Hz, 2H), 7.33 (AA′ part of the AA′BB′ system, J = 8.2 Hz, 2H), 7.67 (BB′ part of the AA′BB′ system, J = 8.2 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 22.2, 37.1, 37.2, 37.3, 37.4, 39.3, 39.4, 57.6, 57.8, 69.9, 71.6, 78.6, 78.7, 79.2, 79.4, 83.1, 83.3, 85.3, 128.4, 130.4, 135.7, 145.1; ESI-MS (*m/z*) 779 $[M + H]^+$, 796 $[M + NH_4]^+$. Anal. Calcd for $C_{31}H_{34}FeN_2O_{10}S_4$ (778.71): C, 47.8; H, 4.40; N, 3.60. Found: C, 48.08; H, 4.51; N, 3.60.

1-Ferrocenylsulfonyl-11-[(4-methylphenyl)sulfonyl]-6-[(4-vinylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-triyne (1abd): A stirred mixture of **10ab** (0.08 g, 0.10 mmol), 4-vinylbenzenesulfonamide (**11**,[15] 0.02 g, 0.10 mmol), anhydrous potassium carbonate (0.09 g, 0.63 mmol), and acetonitrile (20 mL) was refluxed for 7 h (TLC monitoring). The salts were filtered off and the filtrate was evaporated. The oily residue was purified by column chromatography on silica gel with hexane/ethyl acetate (1:1) to afford **1abd** (0.05 g, 66%) as an orange solid; mp 112−114 °C; IR (ATR) 2923, 1345, 1327, 1160 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.44 (s, 3H), 3.72 (br abs, 4H), 3.83−3.94 (m, 8H), 4.39 (br abs, 5H + 2H), 4.55 (br abs, 2H), 5.47 (d, J = 10.8 Hz, 1H), 5.90 (d, J = 17.6 Hz, 1H), 6.76 (dd, J = 17.6 and 10 Hz, 1H), 7.28 (AA′ part of a AA′BB′ system, J = 8.2 Hz, 2H), 7.49 (AA′ part of a AA′BB′ system, J = 8.2 Hz, 2H), 7.63 (BB′ part of a AA′BB′ system, J = 8.2 Hz, 2H), 7.70 (BB′ part of the AA′BB′ system, J = 8.2 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 22.3, 38.1, 38.2, 38.4, 38.5, 38.6, 38.7, 69.9, 71.3, 71.6, 79.3, 79.4, 79.5, 79.6, 79.7, 79.8, 85.3, 118.6, 127.2, 128.5, 128.8, 130.2, 135.8, 137.8, 142.9, 144.8; ESI-MS (*m/z*) 769 $[M]^+$, 792 $[M + Na]^+$, 808 $[M + K]^+$. Anal. Calcd for $C_{37}H_{35}FeN_3O_6S_3$ (769.73): C, 57.73; H, 4.58; N, 5.46. Found: C, 57.41; H, 4.97; N, 5.07.

6,11-Bis[(4-methylphenyl)sulfonyl]-1-ferrocenylsulfonyl-1,6,11-triazacyclopentadeca-3,8,13-triynepalladium-(0) (2aab): 2aab was prepared according to the method previously reported by us.[3] Starting from 6,11-bis[(4-methylphenyl)sulfonyl]-1-ferrocenylsulfonyl-1,6,11-triazaciclopentadeca-3,8,13-triyne (**1aab**,[3] 0.05 g, 0.06 mmol), **2aab** was obtained as an orange solid (0.021 g, 37% yield); mp 135−137 °C dec; IR (ATR) 2924, 1338, 1157 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.29 (s, 6H), 4.10−4.28 (m, 12H + 2H), 4.33 (s, 5H), 4.38 (t, J = 2 Hz, 2H), 7.09 (AA′ part of the AA′BB′ system, J = 8 Hz, 4H), 7.48 (BB′ part of the AA′BB′ system, J = 8 Hz, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 22.1, 37.4, 37.5, 37.6, 69.9, 71.1, 71.3, 74.9, 75.2, 75.4, 85.8, 128.5, 129.9, 135.8, 144.4; ESI-MS (*m/z*) 863 $[M]^+$. Anal. Calcd for $C_{36}H_{35}FeN_3O_6PdS_3 \cdot EtOAc$ (952.23): C, 50.45; H, 4.55; N, 4.41; S, 10.10. Found: C, 50.69; H, 4.69; N, 4.48; S, 9.80.

1,6,11-Tris(ferrocenylsulfonyl)-1,6,11-triazacyclopentadeca-3,8,13-triynepalladium(0) (2bbb): 2bbb was prepared according to the method previously reported by us.[3] Starting from **1bbb** (0.10 g, 0.11 mmol), **2bbb** was obtained as an orange solid (0.049 g, 44% yield); mp 152−154 °C dec; IR (ATR) 2922, 1343, 1134 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.14 (br abs, 18H), 4.32 (br s, 15H), 4.35 (t, J = 1.8 Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 37.5, 69.9, 71.1, 71.3, 75.4, 85.9; ESI-MS (*m/z*) 1051 $[M]^+$. Anal. Calcd for $C_{42}H_{39}Fe_3N_3O_6PdS_3 \cdot 1.5CH_2Cl_2$ (1094.38): C, 44.30; H, 3.59; N, 3.56; S, 8.15. Found: C, 44.66; H, 3.37; N, 3.62; S, 8.00.

1-Ferrocenylsulfonyl-11-[(4-methylphenyl)sulfonyl]-6-[(4-vinylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-triynepalladium(0) (2abd): 2abd was prepared according to the method previously reported by us.[3] Starting from **1abd** (0.051 g, 0.06 mmol), **2abd** was obtained as an orange solid (0.024 g, 41% yield); mp 149−151 °C dec; IR (ATR) 2922, 1341, 1158, 1137 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.29 (s, 3H), 4.05−4.11 (m, 4H), 4.17 (t, J = 1.7 Hz, 2H), 4.21−4.25 (m, 4H), 4.27−4.34 (m, 4H), 4.33 (s, 5H), 4.38 (t, J = 1.7 Hz, 2H), 5.32 (d, J = 11 Hz, 1H), 5.72 (d, J = 18 Hz, 1H), 6.58 (dd, J = 18 and 11 Hz, 1H), 7.11 (AA′ part of a AA′BB′ system, J = 8 Hz, 2H), 7.23 (AA′ part of a AA′BB′ system, J = 8.6 Hz, 2H), 7.49 (BB′ part of two AA′BB′ systems, J = 8.2 Hz, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 22.1, 37.3, 37.4, 37.5, 37.6, 37.7, 37.8, 69.9, 71.1, 71.3, 74.6, 74.7, 74.9, 75.1, 75.6, 75.7, 85.9, 117.9, 126.8, 128.4, 128.9, 129.9, 135.9, 136.0, 137.5, 142.5, 144.4; ESI-MS (*m/z*) 898 $[M + Na]^+$; HRMS calcd for ($C_{37}H_{35}FeN_3O_6PdS_3$ + Na) 897.9964, found 897.9962.

Cycloisomerization of Compounds 1 Mediated by Transition Metals. Synthesis of 2,5,8-Tris[(2,4,6-triisopropylphenyl)sulfonyl]-2,5,8-triazatrindane (3ccc). General Methods. Method A (with $Pd(PPh_3)_4$): A degassed solution of macrocycle **1ccc** (0.05 g, 0.05 mmol) and tetrakis-(triphenylphosphane)palladium(0) (0.067 g, 0.06 mmol) in anhydrous toluene (20 mL) was refluxed for 24 h (TLC monitoring). The solvent was then evaporated and the residue was purified by column chromatography on silica gel with dichloromethane/hexane (polarity from 9:1 to 20:1) to afford **3ccc** (0.043 g, 54%) as a colorless solid; mp 235−237 °C dec; IR (ATR) 2957, 2866, 1301, 1151, 1046 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.20−1.29 (m, 54H), 2.92 (sept, J = 6.8 Hz, 3H), 4.21 (sept, J = 6.6 Hz, 6H), 4.48 (s, 12H), 7.19 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 24.2, 25.5, 30.1, 34.8, 51.6, 124.7, 131.4, 131.7, 152.1, 154.2; ESI-MS (*m/z*) 1017 $[M + NH_4]^+$, 1022 $[M + Na]^+$. Anal. Calcd for $C_{57}H_{81}N_3O_6S_3$ (1000.47): C, 68.43; H, 8.16; N, 4.20. Found: C, 68.18; H, 8.51; N, 4.06.

Method B (with $CpCo(CO)_2$): A degassed solution of macrocycle **1ccc** (0.05 g, 0.05 mmol) and anhydrous *n*-decane (10 mL) was heated at 140 °C for 20 min. Then, cyclopentadienylcobalt dicarbonyl (0.012 mL, 0.05 mmol) was added and the mixture was heated at 140 °C for 1 h (TLC monitoring). After the reaction mixture was cooled to room temperature, a solid precipitated and was filtered off. The precipitate was purified by column chromatography on silica gel with hexane/dichloromethane (1:10) to afford **3ccc** (0.044 g, 88%) as a colorless solid.

Method C (with $Cl_2(PCy_3)_2Ru{=}CHPh$): A degassed solution of macrocycle **1ccc** (0.05 g, 0.05 mmol) and Grubbs' catalyst (0.0028 g, 0.002 mmol, 7% molar) in anhydrous toluene (10 mL) was refluxed for 22 h (TLC monitoring). The solvent was then evaporated and the residue was isolated by column chromatography on silica gel with dichloromethane/hexane (polarity from 9:1 to 10:1) and purified by digestion from *n*-hexane to afford **3ccc** (0.018 g, 36%) as a colorless solid.

Method D (with $RhCl(CO)(PPh_3)_2$): A degassed solution of macrocycle **1ccc** (0.05 g, 0.05 mmol) and chlorocarbonylbis-(triphenylphosphane)rhodium(I) (0.0017 g, 0.0025 mmol, 5% molar) in anhydrous toluene (10 mL) was heated at 65 °C for 18 h (TLC monitoring). The solvent was then evaporated and the residue was chromatographed through silica gel with dichloromethane/hexane (polarity from 9:1 to 10:1) to afford **3ccc** (0.048 g, 96%) as a colorless solid.

5,8-Bis[(4-methylphenyl)sulfonyl]-2-ferrocenylsulfonyl-2,5,8-triazatrindane (3aab): mp 240−242 °C dec; IR (ATR) 2856, 1344, 1161, 1142 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.39 (s, 6H), 4.30 (br abs, 4H), 4.32−4.44 (m, 8H + 2H), 4.42 (s, 5H), 4.63 (t, J = 1.8 Hz, 2H), 7.31 (AA′ part of the AA′BB′ system, J = 8.2 Hz, 4H), 7.72 (BB′ part of the AA′BB′ system, J = 8.2 Hz, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 22.2, 52.6, 52.7, 69.6, 71.6, 71.7, 83.6, 128.2, 130.7, 131.3, 131.4, 131.7, 134.1, 144.7; ESI-MS (*m/z*) 757 $[M]^+$. Anal. Calcd for $C_{36}H_{35}FeN_3O_6S_3$ (757.72): C, 57.06; H, 4.66; N, 5.55. Found: C, 56.81; H, 5.01; N, 5.22.

2,5,8-Tris(ferrocenylsulfonyl)-2,5,8-triazatrindane (3bbb): mp 123−125 °C dec; IR (ATR) 2859, 1341, 1188, 1137 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6) δ 4.31 (s, 12H), 4.38 (s, 15H), 4.41 (br abs, 6H), 4.68 (br abs, 6H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 51.6, 68.6, 69.5, 70.0, 82.9, 130.8; ESI-MS (*m/z*) 945 $[M]^+$, 946 $[M + H]^+$, 968 $[M + Na]^+$. Anal. Calcd for $C_{42}H_{39}Fe_3N_3O_6S_3$ (945.51): C, 53.35; H, 4.16; N, 4.44. Found: C, 53.16; H, 4.26; N, 4.30.

2-Ferrocenylsulfonyl-8-[(4-methylphenyl)sulfonyl]-5-[(4-vinylphenyl)sulfonyl]-2,5,8-triazatrindane (3abd): mp 170−172 °C dec; IR (ATR) 2854, 1343, 1161, 1142, 1096 cm^{-1};

(15) Cortés, J.; Moreno-Mañas, M.; Pleixats, R. *Eur. J. Org. Chem.* **2000**, 239−243.

^{1}H NMR (200 MHz, $CDCl_3$) δ 2.39 (s, 3H), 4.25−4.45 (m, 14H), 4.42 (s, 5H), 4.63 (br abs, 2H), 5.42 (d, J = 10.9 Hz, 1H), 5.85 (d, J = 17.6 Hz, 1H), 6.71 (dd, J = 17.6 and 10.9 Hz, 1H), 7.30 (AA′ part of a AA′BB′ system, J = 8 Hz, 2H), 7.51 (AA′ part of a AA′BB′ system, J = 8.3 Hz, 2H), 7.71 (BB′ part of a AA′BB′ system, J = 8 Hz, 2H), 7.78 (BB′ part of a AA′BB′ system, J = 8.3 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 22.2, 52.6, 52.7, 69.6, 71.6, 71.7, 83.6, 118.4, 127.6, 128.2, 128.6, 130.7, 131.3, 131.4, 131.5, 131.7, 131.8, 134.2, 135.8, 135.9, 143.0, 144.7; ESI-MS (*m/z*) 769 $[M]^+$. Anal. Calcd for $C_{37}H_{35}FeN_3O_6S_3$ (769.73): C, 57.73; H, 4.58; N, 5.46. Found: C, 57.33; H, 4.78; N, 5.12.

***(E)*-1,6,11-Tris[(2,4,6-triisopropylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3-ene-8,13-diyne (4ccc). General Method:** A stirred mixture of **12ccc**[3] (0.40 g, 0.42 mmol), potassium carbonate (0.30 g, 2.10 mmol), and acetonitrile (40 mL) was refluxed for 10 min. Then, a solution of (*E*)-1,4-dibromo-2-butene (0.11 g, 0.49 mmol) in acetonitrile (20 mL) was added to the reaction mixture. The reaction was heated and monitored by TLC until completation (4 h). The salts were filtered off and the filtrate was evaporated. The residue was purified by column chromatography on silica gel with hexane/ethyl acetate (10:1) to afford **4ccc** (0.32 g, 75%) as a colorless solid; mp 218−220 °C dec; IR (ATR) 2959, 2929, 1461, 1363, 1317, 1150 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.20−1.30 (m, 54H), 2.90−2.96 (m, 3H), 3.89 (br abs, 4H), 4.01 (s, 4H), 4.04 (s, 4H), 4.05−4.13 (m, 6H), 6.01 (br abs, 2H), 7.18 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 24.2, 25.5, 29.9, 30.0, 34.9, 36.8, 37.7, 49.3, 79.9, 80.7, 124.7, 124.8, 130.4, 130.8, 130.9, 152.4, 152.6, 154.1, 154.4; ESI-MS (*m/z*) 1002 $[M + H]^+$. Anal. Calcd for $C_{57}H_{83}N_3O_6S_3{\cdot}Et_2O$ (1076.61): C, 68.05; H, 8.71; N, 3.90; S, 8.94. Found: C, 67.71; H, 9.03; N, 4.18; S, 9.00.

***(E)*-1,6,11-Tris[(4-methylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3-ene-8,13-diyne (4aaa):** mp 210−212 °C; IR (ATR) 3065, 2917, 1336, 1156 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.40 (s, 3H), 2.45 (s, 6H), 3.61 (br abs, 4H), 3.81 (s, 4H), 3.94 (s, 4H), 5.34−5.45 (m, 2H), 7.27 (AA′ part of a AA′BB′ system, J = 8.5 Hz, 2H), 7.33 (AA′ part of a AA′BB′ system, J = 8.2 Hz, 4H), 7.60 (BB′ part of a AA′BB′ system, J = 8.5 Hz, 2H), 7.67 (BB′ part of a AA′BB′ system, J = 8.2 Hz, 4H); ^{13}C NMR (50 MHz, DMSO-d_6) δ 20.9, 21.0, 36.8, 37.7, 49.3, 79.0, 79.2, 127.2, 127.5, 128.8, 129.7, 135.1, 136.1, 143.7; ESI-MS (*m/z*) 666 $[M + H]^+$, 683 $[M + NH_4]^+$. Anal. Calcd for $C_{33}H_{35}N_3O_6S_3$ (665.85): C, 59.53; H, 5.30; N, 6.31; S, 14.45. Found: C, 59.26; H, 5.34; N, 6.22; S, 14.08.

***(Z)*-1,6,11-Tris[(4-methylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3-ene-8,13-diyne (5aaa):** mp 194−196 °C dec; IR (ATR) 3029, 2928, 1332, 1155 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.40 (s, 3H), 2.44 (s, 6H), 3.58 (d, J = 4.6 Hz, 4H), 3.77 (s, 4H), 3.89 (s, 4H), 5.46 (t, J = 4.6 Hz, 2H), 7.16 (AA′ part of a AA′BB′ system, J = 8.3 Hz, 2H), 7.32 (AA′ part of a AA′BB′ system, J = 8.2 Hz, 4H), 7.43 (BB′ part of a AA′BB′ system, J = 8.3 Hz, 2H), 7.70 (BB′ part of a AA′BB′ system, J = 8.2 Hz, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 22.2, 36.6, 38.7, 43.1, 79.3, 80.0, 128.3, 128.4, 130.2, 130.3, 136.7, 144.8; ESI-MS (*m/z*) 666 $[M + H]^+$, 683 $[M + NH_4]^+$; HRMS calcd for ($C_{33}H_{35}N_3O_6S_3$ + Na) 688.1580, found 688.1563.

***(Z)*-1,6,11-Tris[(2,4,6-triisopropylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3-ene-8,13-diyne (5ccc):** mp 246−248 °C dec; IR (ATR) 2959, 1318, 1151 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.19−1.30 (m, 54H), 2.92 (sept, J = 7.0 Hz, 3H), 3.93 (s, 4H), 4.00−4.15 (m, 6H), 4.03 (s, 4H), 4.07 (s, 4H), 5.68 (t, J = 4.37 Hz, 2H), 7.18 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 24.3, 25.5, 25.6, 30.1, 35.0, 35.9, 37.5, 42.3, 80.2, 80.5, 124.8, 130.4, 130.8, 152.5, 152.6, 154.4, 154.5; ESI-MS (*m/z*) 1002 $[M + H]^+$, 1019 $[M + NH_4]^+$; HRMS calcd for ($C_{57}H_{83}N_3O_6S_3$ + Na) 1024.5336, found 1024.5308.

***trans*-2,5,8-Tris[(4-methylphenyl)sulfonyl]-3a,3b-dihydro-1*H*-2,5,8-triazatrindane (13aaa):** mp 144−146 °C dec; IR (ATR) 2925, 2851, 1342, 1160, 1092 cm^{-1}; ^{1}H NMR (200 MHz, CD_2Cl_2) δ 2.36 (s, 3H), 2.41 (s, 6H), 2.50−2.60 (m, 4H), 3.50 (d, J = 14.9 Hz, 2H), 3.75 (br abs, 6H), 3.95 (d, J = 14.9 Hz, 2H), 7.24 (AA′ part of a AA′BB′ system, J = 8 Hz, 2H), 7.34 (AA′ part of a AA′BB′ system, J = 8.2 Hz, 4H), 7.55−7.70 (m, 6H); ^{13}C NMR (50 MHz, DMSO-d_6) δ 20.7, 20.9, 42.9, 48.5, 49.4, 53.4, 125.5, 126.8, 127.7, 129.4, 129.9, 132.3, 143.5, 143.7; ESI-MS (*m/z*) 666 $[M + H]^+$, 683 $[M + NH_4]^+$, 688 $[M + Na]^+$, 704 $[M + K]^+$. Anal. Calcd for $C_{33}H_{35}N_3O_6S_3{\cdot}$EtOAc (753.95): C, 58.94; H, 5.75; N, 5.57. Found: C, 58.58; H, 5.41; N, 5.99.

***trans*-2,5,8-Tris[(2,4,6-triisopropylphenyl)sulfonyl]-3a,3b-dihydro-1*H*-2,5,8-triazatrindane (13ccc):** mp 151−153 °C dec; IR (ATR) 2956, 2867, 1305, 1151, 1045 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 1.15−1.30 (m, 54H), 2.85 (br abs, 2H), 2.92 (sept, J = 7.0 Hz, 3H), 3.02 (br abs, 2H), 3.67 (br abs, 2H), 3.92 (s, 8H), 4.15 (sept, J = 6.9 Hz, 6H), 7.19 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) 23.5, 24.8, 29.4, 34.1, 44.2, 47.2, 47.9, 52.2, 123.9, 126.8, 127.8, 130.5, 151.4, 153.5; ESI-MS (*m/z*) 1002 $[M + H]^+$, 1024 $[M + Na]^+$. Anal. Calcd for $C_{57}H_{83}N_3O_6S_3{\cdot}$EtOAc (1090.59): C, 67.18; H, 8.41; N, 3.85; S, 8.82. Found: C, 67.26; H, 8.22; N, 4.04; S, 8.54.

***cis*-2,5,8-Tris[(4-methylphenyl)sulfonyl]-3a,3b-dihydro-1*H*-2,5,8-triazatrindane (14aaa):** mp 152−154 °C dec; IR (ATR) 2923, 2853, 1339, 1305, 1157, 1091 cm^{-1}; ^{1}H NMR (200 MHz, CD_2Cl_2) δ 2.30−2.33 (m, 2H), 2.32 (s, 3H), 2.42 (s, 6H), 2.84 (br abs, 2H), 3.40−4.00 (m, 10H), 7.05 (AA′ part of a AA′BB′ system, J = 8.2 Hz, 2H), 7.35 (AA′ part of a AA′BB′ system, J = 8.2 Hz, 4H), 7.52 (BB′ part of a AA′BB′ system, J = 8.2 Hz, 2H), 7.65 (BB′ part of a AA′BB′ system, J = 8.2 Hz, 4H); ^{13}C NMR (50 MHz, CD_2Cl_2) 22.0, 37.8, 48.6, 48.9, 50.9, 124.9, 126.1, 128.1, 128.2, 130.5, 130.7, 133.5, 134.5, 144.9; ESI-MS (*m/z*) 666 $[M + H]^+$, 688 $[M + Na]^+$; HRMS calcd for ($C_{33}H_{35}N_3O_6S_3$ + Na) 688.1580, found 688.1603.

***cis*-2,5,8-Tris[(2,4,6-triisopropylphenyl)sulfonyl]-3a,3b-dihydro-1*H*-2,5,8-triazatrindane (14ccc):** mp 146−148 °C dec; IR (ATR) 2957, 2869, 1313, 1151, 1046 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.10−1.40 (m, 54H), 2.77 (br abs, 2H), 2.90−3.00 (m, 3H), 3.22 (br abs, 2H), 3.45 (br abs, 2H), 3.81 (d, J = 13.3 Hz, 2H), 3.88 (d, J = 13.3 Hz, 2H), 3.91 (d, J = 13.3 Hz, 2H), 3.99 (d, J = 13.3 Hz, 2H), 4.00−4.30 (m, 6H), 7.19 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.5, 24.8, 29.3, 29.4, 34.2, 38.0, 46.4, 47.3, 48.5, 123.9, 124.6, 125.9, 130.3, 130.7, 151.3, 151.4, 153.4, 153.6; ESI-MS (*m/z*) 1002 $[M + H]^+$. Anal. Calcd for $C_{57}H_{83}N_3O_6S_3{\cdot}$EtOAc (1090.59): C, 67.18; H, 8.41; N, 3.85; S, 8.82. Found: C, 66.97; H, 8.38; N, 4.07; S, 8.76.

Crystal Structure Determination. Yellow crystal needles of **3abd**·1.5CH_2Cl_2 were obtained by slow diffusion of *n*-hexane into a dichloromethane/ethyl acetate solution of the complex. Crystal structure determination for **3abd**·1.5CH_2Cl_2 was 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 measurement was made in the range of 1.65 to 31.52 in theta. Full sphere data were collected with ω and φ scans. Data collection was done with the Smart V. 5.060 (BrukerAXS 1999) program, data reduction with the Saint + Version 6.02 (Bruker AXS 1999) program, and absorption correction with the SADABS (Bruker AXS 1999) program. A crystal structure solution for **3abd**·1,5CH_2Cl_2 was achieved using direct methods such as those used in SHELXTL Version 5.10 (Sheldrick, Universtität Göttingen (Germany), 1998) and visualized using an 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 SHELXTL program (Version 5.10) (Sheldrick, Universtität Göttingen (Germany),1998). All non-hydrogen atoms were refined including anisotropic displacement parameters. A total of 1.5 molecules of dichloromethane could be found, highly disordered, and in different positions and occupation ratios.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of compounds **2abd**, **5aaa**, **5ccc**, and **14aaa** and details of the structure determination, including atomic coordinates, bond lengths and angles, thermal parameters, least-squares planes, and interatomic contacts of complexes **3abd**. This material is available free of charge via the Internet at http://pubs.acs.org. The supplementary crystallographic data for this paper (CCDC 262952) can also 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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