(not depicted) with Ru^{III} adduct [Ru(**4**)Cl_3] gave the anticipated Ru^{II} complex **9**, which exhibited nearly identical ^1H and ^{13}C NMR spectra to that of complex **3**. Thus, addition of the bromo building block **10** to the bis-Ru^{III} adduct **7** afforded the anticipated mixed monomer macrocycle **11** (Scheme 2). Evidence for its formation includes a symmetrically similar yet expectedly broadened ^1H NMR spectrum corresponding exactly to that of the hexamethyl analogue **8**; HETCOR experiments further support the structure. These experiments suggest the potential to access larger and more complex macrocycles as well as other architectures.

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$$A(r) = A(a)e^{\omega^2 M(1-\rho\nu)(r^2-a^2)/2RT} \quad (1)$$

frequency [rad s^{-1}], M the molar mass, ρ the solvent density, ν the solute partial specific volume, r the radius from the center of the rotor, a the radius at the meniscus, R the gas constant, and T the temperature in Kelvin. The absorbance profile of a multicomponent system has additional exponential growth terms. A Parr DMA58 precision densitometer was used to determine the partial specific volume.
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Synthesis of the First [3_4]Allenophane: 1,3,10,12,19,21,28,30-Octamethyl-[3.3.3.3]paracyclophan-1,2,10,11,19,20,28,29-octaene**

Stephan Thorand, Fritz Vögtle, and Norbert Krause*

Dedicated to Professor Armin de Meijere on the occasion of his 60th birthday

Allenes belong to the most interesting target molecules of organic chemistry because of their axial chirality and their high reactivity. Although numerous achiral and chiral allenes with different substitution patterns have been synthesized,[1] several types of allenes with unusual topologies and properties are still unknown. Among these are oligomeric cyclic arylallenes which represent a new class of cyclophanes[2]

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("allenophanes") and which should possess interesting properties as chiral ligands/hosts for metal ions and small guest molecules,[3, 4] also because they are axially and planar chiral when substituted suitably. Additionally, investigations of ring strain and circular dichroism[5] should provide information about the interaction between the π-electron systems of the aromatic rings and the allenic bridges. The few allenophanes reported until now are either ansa compounds, that is, cyclophanes with only one bridged arene ring,[6] or macrocycles with only one allene bridge.[7] We now report the first synthesis of a "true" allenophane bearing several aromatic rings and allenic bridges, that is, of the [3$_4$]allenophane 1,3,10,12,19,21,28,30-octamethyl[3.3.3.3]paracyclophan-1,2,10,-11,19,20,28,29-octaene (**1**). This hydrocarbon exists as four diastereomers with different topologies (Figure 1)[8] which should show an individual complexating ability.

Our synthesis starts with the aromatic building blocks 4-trimethylsilylethynylbenzaldehyde and -acetophenone (**3**), which were prepared in high yield by using a new variant of the Sonogashira-coupling procedure developed by us

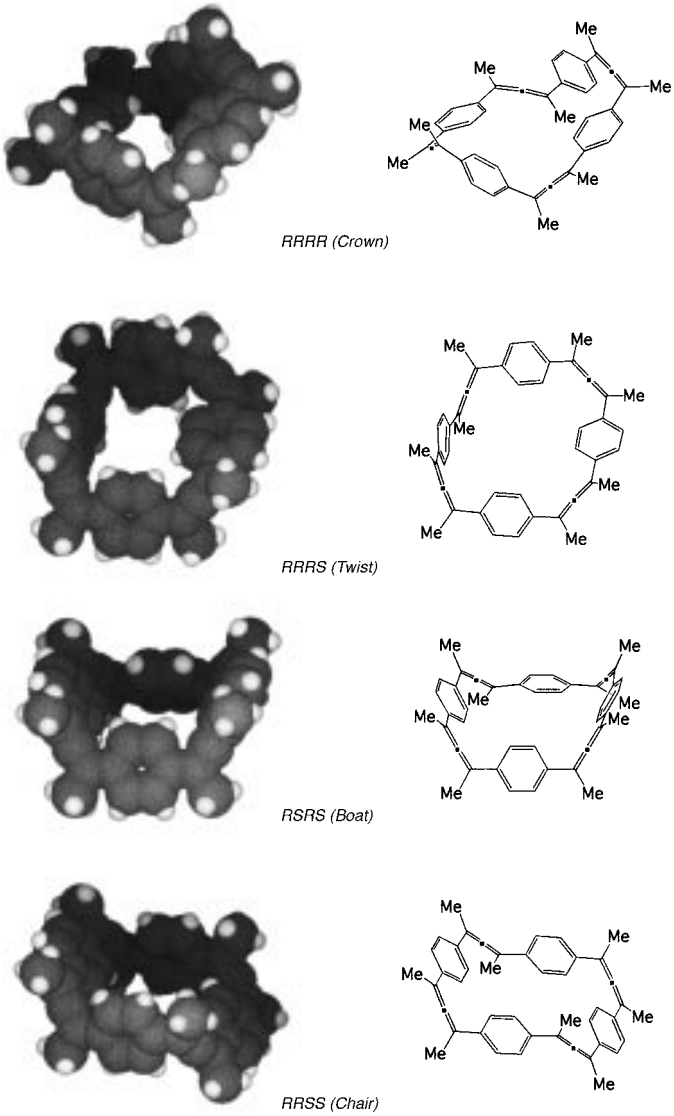

Figure 1. Diastereomers of allenophane **1**.

(Scheme 1).[9] The former compound was acetalized with 1,3-propanediol and desilylated to **2** with K_2CO_3/methanol. Attempts to add the lithium acetylide of **2** to **3** gave the desired product **4** only in about 45% yield; it seems that enolization of the ketone by the strongly basic acetylide prevails. This problem could be solved by transmetalation to the less basic titanium acetylide[10] which provided **4** in 89% yield. Acylation of **4** was followed by introduction of the first allene moiety, making use of an S_N2' substitution with methylmagnesium bromide in the presence of copper(I) iodide and lithium bromide.[11] Diarylallene **6** was obtained with 88% yield and deprotected chemoselectively to **7** or **8** with standard methods. Lithiation of **7** and addition to **8** then gave the propargylic alcohol **9**. The alcohol **9** was tranformed into the tertiary acetate **12** by oxidation with activated manganese dioxide, followed by addition of methyllithium and acylation. Another S_N2' substitution gave trisallene **13** with good yield (85%) which was then deprotected at both termini to provide **14** (Scheme 2).

In the key step of the synthesis, this had to be cyclized to the 28-membered macrocycle **15**. Among different procedures which were tested for this purpose, addition of **14** to a diluted solution of potassium hexamethyldisilazide in THF at $-80\,^{\circ}C$ gave the best results (see Experimental Section). The macrocycle **15** was thus obtained in 52% yield and transformed into the propargylic acetate **18** with the usual sequence of oxidation, addition of MeLi, and acylation; finally, the fourth allenic bridge was introduced by another S_N2' substitution with MeMgBr. Allenophane **1** was thus synthesized over 16 steps in 5.0% overall yield.

The synthesis of **1** presented here is not stereoselective; therefore, trisallene **13** was obtained as a mixture of four diastereomers, resulting in very complex NMR spectra of this compound and of the subsequent products **14**–**18**. In contrast, only one set of signals was observed for allenophane **1** in the ^1H ($\delta = 7.33$, 2.26) and ^{13}C NMR spectrum ($\delta = 207.0$, 134.8, 125.5, 102.5, 15.8); even addition of the shift reagents [Eu(fod)$_3$]/[Ag(fod)][12] did not result in a splitting of the resonances (fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione). Attempts to prove the existence of the four diastereomers shown in Figure 1 by HPLC failed due to the low solubility of the compound. We are currently working on the diastereo- and enantioselective synthesis of the isomers of **1**, making use of the high *anti*-stereoselectivity of the S_N2' substitution of derivatives of chiral propargylic alcohols.[1, 13] Additionally, we intend to study the use of the acyclic oligomeric arylallenes of the type **13**/**14** as precursors for helically chiral polymers which are of high current interest as model compounds for biologically relevant receptors and catalysts.[14] Also, macrocyclic hydrocarbons such as **1** may be useful as wheels for rotaxanes.

Experimental Section

Cyclization of **14**: Potassium hexamethyldisilazide (50 mg, 0.25 mmol) was dissolved in THF (40 mL), and the resulting solution was cooled to $-80\,^{\circ}C$. A solution of **14** (70 mg, 0.125 mmol) in THF (10 mL) was then added within 20 min. Stirring at $-80\,^{\circ}C$ was continued for 40 min; hydrolysis with saturated NH_4Cl solution was followed by extraction with diethyl ether (three times). The combined organic layers were washed once with brine

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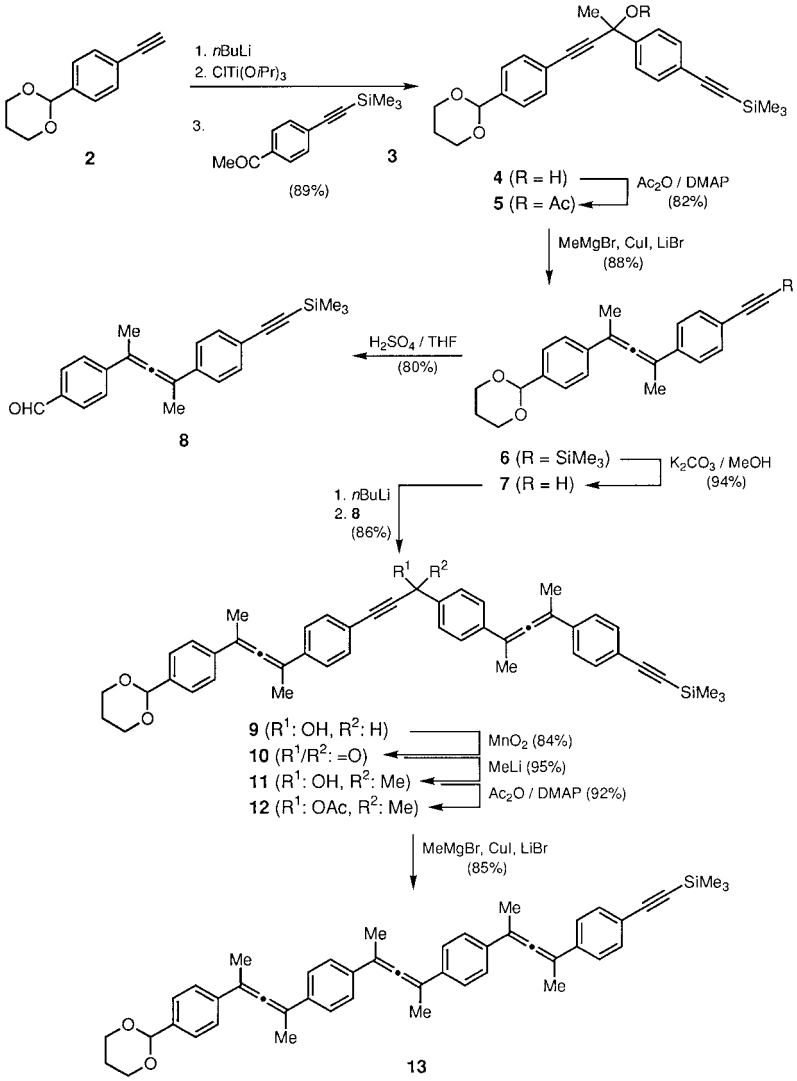
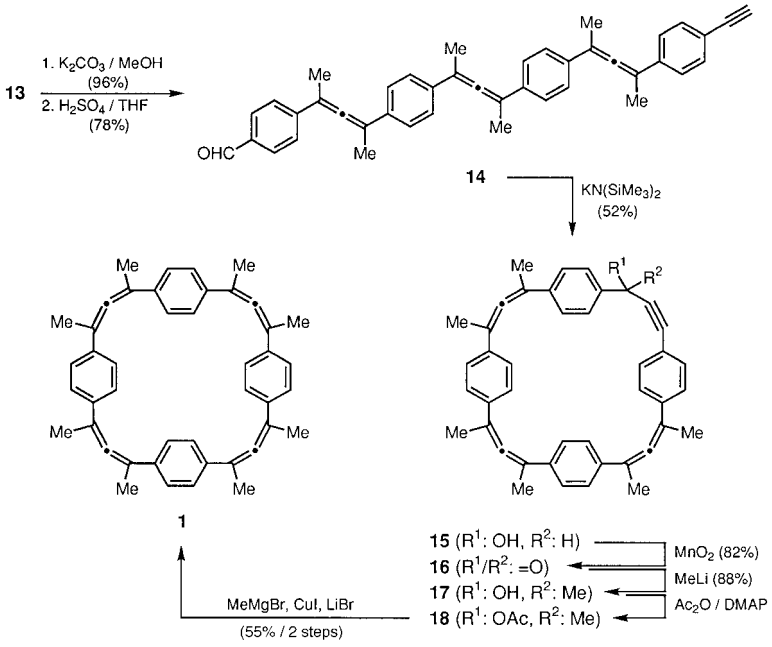


Scheme 1. Synthesis of the trisallene **13**. DMAP = 4-dimethylaminopyridine.



Scheme 2. Conclusion of the synthesis of **1**: Cyclization and final reactions on the macrocyclic framework.

and dried with $MgSO_4$; the solvent was distilled off in vacuo. Purification of the crude product by chromatography (SiO_2, toluene) gave **15** (36 mg, 52%) as a colorless solid.

Spectroscopic data of 1,3,10,12,19,21,28,30-octamethyl-[3.3.3.3]paracyclophan-1,2,10,11,19,20,28,29-octaene (**1**): ^{1}H NMR (500 MHz, CD_2Cl_2): $\delta = 7.33$ (s, 16H, Aryl-H), 2.26 (s, 24H, CH_3); ^{13}C NMR (125 MHz, CD_2Cl_2): $\delta = 207.0$ (×), 134.8 (×), 125.5 (+), 102.5 (×), 15.8 (+); IR (KBr): $\tilde{\nu} =$ 2982 – 2852, 1928, 1602, 1502, 833 cm^{-1}; MS (EI, 70 eV): *m*/*z* (%): 568 (100, $[M]^+$), 553 (50); high-resolution MS: calcd: 568.3129, found: 568.3123. ((×) and (+) denote the phases in the DEPT spectrum.)

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