The homogeneity of the hydrogenation was monitored by the addition of a tenfold excess of cyclohexene to the reaction mixture in several cases. Cyclohexene is not or only very slowly hydrogenated by homogeneous Pd species, but is readily hydrogenated by colloidal or heterogeneous Pd. As we did not observe the formation of any cyclohexane during the hydrogenation of the alkynes, it can be concluded that the Pd(bian)-catalyzed hydrogenation reaction is homogeneous.[15]

The mechanism of this selective hydrogenation of alkynes is as yet unclear. The complexes **I** should be considered precatalysts, and the actual catalyst is probably a [Pd(bian)(alkyne)] complex **II** (Scheme 1). The stability of **II** relative to the corresponding alkene complex **I** is probably important for the observed chemoselectivity of hydrogenation. For most or all alkynes a high ratio **II**/**I** would be expected. Hydrogenation could readily take place by addition of hydrogen to **II** and subsequent insertion/elimination or by a pairwise transfer of hydrogen atoms. The latter was substantiated in similar hydrogenations by means of the *para*-hydrogen-induced polarization in ^{1}H and ^{2}H NMR spectroscopy during hydrogenation.[16] Currently, we are trying to extend the scope and to elucidate the mechanism of the reaction.

Experimental Section

Typical procedure for the catalytic hydrogenation of alkynes: **Ia**[11b] (25 mg, 0.04 mmol) and the alkyne (4.0 mmol) were added to 50 mL of dry THF in a Schlenk tube under nitrogen atmosphere. The solution was then subjected to a hydrogen atmosphere of 1 bar by first flushing with hydrogen and then slowly blowing hydrogen over the surface while the solution was vigorously stirred at 20 °C. The reaction was monitored by GC (Varian 3300; DB-5 column) and stopped when all alkyne had been consumed (conversion 99.5 – 100 %). The composition of the reaction mixture was determined by GC and ^{1}H NMR spectroscopic analysis.

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Self- and Directed Assembly of Hexaruthenium Macrocycles**

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Elegant work in the area of self-assembly by Stang,[1] Lehn et al.,[2] and many others[3–7] has prompted our investigation of the potential to spontaneously construct Ru-based (macro)-molecules. More specifically, our goal involved the design and preparation of polyterpyridyl ligands that would form the basis of a "modular building block set"[8] capable of being used to access "higher order" (fractal) architectures. Herein we report the construction of a bis(terpyridyl) monomer that facilitates the preparation of hexaruthenium macrocycles.

Linear bis(terpyridyl) monomers have been employed for the formation of layered polyelectrolyte films,[9] Ru^{II}-based dendrimers,[10] helicating ligands,[11] grids,[12] racks,[13] and photoactive molecular-scale wires,[14] to mention but a few. Whereas progress in directed synthesis of cyclic rigid structures[15] can be found in "shape-persistent" phenylacetylenes,[16–18] diethynylbenzene macrocycles,[19] and a hexagon containing 24 phenylene units,[20] advances in self-assembly have yielded, for example, chiral[21] and achiral circular

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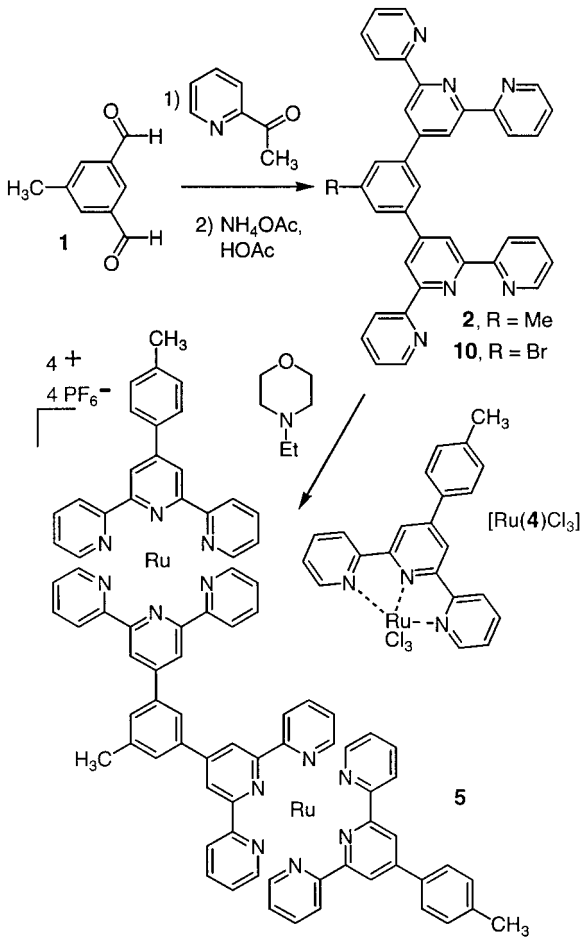
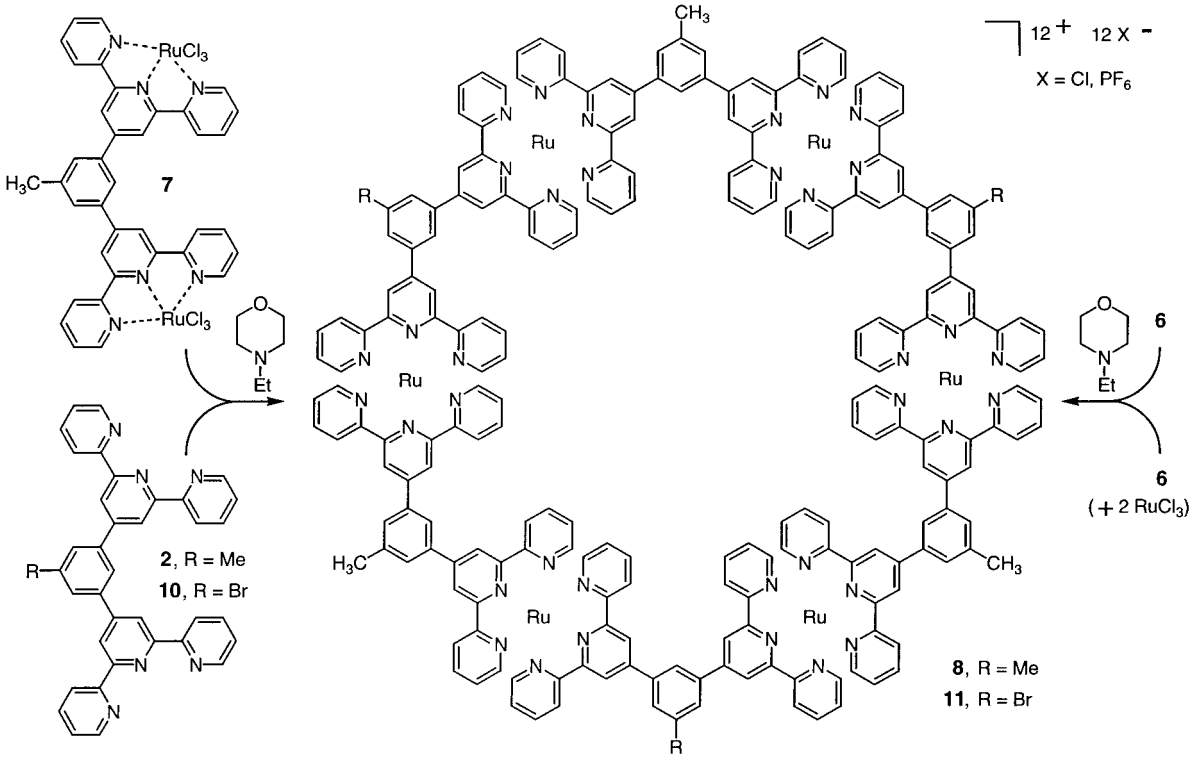
helicates,[22] cylindrical cage structures,[23] Pt-coordinated bipyridyl squares,[24] metal-templated [2]catenanes,[25, 26] and cyclic porphyrin trimers.[27]

Our strategy involved the preparation of a bis(terpyridyl) monomer possessing a 60° angle with respect to the two ligating moieties. This would facilitate the assembly of six building blocks with six connecting metals in the ubiquitous benzenoid architecture. The potential to synthesize such constructs, with little equilibration (metal–ligand exchange) under mild physicochemical conditions, is predicated on the unique strength of the terpyridine–Ru coordination.[28]

Synthesis of the requisite building block began with treatment of the known dialdehyde[29] **1** with excess 2-acetylpyridine[30] and base (1N NaOH followed by NH_4OAc and acetic acid to afford the desired angular bis(terpyridine) **2** (66% yield; Scheme 1). Confirmation of this structure included the diagnostic ^1H NMR signals at $\delta = 7.38$ (dd; 5,5″-H), 7.82 (s; 4,6-Ar), and 8.83 (s; 3′,5′-H). Reaction of hexagon precursor **2** with two equivalents of $RuCl_3 \cdot n H_2O$ produced the minimally soluble, paramagnetic bis-Ru^{III} adduct **7** (Scheme 2), which was treated without further purification with one equivalent of monomer **2** under reducing conditions (*N*-ethylmorpholine) to yield the self-assembled, diamagnetic, hexameric Ru^{II} complex **8** (40% yield; Table 1). The ^1H NMR spectrum (Figure 1b) of the purified material revealed a single aliphatic resonance at $\delta = 2.93$ (CH_3), which suggested the presence of only one type of monomeric unit, which is not the expected case for a linear oligomer. Other diagnostic spectral attributes (^1H NMR) included upfield and downfield shifts, repectively, of the 6,6″-H signals ($\delta = 7.62$; $\Delta\delta = -1.15$) and the 3′,5′-H signals ($\delta =$



Scheme 1. Synthesis of the key monomer **2** and the Ru^{II} complex **5** that aided in structural elucidation of the metallomacrocycles.



Scheme 2. Self- and directed-assembly of macrocycles **8** and **11**.

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Table 1. Selected data for compounds **2**, **3**, **5**, **6**, **8**, **10**, and **11**.

2: ^{1}H NMR ($CDCl_3$): $\delta = 2.59$ (s, 3H, CH_3), 7.38 (dd, $J = 6$ Hz, 4H, $H^{5,5''}$), 7.82 (s, 2H, $H^{4,6}_{Ar}$), 7.91 (dd, $J = 8$ Hz, 4H, $H^{4,4''}$), 8.22 (s, 1H, H^{2}_{Ar}), 8.71 (d, $J = 8$ Hz, 4H, $H^{3,3''}$), 8.77 (d, $J = 4$ Hz, 4H, $H^{6,6''}$), 8.83 (s, 4H, $H^{3',5'}$); ^{13}C NMR ($CDCl_3$): $\delta = 21.60$(CH_3), 119.24 ($C^{3'}$), 121.50 (C^{5}_{Ar}), 121.71 (C^{3}), 123.53 (C^{2}_{Ar}), 123.94 (C^{5}), 128.94 (C^{6}_{Ar}), 136.97 (C^{4}), 139.48 (C^{1}_{Ar}), 149.20 (C^{6}), 150.31 ($C^{4'}$), 155.97 (C^{2}), 156.20 ($C^{2'}$); ESI-MS: m/z: 555 [$M + H^+$]; m.p. 187–188 °C (decomp); elemental analysis calcd for $C_{37}H_{26}N_6$: C 80.14, H 4.69, N 15.16; found: C 79.34, H 4.84, N 18.9

3: ^{1}H NMR (CD_3CN): $\delta = 2.74$ (s, 3H, CH_3), 7.37 (dd, 2H, $H^{5,5''}$), 7.62 (d, 2H, $H^{6,6''}$), 7.78 (d, 2H, $H^{3,5}_{Ar}$), 8.14 (dd, 2H, $H^{4,4''}$), 8.31 (d, 2H, $H^{2,6}_{Ar}$), 8.83 (d, 2H, $H^{3,3''}$), 9.19 (s, 2H, $H^{3',5'}$); ^{13}C NMR (CD_3CN): $\delta = 21.91$ (CH_3), 122.83 ($C^{3'}$), 125.94 (C^{3}), 128.89 (C^{5}), 129.14 (C^{2}_{Ar}), 131.77 (C^{3}_{Ar}), 135.39 (C^{4}_{Ar}), 139.47 (C^{4}), 142.52 (C^{1}_{Ar}), 149.75 ($C^{4'}$), 153.91 (C^{6}), 156.88 (C^{2}), 159.74 ($C^{2'}$); MALDI-TOF-MS: m/z: 892 [$M - PF_6$], 747 [$M - 2PF_6$]

5: ^{1}H NMR (CD_3CN): $\delta = 2.68$ (s, 6H, CH_3 (**4**)), 2.96 (s, 3H, CH_3 (**2**)), 7.35 (dd, 8H, $H^{5,5''}$ (**4** + **2**)), 7.62 (m, 8H, $H^{6,6''}$ (**4** + **2**)), 7.74 (d, 4H, $H^{3,5}_{Ar}$ (**4**)), 8.12 (m, 8H, $H^{4,4''}$ (**4** + **2**)), 8.28 (d, 4H, $H^{2,6}$ (**4**)), 8.49 (s, 2H, $H^{4,6}_{Ar}$ (**2**)), 8.82 (d, 4H, $H^{3,3''}$ (**4**)), 8.92 (d + s, 5H, $H^{3,3''} + H^{2}_{Ar}$ (**2**)), 9.17 (s, 4H, $H^{3',5'}$ (**4**)), 9.40 (s, 4H, $H^{3',5'}$ (**2**)); ^{13}C NMR (CD_3CN): $\delta = 20.41$, 20.77 (CH_3 (**4** + **2**)), 121.35, 121.83 ($C^{3'}$ (**4** + **2**)), 124.30, 124.51 (C^{3} (**4** + **2**)), 127.50 (C^{5} (**4** + **2**)), 127.70 (C^{2}_{Ar} (**4** + **2**)), 130.26 (C^{3}_{Ar} (**4**) + C^{6}_{Ar} (**2**)), 133.89 (C^{4}_{Ar} (**4**) + C^{5}_{Ar} (**2**)), 138.03 (C^{4} (**4** + **2**)), 141.02 (C^{1}_{Ar} (**4** + **2**)), 147.55, 148.39 ($C^{4'}$ (**4** + **2**)), 152.46 (C^{6} (**4** + **2**)), 155.34, 155.60 (C^{2} (**4** + **2**)), 158.23 ($C^{2'}$ (**4** + **2**)); MALDI-TOF-MS: m/z: 1837 [$M - PF_6$], 1692 [$M - 2PF_6$], 1547 [$M - 3PF_6$]

6: ^{1}H NMR (CD_3OD): $\delta = 2.79$ (s, 3H, CH_3), 2.94 (s, 6H, CH_3), 7.40–9.76 (m, aromatics and terpyridines, 69H); ^{13}C NMR (CD_3OD): $\delta = 20.89$, 122.01, 122.60, 125.19, 125.69, 128.01, 130.54, 136.84, 138.51, 141.32, 148.76, 149.25, 152.40, 156.12, 158.97; MALDI-TOF-MS: m/z: 1864 [$M - 4Cl$]

8: ^{1}H NMR (CD_3CN): $\delta = 2.93$ (s, 3H, CH_3), 7.31 (dd, 4H, $H^{5,5''}$), 7.62 (d, 4H, $H^{6,6''}$), 8.06 (dd, 4H, $H^{4,4''}$), 8.41 (s, 2H, $H^{4,6}_{Ar}$), 8.87 (d + s, 5H, $H^{3,3''} + H^{2}_{Ar}$), 9.37 (br s, $H^{3',5'}$, 4H); ^{13}C NMR ([D_6]DMSO): $\delta = 21.54$ (CH_3), 121.83 ($C^{3'}$), 124.62 (C^{5}_{Ar}), 125.09 (C^{3}), 127.96 (C^{2}_{Ar}), 130.32 (C^{5}), 137.60 (C^{4}_{Ar}), 138.24 (C^{4}), 140.10 (C^{1}_{Ar}), 146.86 ($C^{4'}$), 152.24 (C^{6}), 155.25 (C^{2}), 158.14 ($C^{2'}$); elemental analysis calcd for $C_{222}H_{156}N_{36}Ru_6P_{12}F_{72} \cdot 8H_2O$: C 45.82, H 2.96, N 8.67; found: C 45.86, H 2.98, N 8.68; MALDI-TOF-MS: m/z: 5544 [$M - PF_5$], 5400 [$M - PF_6 - PF_5$], 5292[$M - 3PF_5$], 5166 [$M - 4PF_5$], 5020 [$M - 4PF_5 - PF_6$] (results were interpreted as the loss of either PF_5 alone or as both PF_5 and PF_6 together)[34]

10: ^{1}H NMR ($CDCl_3$): $\delta = 7.41$ (dd, $J = 6$ Hz, 4H, $H^{5,5''}$), 7.94 (dd, $J = 8$ Hz, 4H, $H^{4,4''}$), 8.15 (s, 2H, $H^{2,6}_{Ar}$), 8.30 (s, 1H, H^{4}_{Ar}), 8.73 (d, $J = 8$ Hz, 4H, $H^{3,3''}$), 8.78 (d, $J = 5$ Hz, 4H, $H^{6,6''}$), 8.81 (s, 4H, $H^{3',5'}$); ^{13}C NMR ($CDCl_3$): $\delta =$ 119.23 ($C^{3'}$), 121.62 (C^{3}), 123.90 (C^{4}_{Ar}), 124.18 (C^{5}), 125.23 (C^{1}_{Ar}), 130.96 (C^{2}_{Ar}), 137.12 (C^{4}), 141.63 (C^{3}_{Ar}), 148.88 ($C^{4'}$), 149.33 (C^{6}), 156.10 (C^{2}), 156.33 ($C^{2'}$); ESI-MS: m/z: 620 [$M + H^+$]; m.p. 308–309 °C

11: ^{1}H NMR (CD_3CN): $\delta = 2.90$ (s, 3H, CH_3 (**2**)), 7.30 (m, 8H, $H^{5,5''}$ (**2** + **10**)), 7.60 (d, 8H, $H^{6,6''}$ (**2** + **10**)), 8.05 (dd, 8H, $H^{4,4''}$ (**2** + **10**)), 8.41 (s, 2H, $H^{4,6}_{Ar}$ (**2**)), 8.75 (s, 2H, $H^{2,6}_{Ar}$ (**10**)), 8.85 (d + s, 9H, $H^{3,3''}$ (**10** + **2**) + H^{2}_{Ar} (**2**)), 9.18 (s, 1H, H^{4}_{Ar} (**10**)), 9.43 (s, 8H, $H^{3',5'}$ (**2** + **10**)); ^{13}C NMR ([D_6]DMSO): $\delta = 22.01$ (CH_3 (**2**)), 122.79 ($C^{3'}$ (**2** + **10**)), 124.84 (C^{5}_{Ar} (**2**)), 125.88 (C^{3}, (**2** + **10**)), 127.11 (C^{4}_{Ar}, **10**), 128.50 (C^{5} (**2** + **10**) + C^{2}_{Ar} (**2**)), 131.05, (C^{6}_{Ar} (**2**)), 132.10 (C^{1}_{Ar}, **10**), 132.66 (C^{2}_{Ar} (**10**)), 138.47 (C^{3}_{Ar} (**10**)), 138.84 (C^{4} (**2** + **10**)), 140.49 (C^{1}_{Ar} (**2**)), 146.15 ($C^{4'}$ (**10**)), 147.99 ($C^{4'}$ (**2**)), 153.00 (C^{6} (**2** + **10**)), 156.04 (C^{2} (**2** + **10**)), 158.89 ($C^{2'}$ (**2** + **10**))

9.37; $\Delta\delta = +0.54$) relative to the corresponding signals in the uncomplexed ligand (Figure 1a). COSY and HETCOR spectra of the biscoordinating ligand **2** and the self-assembled macrocycle **8** verified the peak assignments and coupling patterns. Hexamer **8**, isolated as the $12Cl^-$ salt, was soluble in MeOH and hot H_2O, while conversion into the $12PF_6^-$ salt facilitated solubilization in MeCN, acetone, and DMSO.

Initially, further characterization of the key monomer **2**, as well as the bis(terpyridyl)–Ru^{II} connective moieties, was provided by the formation of the mono- and di-Ru^{II} complexes **3** and **5** (Scheme 1). Reaction of 4′-(4-methylphenyl)-2,2′:6′,2″-terpyridine (**4**)[31] with $RuCl_3 \cdot n H_2O$ (→[Ru(**4**)Cl_3]; Scheme 1) followed by addition of the unmetalated mono-and

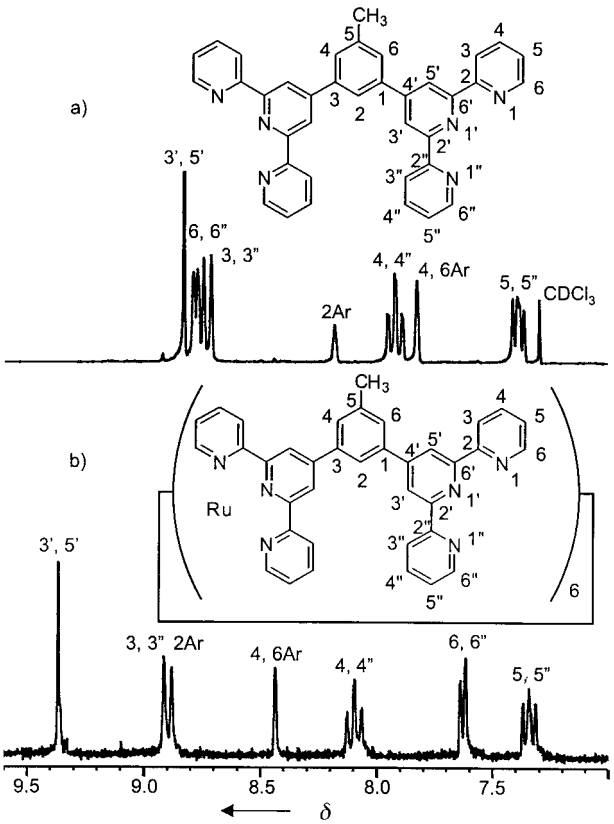
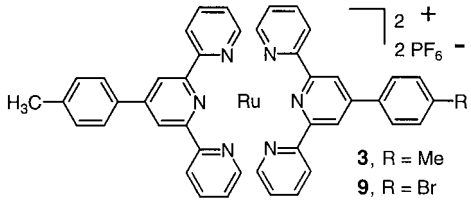


Figure 1. ^{1}H NMR spectra of the bis(terpyridyl) ligand **2** (a) and the self-assembled hexa-Ru^{II} complex **8** (b).



bis-terpyridyl ligands (**4** and **2**) afforded the desired complexes (**3** and **5**, respectively). As in the case of hexamer **8**, complexes **3** and **5** exhibited a downfield shift (^{1}H NMR) of the 3′,5′-H resonances (**3**, δ=9.19, $\Delta\delta = +0.36$; **5**, $\delta = 9.17$, $\Delta\delta = +0.34$) and an upfield shift of the 6,6″-H signals (**3** and **5**, $\delta = 7.62$; $\Delta\delta = -1.15$). Bisruthenium complex **5** was also prepared employing ligand **7** followed by capping with the free monoterpyridine **4**.

In order to ensure structural verification of macrocycle **8**, a stepwise, directed route to the material was devised. Subsequently, the diamagnetic tris-oligomer **6** was prepared from building block **2** by sequential treatment with two equivalents of $RuCl_3 \cdot n H_2O$ and then unmetalated monomer **2** (Scheme 3). The ^{1}H NMR spectrum of trimer **6** showed a complex pattern of broadened absorptions in the aromatic region ($\delta = 9.76$–7.40) as well as the two anticipated singlets arising from the nonequivalent methyl groups ($\delta = 2.79$ (3H);

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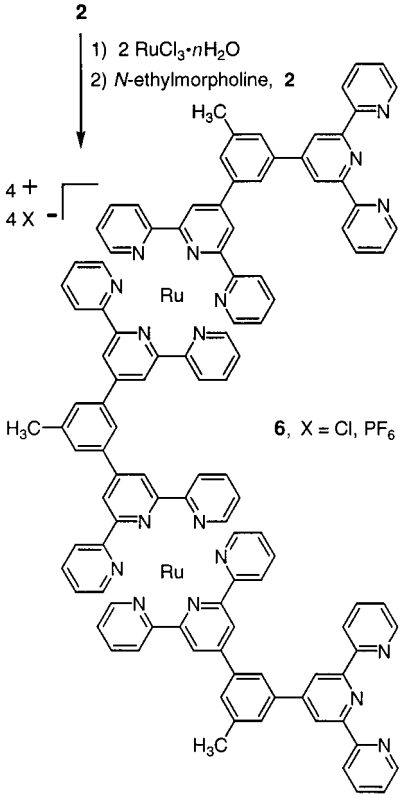

Scheme 3. Construction of bis-Ru^{II} trimer **6** used in the directed synthesis of macrocycle **8**.

2.94 (6H)). Finally, reaction of the oligomer **6** with one equivalent of **7** (Scheme 2) yielded a material possessing identical spectral and physical characteristics to that of the self-assembled hexamer **8**. Notably, TLC on silica gel of the macrocycle **8** prepared by both procedures, eluting with a mixture of CH_3CN and aqueous KNO_3, exhibited identical R_f values (0.55), while the UV extinction coefficients (ε) exhibited a 5.1, 5.5, and 5.8 fold increase for λ_{max} at 290, 312, and 496 nm, respectively (Table 2), relative to the analogously measured coefficients for the mono-Ru^{II} complex **3**. Molecular modeling of macrocycle **8** revealed a diameter of 37.5 Å, a minimum inner void distance of 17.5 Å, and a distance between adjacent Ru metals of 13.5 Å.

Table 2. UV absorption data of complexes **3** and **8**.

Complex	λ_{max} [nm]	ε
3	284	58900
	310	66100
	486	24800
8	290	322900
	312	336800
	496	143400

Figure 2 shows analytical ultracentrifugation absorption profiles at equilibrium[32] for hexamer **8** (obtained from the reaction mixture derived from the self assembly of **7** and **2**) at a concentration of 0.5% in acetonitrile. The data can be fitted equally well with a floating baseline term and a single exponential (Figure 2b), which indicates an average molecular weight of $M = 3250 \pm 100$, or with a two-exponential term and no floating baseline (Figure 2a), which yields $M = 1340 \pm 200$ (78% of chromophores) and $M = 5600 \pm 900$ (22% of chromophores). We assume that both species have the same partial specific volume. Figure 2 also shows the fitted profiles in both cases. The baseline is strikingly large for the single exponential fit with a floating baseline. This result suggests a nonsedimenting component (perhaps small, chromophoric ions) along with structures whose average mass falls only slightly short of the expectation for **8** ($M = 5670$ or 3930 without counterions). The two-exponential fit without floating baseline (Figure 2a) suggests an alternate viewpoint, in which significant amounts of fully formed **8** (22% by chromophoric response) coexist with a mixture of low molecular mass species comparable in mass to either **7** or **2**. This very high concentration was chosen to facilitate comparison with the NMR results (typically 0.5% for ^{1}H and 2.5% for ^{13}C) and requires investigation at wavelengths away from the maximum absorptions in the spectrum. By using more normal concentrations (0.006–0.02%) in the analytical ultracentrifuge the data are fitted well by a single exponential with a small floating baseline (Figure 2c) and molecular weights of $M \approx 2600 \pm 200$, approximately half that expected for **8**. These solutions are sufficiently dilute to yield molecular parameters without undue influence from thermodynamic nonideality.

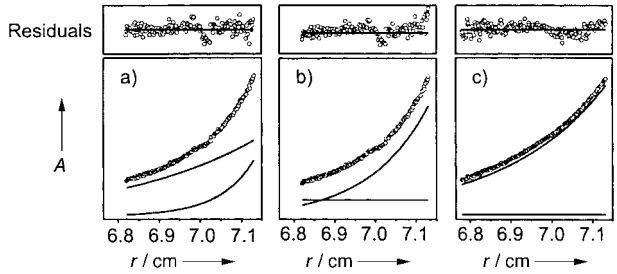

Figure 2. a) Concentration profile (A = absorbance, r = radius) for 0.5 wt% of **8** showing individual fits corresponding to two species; b) profile for 0.5 wt% and the fit to one species and a single baseline term; c) profile for 0.006 wt% and the fit to one species with a single baseline term.

In an effort to modify the generally poor solubility of macrocycle **8**, as well as provide organizational scaffolding for the formation of a noncovalently-bonded network, the counter ions in $\mathbf{8}^{12+}(12\,Cl^-)$ were exchanged with a dodecacarboxylate-terminated dendrimer[33] to give $\mathbf{8}^{12+}[C(CH_2OCH_2CH_2CONHC(CH_2CH_2CO_2^-)_3]_4)$, which is an extremely insoluble assembly. However, a 1:1 mixture of hexamer **8** and a third generation carboxylate-terminated dendrimer gave $\mathbf{8}^{12+}$(G3-108-CO_2^-), which produced a deep red solution in D_2O (25 °C), allowing verification of its structure by ^{1}H NMR spectroscopy. The use of compact, charge concentrated, (pseudo)spherical dendrimers possessing uniquely positioned anionic counterion character affords a convenient circumvention of the spatial randomness of traditional simple counterions in such complexes.

These results prompted the construction of heteroleptic macrocycles. Bromo analogues of **2** and **4** were prepared starting with 5-bromo-*m*-xylene or 4-bromobenzaldehyde, respectively. Reaction of the bromomonoterpyridyl ligand

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(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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