Organometallic Macrocycles

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Organometallic Macrocycles and Cyclic Polymers by the Bipyridine-Initiated Photolytic Ring Opening of a Silicon-Bridged [1]Ferrocenophane**

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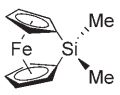
Cyclic organic polymers are challenging synthetic targets, and such materials show interesting and important differences in physical and chemical properties compared to their linear counterparts.[1] Although inorganic macrocyclic species have received significant attention, examples of cyclic inorganic polymers are quite scarce.[1,2] Organometallic macrocycles are even less common, and cyclic organometallic polymers are extremely rare.[3,4] Silicon-bridged [1]ferrocenophanes (sila[1]ferrocenophanes), such as **1**, possess substantial ring



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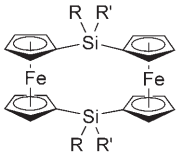

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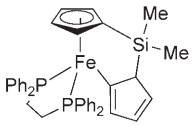

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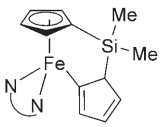
strain, and their ability to undergo ring-opening polymerization (ROP) to give linear oligo- and polyferrocenylsilanes (PFSs) has been well-studied.[5] In contrast, cyclic analogues of PFSs, the [1^n]ferrocenophanes,[6] are much less explored. The smallest of these cyclic species are the disila-[1.1]ferrocenophanes **2**;[7] these species as well as many other [1.1]ferrocenophanes with bridging atoms other than silicon are well-known.[8] Nevertheless, analogues with larger ring sizes are more difficult to prepare, and only a few examples have been reported.[9,10] Accordingly, the preparation of high-molecular-weight cyclic organometallic polymers, such as cyclic PFS, remains a substantial synthetic challenge.[4]

Recently, we developed photocontrolled ring-opening polymerizations of sila[1]ferrocenophanes (such as **1**) involving iron–cyclopentadienyl (Fe–Cp) bond cleavage; these reactions proceed in the presence of $[C_5H_5]^-$ anions and provide a controlled route to new PFS homopolymers and block copolymers.[11–13] When 1,2-bis(diphenylphosphino)-ethane (dppe) was used in place of the Na$[C_5H_5]$ initiator at 5 °C, photolysis afforded ring-slipped species **3** as the sole product, and no polymer was detected.[11] To explore the generality of this unusual chemistry, we studied the analogous reaction in the presence of a bidentate N-donor ligand, 4,4′-dimethyl-2,2′-bipyridine (Me_2bpy), as an initiator.[14]



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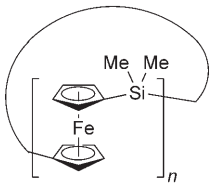

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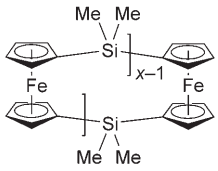

6$_x$

Photolysis of ferrocenophane **1** in the presence of a stoichiometric quantity of Me_2bpy was performed for 2 h at 35 °C in THF, and the initially red solution turned orange-brown. Surprisingly, analysis of the reaction mixture by ^{1}H NMR spectroscopy showed the complete conversion of ferrocenophane **1** into multiple products, including a polymer fraction (PFS **5**, 24 %) and cyclic dimer **6**$_2$.[2,15,16] The presence of cyclic dimer **6**$_2$ and the moderate yield of PFS **5** prompted us to search for other cyclic oligomers in the reaction mixture:[17] pure cyclic dimer **6**$_2$, cyclic pentamer **6**$_5$, and cyclic hexamer **6**$_6$ were obtained after extraction with hexanes and purification by flash chromatography. Cyclic oligomers **6**$_5$ and **6**$_6$ are rare examples of [1^n]ferrocenophanes containing more than two ferrocene units; they are also analogues of the linear oligoferrocenylsilanes that we have synthesized by the anionic oligomerization of ferrocenophane **1**.[18]

Cyclic pentamer **6**$_5$ and cyclic hexamer **6**$_6$ were fully characterized using NMR spectroscopy and X-ray crystallography.[16] As expected, the NMR spectra of these cyclic oligoferrocenylsilanes are much simpler than those of their linear analogues. For example, the ^{1}H NMR spectrum of cyclic pentamer **6**$_5$ shows only two triplets for Cp protons at $\delta = 4.24$ and 4.04 ppm and a singlet for methyl protons at $\delta =$ 0.46 ppm.

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

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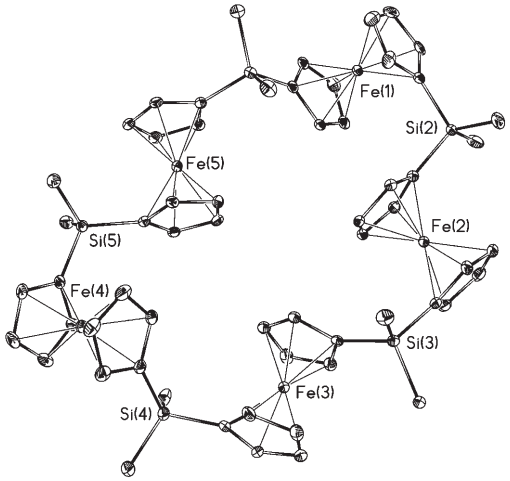


Figure 1. Molecular structure of $\mathbf{6}_5$. Thermal ellipsoids are set at the 30% probability level; hydrogen atoms have been removed for clarity.

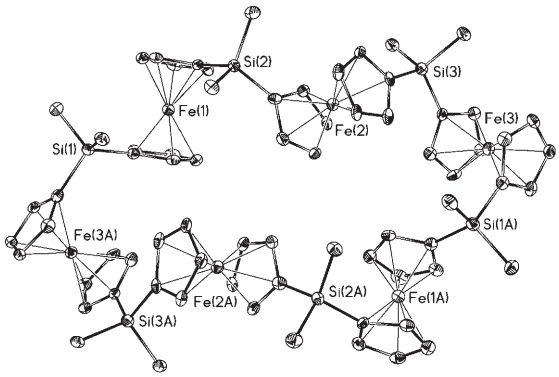
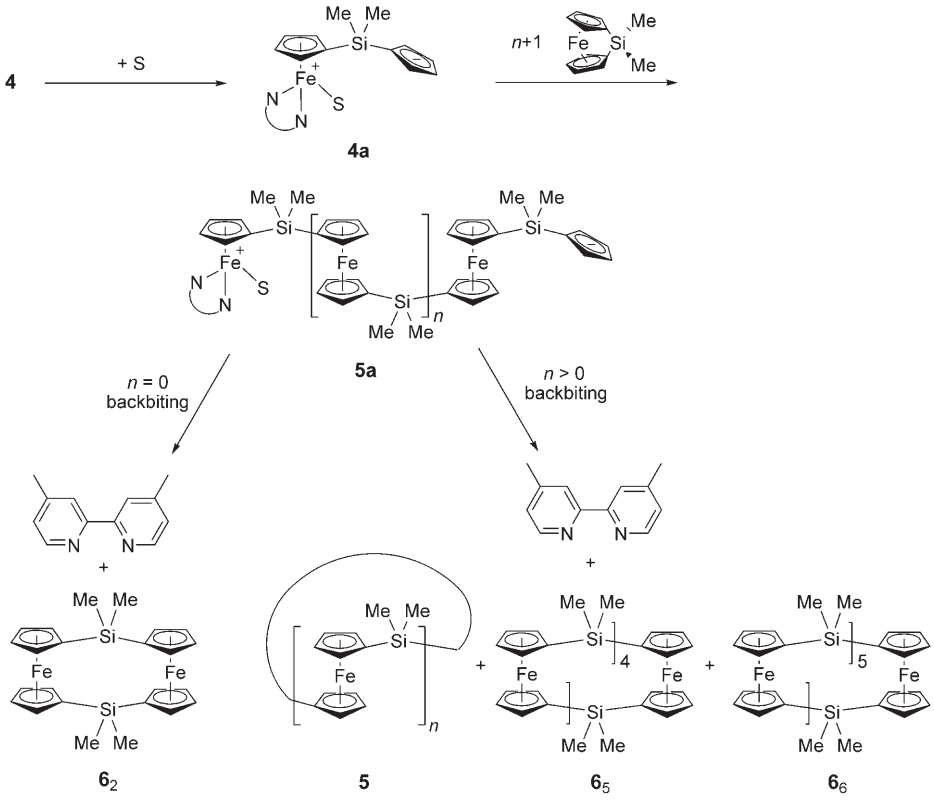


Figure 2. Molecular structure of $\mathbf{6}_6$. Thermal ellipsoids are set at the 30% probability level; hydrogen atoms have been removed for clarity.

Single crystal X-ray diffraction studies were performed to confirm the structures of cyclic oligomers $\mathbf{6}_5$ and $\mathbf{6}_6$ (Figures 1 and 2).[16] The Fe–C and Si–C bond distances in $\mathbf{6}_5$ and $\mathbf{6}_6$ are similar to those of previously reported linear oligoferrocenylsilanes.[18–20] The intramolecular Fe···Fe separations in $\mathbf{6}_5$ range from 5.9038(7) Å [*d*(Fe(1)···Fe(2))] to 6.3426(7) Å [*d*(Fe(5)···Fe(1))], and the corresponding distances in $\mathbf{6}_6$ range from 5.6395(17) Å [*d*(Fe(2)···Fe(3))] to 6.1069(18) Å [*d*(Fe(1)···Fe(2))]. These iron–iron distances are comparable to those in the linear oligoferrocenylsilanes.[18–20]

Analysis of the isolated PFS **5** by gel permeation chromatography (GPC) gave an estimate of $M_n = 11\,900$ and PDI = 2.12 (M_n = number-average molecular weight, PDI = polydispersity index) versus polystyrene standards. As it seemed highly likely that this material was also cyclic, we studied its microstructure by MALDI-TOF mass spectrometry.[21] This experiment confirmed the cyclic nature of PFS **5** (Figure 3). Only peaks that are integer multiples of the molecular weight of **1** were present, indicating a lack of end groups in the polymer. Interestingly, two populations of PFS **5** with different average chain lengths were observed, which presumably arise from backbiting and chain extension reactions that disrupt chain propagation in a random fashion (Scheme 1).

Scheme 1 illustrates a possible mechanism for the photolysis of ferrocenophane **1** in the presence of a stoichiometric amount of Me_2bpy. The formation of polymeric products **5** in this reaction indicated that chain propagation is faster than the initiation of ferrocenophane **1**. After initial Me_2bpy coordination and Cp ring slippage to give **4** (not observed), the η^1-coordinated Cp ring dissociates from the iron center (**4a**, not observed), and the free Cp anion induces rapid chain propagation to yield polymer **5a**. The $[CpFe(Me_2bpy)S]^+$ end group of PFS **5a** is likely unstable, and the pendent Cp anion can attack the iron center in the other end group in a backbiting reaction. This process releases Me_2bpy and yields cyclic oligoferrocenylsilanes of various ring sizes. Compared to the photolysis of ferrocenophane **1** in the presence of dppe,[11] the propensity for backbiting during



Scheme 1. Possible mechanism for the photolysis of ferrocenophane **1** in the presence of Me_2bpy. S = solvent, $\widehat{NN} = Me_2bpy$.

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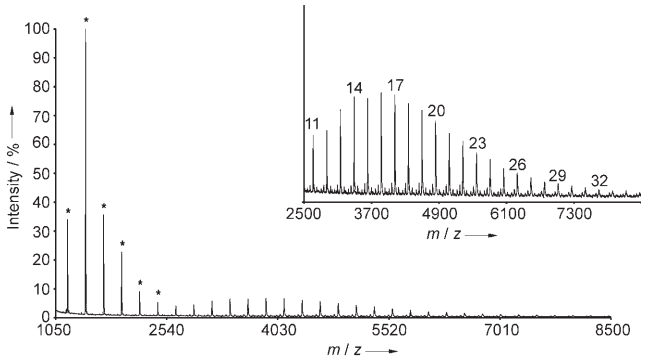


Figure 3. MALDI-TOF mass spectrum of PFS **5**. The asterisks indicate the lower-molecular-weight population of polymer chains. The inset contains the spectrum for the higher-molecular-weight population; the number above each peak corresponds to the degree of polymerization for that oligomer.

chain growth in the Me_2bpy reaction is presumably a consequence of the weaker binding strength of Me_2bpy at the soft Fe^{II} center.

Cyclic oligoferrocenylsilanes are also useful electrochemical models to explain the two-wave redox behavior of the PFS high polymer in cyclic voltammetry. Our previous work on linear oligoferrocenylsilanes is fully consistent with the following explanation: oxidation of the Fe^{II} centers to Fe^{III} initially occurs at alternating iron sites along the chain, and the remaining sites are oxidized at a higher potential.[18] We were therefore interested in comparing the electrochemical properties of cyclic oligomers $\mathbf{6}_5$ and $\mathbf{6}_6$ to those of the linear oligomers. The results of cyclic voltammetry experiments are given in Figure 4 and in Table S1 in the Supporting Information.

The electrochemical behavior of cyclic pentamer $\mathbf{6}_5$ and cyclic hexamer $\mathbf{6}_6$ are consistent with the proposed model (Scheme 2).[18] As anticipated, we observed three waves with

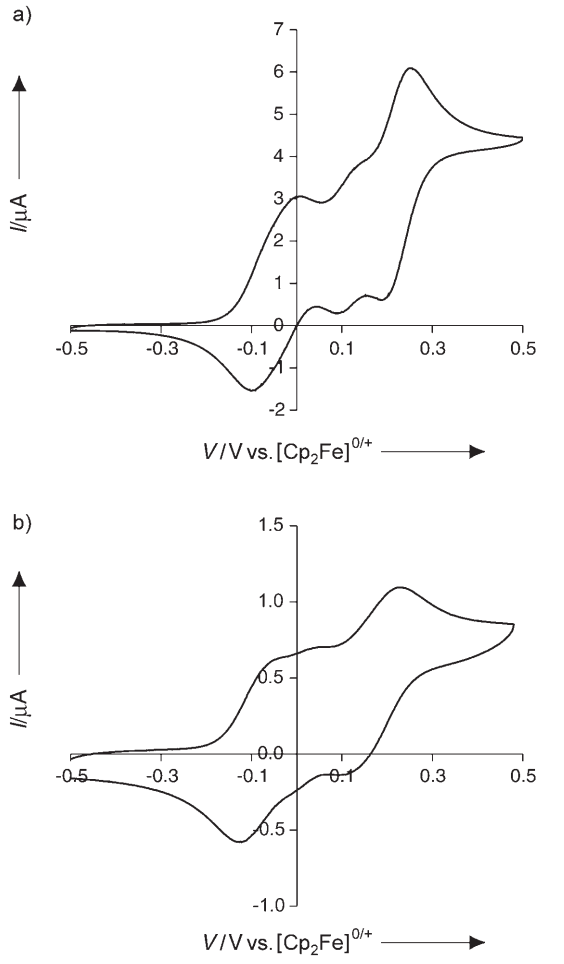
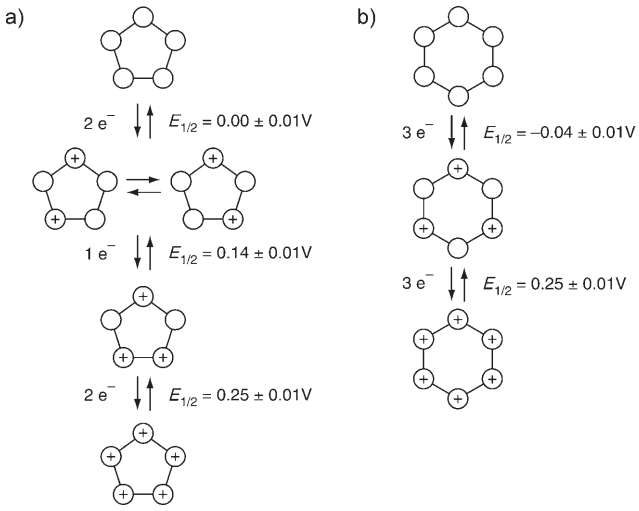


Figure 4. Cyclic voltammograms of a) cyclic pentamer $\mathbf{6}_5$ and b) cyclic hexamer $\mathbf{6}_6$ at a scan rate of 25 $mV\,s^{-1}$. A 1:1 mixture of CH_2Cl_2 and CH_3CN was used as solvent and $[NBu_4][PF_6]$ was the supporting electrolyte.



Scheme 2. a) Redox behavior of cyclic pentamer $\mathbf{6}_5$. b) Redox behavior of cyclic hexamer $\mathbf{6}_6$. Each circle represents a ferrocene unit; potentials are given relative to $[Cp_2Fe]^{0/+}$.

an approximate ratio of 2:1:2 for the odd-numbered cyclic oligomer ($\mathbf{6}_5$) and two waves with an approximate ratio of 1:1 for the even-numbered cyclic oligomer ($\mathbf{6}_6$). The differences between the first and last oxidation potentials for each cyclic oligomer, 0.27 ± 0.02 V, agree with reported values for linear analogues.[18] This agreement suggests that the values of the initial and final potentials do not depend on the number of intervening redox events.

Significantly, performing the photolysis of ferrocenophane **1** and Me_2bpy in THF for 2 h at a lower temperature (5 °C rather than 35 °C) leads to substantially higher yields of polymer **5** (ca. 54 % relative to cyclic oligomers) with higher molecular weights ($M_n = 28400$, PDI = 1.46). This result suggests that our new method offers unprecedented opportunities to access cyclic PFS with different molecular weights; this protocol may also be applicable to other related strained metallorings containing other metals, π-hydrocarbon ligands, and bridging groups.[5b] We are currently examining other bidentate ligands to access higher homologues of oligoferrocenylsilanes $\mathbf{6}_x$.

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[15] The degree of polymerization for each oligoferrocenylsilane is indicated by a subscript in its compound number. For example, $\mathbf{6}_2$ refers to the cyclic dimer disila[1.1]ferrocenophane.

[16] See the Supporting Information for full experimental details.

[17] The reaction mixture contains PFS **5** and various cyclic oligoferrocenylsilanes in approximately the following amounts (determined from integrations of the methyl signals in the ^{1}H NMR spectrum, average of three experiments): PFS **5** 24%, cyclic dimer $\mathbf{6}_2$ 17%, cyclic pentamer $\mathbf{6}_5$ 21%, cyclic hexamer $\mathbf{6}_6$ 9%.

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