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Ferrocenophanes with gallium and silicon as alternating bridges†

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[1.1]Ferrocenophanes with gallium and silicon in bridging positions have been prepared in yields of 29 and 41%, respectively. From the same reactions, polymer-containing fractions were isolated (31% in each case) and shown to be comprised of linear and cyclic species with up to 16 ferrocene units (MALDI-TOF analysis).

During the last two decades, [1]ferrocenophanes ([1]FCPs; Scheme 1) were developed as a class of precursors for the preparation of well-defined metallopolymers.¹ The most researched strained sandwich compounds are silicon-bridged [1]FCPs, which were also the first reported [1]FCPs.² The related [1.1]FCPs (Scheme 1) are an even older class of compounds, which were described as early as 1956.³ During the 1980s, carbon-bridged [1.1]FCPs were intensively investigated as it was found that the *syn* conformer of the CH₂-bridged species catalyzed the formation of dihydrogen in aqueous acidic solutions.⁴ To date, the family of [1.1]FCPs has a significant number of members with heteroatom-bridged species known for B, Al, Ga, In, Si, Sn, Pb, P, As, S, Zn, and Hg.⁵

Recently, we developed a synthetic methodology that allowed the preparation of the first [1.1]FCPs bridged by different elements.⁵ The first silastanna[1.1]ferrocenophanes were synthesized (Scheme 2), but could only be obtained in low yields [2_1 (R = Et, R' = Me): 3%; 2_1 (R = R' = Me): 7%]. Furthermore, [1.1.1.1]FCPs (2_2) with alternating silicon and tin in bridging positions were isolated and MALDI-TOF mass analysis showed the presence of cyclic (2_n) and linear polymers



Scheme 1 [1]Ferrocenophanes and [1.1]ferrocenophanes.



Scheme 2 Linear and cyclic poly(ferrocenes) with alternating bridges.⁵

 $(\mathbf{3}_{\mathbf{m}})$ with up to 20 ferrocene units.⁵ Cyclic poly(ferrocenes) of this size are very rare and only photocontrolled ringopening polymerization (ROP) of the Me₂Si-bridged [1]FCP (Scheme 1) has yielded larger macrocycles (with more than 40 repeating units) to date.⁶

Metal-containing polymers have shown utility as precursors to functional ceramic materials. For example, cross-linked poly(ferrocenylsilane)-based materials yielded shape-retaining ceramics with tunable magnetic properties.⁷ Similarly, pyrolysis of short cylindrical micelles with a cross-linked polyisoprene shell and a poly(ferrocenylsilane) core resulted in nanoscale magnetic ceramics.⁸ More recently, low-molecular-weight ferrocene-platinum-containing polymers were employed to pattern surfaces with FePt alloy nanoparticles for ultrahighdensity magnetic data storage applications.⁹ In each case, the predetermined composition of the polymers employed played an important role in the properties of the resulting ceramics. Although recent results in this area have been impressive, there remains a need for synthetic methods that allow for variation in the composition of pre-ceramic metal-containing polymers. For example, pyrolysis of metal-containing polymers containing gallium and iron may lead to magnetostrictive ceramic materials that undergo changes in shape or dimensions during magnetization.¹⁰

Within this report we present a novel synthetic method towards unsymmetrically bridged [1.1]FCPs containing silicon and gallium bridging moieties, which also yield linear and cyclic polymers of similar composition. These results complement our efforts to develop gallium- and aluminum-containing metallopolymers through ROP methodologies.¹¹

As illustrated in Scheme 3, lithiation of the Me_2Si- bridged dibromide 1^{Me} followed by the addition of gallium

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Scheme 3 Synthesis of silagalla[1.1]ferrocenophanes 6a and 6b.



Fig. 1 Molecular structure of **6b** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected atom-atom distances [Å] for **6b** (see ESI for **6a**): Ga1-N1 2.1626(16); Ga1-C1 1.973(2); Ga1-C20 1.958(2); Ga1-C35 1.9566(19); Fe1...Fe2 5.3147(4).

dichlorides (4 or 5), equipped with non-encumbered ligands, gave the targeted silagalla[1.1]ferrocenephanes **6a** and **6b**. \ddagger^{12} The isolated yields of 29 (6a) and 41% (6b) are significantly higher than those of their silicon-tin counterparts 2_1 (Scheme 2; 3 and 7%).⁵ Single-crystal X-ray analysis revealed that compounds 6a and 6b exist as anti isomers in the solid state (Fig. 1 and Scheme 1). This is expected as their symmetrically bridged cousins, the disila[1.1]ferrocenophane $(ER_x = SiMe_2)^{13}$ and the digalla[1.1]ferrocenophane (ER_x = GaAr'),¹⁴ exhibit the same conformation. The bond lengths around the two bridging elements are very similar to those of the symmetrically bridged species.^{13,14} Species **6b** is unsymmetrically bridged by a short Si linkage (C25···C30 3.120(3) Å) and a slightly longer Ga linkage $(C20 \cdot \cdot C35 3.347(3) \text{ Å})$. The Cp rings of each ferrocenediyl unit deviate from coplanarity: tilt angles between least square planes of the C atoms of the Cp rings are 5.07(12) (Fe1) and 4.35(12)° (Fe2). The molecular structure of **6a** in the solid state is very similar to that of **6b** (see ESI).

Species **6a** and **6b** both show similar pattern in their NMR spectra. For example, the ¹H NMR spectra show 8 signals of equal intensity for all 16 Cp protons revealing the presence of a two-fold symmetry element. This is consistent with the molecular structures found in the solid state, if one considers that inversion of the envelope conformation of the chelating five-membered rings (Ga1-C1-C2-C7-N1) occurs fast in solution, resulting in time-averaged C_s -symmetrical species. The known dimethylsila[1.1]ferrocenophane¹³ is a fluxional molecule in solution, exhibiting fast *anti*-to-*anti* isomerization (Scheme 4).

This degenerate isomerization of two C_{2h} -symmetrical species creates a *pseudo*-mirror plane (σ_h) resulting in D_{2h} symmetrical molecules on time-average and 2 instead of the expected 4 signals for all Cp protons are observed. Such a fluxional behavior is characteristic of [1.1]FCPs and usually observed for *syn*- as well as for *anti* isomers. This dynamic behavior was first described for the carbon-bridged species,



Scheme 4 *anti*-to-*anti* Isomerization of the known Me₂Si-bridged [1.1]FCP, resulting in swapping of positions of related H' and H'' atoms.

which have been coined "molecular acrobats".^{4,15} However, the known Ar'E-bridged [1.1]FCPs (E = Al, Ga, In) do not exhibit higher symmetries on time-average in proton NMR spectra (500 MHz). For the indium-bridged species an anti-toanti isomerization still occurs at ambient temperature, which was shown by exchange proton NMR spectroscopy (EXSY).¹⁶ For group-13-bridged [1.1]FCPs equipped with intramolecularly coordinating ligands, the anti-to-anti isomerization must involve a breakage of the E-N donor bond, rotation of the ligand about the $E-C^{ipso}$ bond, and reformation of the E-N donor bond which is accompanied by an inversion at the group 13 element. Such a dynamic process is faster for indium compared with aluminum or gallium species, as indium forms the weakest donor bond with nitrogen within the series. Against this background, we measured ¹H NMR spectra of **6a** and **6b** in $[D_8]$ toluene in the temperature range of r.t. to 80 °C (500 MHz), but could not find any indication of fluxional behavior. Thus, we conclude that the galliumcontaining moiety does not allow for a fast isomerization, even though the Me₂Si linkage is very flexible.

Cyclic voltammetry of **6a** and **6b** at r.t. revealed the presence of two well-resolved oxidation waves, showing an expected sequential oxidation of the two iron centers (Fig. 2). The separation of these waves, $\Delta E^{\circ'}$, provides a measure of the interaction between the two iron-redox centers.¹⁷ Species **6a** and **6b** are hybrids of the symmetrically bridged disila[1.1]ferrocenophane (ER_x = SiMe₂) and digalla[1.1]ferrocenophane (ER_x = GaAr') and it is not surprising that their $\Delta E^{\circ'}$ of 0.27 V falls between that of 0.25 V (ER_x = SiMe₂)^{13b} and 0.30 V (ER_x = GaAr').¹⁴

Proton NMR spectra of reaction mixtures from which the [1.1]FCPs **6a** and **6b** were extracted into hexane (29 and 41%; Scheme 3) showed broad peaks indicating the formation of oligomers or polymers. The hexane insoluble fractions were purified by precipitation from toluene solutions into hexane, resulting in isolated yields of 31% in both cases. GPC analysis of these fractions, **6a**_x and **6b**_x, showed broad molecular weight distributions and average molecular weights M_w of 3.08 kD (**6a**_x) and 7.05 kD (**6b**_x). A clearer picture of the character of these mixtures could be uncovered by MALDI-TOF mass analysis,



Fig. 2 Cyclic voltammogram of **6a** (1 mM) in CH₂Cl₂ (0.1 M NBu₄PF₆; scan rate = 50 mV s⁻¹; $E^{-\gamma}$ = 0.121 and 0.149 V).





Fig. 3 MALDI-TOF mass spectrum of $6a_x$ (* indicates unassigned peaks).

which showed cyclic and linear polymers. Fig. 3 depicts the mass spectrum for mixture $6a_x$ with four different series of species. Cyclic ferrocenophanes $(6a_n)$ with up to 12 ferrocenediyl moieties (n = 6) were detected. Furthermore, three series of linear species were found: one series with only Cp end groups $(7a_m; m = 1-8)$, one with one GaAr'Cl end group $(8a_m; m = 1-7)$, and one with one GaAr'Br end group $(9a_m; m = 1-7)$. Similar series of species were detected for the mixture $6b_x$, showing compounds with up to 14 ferrocenediyl moieties; however, only the series of cyclic species was less pronounced than for $6a_x$ (see ESI).

The presence of bromide-containing end groups (Fig. 3; series $9a_m$) was unexpected. These species must have formed from the respective chlorides (series 8am) through a Cl/Br exchange reaction. Recently, we discovered that such a Cl/Br exchange happened during the course of the synthesis of the intramolecularly stabilized gallium compound MxGaCl₂.¹⁸ A similar exchange was reported in the literature for the Mes*GaCl₂, where the authors speculated that unreacted starting compound Mes*Br was the direct source of bromide.¹⁹ In the course of the synthesis of MxGaCl₂, we found some indication that LiBr reacted with MxGaCl₂ to give MxGaClBr and MxGaBr₂. Therefore, we speculate that in the reaction mixtures (Scheme 3) LiBr formed and acted as the reagent for the Cl/Br exchange. In analogy to the well-known reaction of tBuLi and tBuBr, some fraction of species with lithiated Cp groups might have reacted with the formed *n*BuBr to give LiBr, butene and protonated Cp end groups. Alternatively, substitution could occur to give LiBr and butylated Cp; however, butyl-containing compounds were not detected.

The new methodology described here has allowed the synthesis of the first examples of poly(ferrocene)s with alternating silicon and gallium in bridging positions. Such species would be very difficult to obtain through ROP of respective sila- and galla[1]ferrocenophanes: the required gallium species are unknown and, in addition, a perfect control over the copolymerization would be needed. The discovered Cl/Br exchange shows that unwanted side reactions occurred, which probably lead to chain growth termination. Future activities will be concentrated on further optimizations of the metallation

of 1^{Me} so that chain growth termination can be suppressed, as well as the evaluation of the polymers described as precursors to magnetostrictive ceramic materials.

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Notes and references

‡ To improve solubilities of [1.1]FCPs, the Ar' ligand $(2-Me_2NCH_2C_6H_4)$ was equipped with a *p*-Me₃Si group. This tactic had been applied successfully to [1.1]metallarenophanes by introducing a *p*-tBu group (see ref. 12). However, the solubilities of **6a** and **6b** are very similar.

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