ORGANOMETALLICS-

Deltoid versus Rhomboid: Controlling the Shape of Bis-ferrocene Macrocycles by the Bulkiness of the Substituents

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S Supporting Information

ABSTRACT: Precise structural control of heteroannularly disubstituted ferrocene (Fc) structures is very challenging as the high rotational mobility of the Fc unit allows a large conformational diversity. Herein we present the syntheses, characterization, and electrochemical investigation of two complementary bis-ferrocene macrocycles, built up via Sonogashira cross coupling and intramolecular ring-closing reaction. While the X-ray structure of 1,2-ethynylbenzene bridged bis-ferrocene complex 1 shows a deltoidal conformation, a stretched oriented rhomboidal bis-ferrocene metallacycle **2** is formed when the peripheral benzene rings are decorated with bulky *tert*-butylsulfanyl groups. VT-NMR



spectroscopy is used to assign the rotation of the embedded Fc units in rhomboid 2. Moreover, cyclic voltammetry (CV) of deltoid 1 and rhomboid 2 indicate that electronic communication between both ferrocenyl groups can be neglected, while the electrostatic through space coupling is significant.

INTRODUCTION

Over the past few decades, fascinating macrocycles comprising ferrocenes as functional units have been reported such as a molecular scissors,¹ tweezers,² and springs.³ Chiral structures resembling Escher's endless staircase⁴ or ferrocene (Fc)terminated helicene⁵ are remarkable examples of how the 3D scaffold of ferrocene is used as structure providing "shaping" synthon. Moreover, the stable and reversible redox chemistry of ferrocene has been exploited in molecular wires,⁶ sensors,⁷ and switches.⁸ Furthermore, substituents on the cyclopentadienyl (Cp) rings enable the fine-tuning of the energy states involved. Owing to its extensive use in numerous areas of applied science, we became interested in the structural control over the embodied ferrocene units as part of the functional application.⁹ We experienced the precise construction of discrete and shapepersistent ferrocene macrocycles as challenging, in particular when ferrocene is integrated as heteroannularly disubstituted subunit and the Cp-Fe-Cp junction is part of the macrocycle such that its rotational freedom allows for a large structural diversity.

Among these considerations, we became interested in macrocycles comprising two ferrocene units which on the one side will increase the structural variation problematic but on the other give access to potentially mixed-valence compounds with exciting intramolecular redox properties. To minimize the structural diversity and to maximize the extent of

Coulomb interactions between both ferrocene subunits, bis-Fc macrocycles consisting of small and rigid scaffolds moved into the focus of interest. Due to our experience with macrocycles consisting of ethynyl interlinked aryl subunits,¹⁰⁻¹⁵ we became interested in 1,2-diethynylbenzene bridges to combine two Fc subunits in a compact fashion favoring intramolecular Coulomb interactions. Such a linker was already reported by Diallo et al., where in a series of Fc-terminated compounds, 1,2-bis-(ferrocenylethynyl)-benzene (3 in Figure 1) exhibited interesting electrostatic interaction characteristics.¹⁶ In their study they showed that the two ferrocenyl groups turn out of plane in order to minimize the electrostatic repulsion upon oxidation. This pioneering study even increased our interest in cyclic derivatives, as the fixation of the Fc subunits within a macrocyclic framework should limit their ability to sidestep in order to avoid electrostatic repulsion. Interestingly, two macrocyclic structures comprising two ferrocenes heteroannularly interlinked by two ortho-diethynyl benzene linkers are possible, which are both presented in this work.

In particular, we describe the syntheses, full characterization, and electrochemical investigation of deltoidal shaped bisferrocene **1** with both *ortho*-diethynyl benzene linkers stacked on top of each other which we thus entitled "deltoid" and of

Received: December 8, 2016



1,2-bis(ferrocenylethynyl)-benzene

Figure 1. Structures of bis-ferrocene macrocycles deltoid 1 and rhomboid 2, together with 1,2-bis(ferroceneyl-ethynyl)-benzene 3.

macrocycle 2 with both *ortho*-diethynyl benzene linkers on opposed sides of the double Fc junction which we simply call "rhomboid". In the case of rhomboid 2, we further analyze the dynamic structural behavior by NMR analyses. Both target structures differ in their spatial arrangement and consequently also in the symmetry elements involved. As the R substituents of deltoid 1 are hydrogen atoms, the structure has a mirror plane comprising both Fe atoms of the ferrocene junctions, and a C_2 -axis going through the middle of the connection between both Fe atoms and a point in the middle between both parallel benzene units. In the case of rhomboid 2, both R substituents are bulky *tert*-butylsulfanyl groups, and the symmetry element is an inversion point between both Fe-atoms of the ferrocene junctions.

Cyclization Strategy. After several unsuccessful attempts to assemble bis-ferrocene macrocycles by dimerizing suitably functionalized ferrocene derivatives, we decided for a stepwise assembly of both bridging linkers. While such a synthetic strategy guarantees good control over the formed connections, it comes with a considerable increase in the number of consecutive reaction steps required, even comprising statistical steps with limited atom economy. In contrast, the subsequent formation of the second linker can also be considered as opportunity to control the spatial arrangement of the macrocycle. As sketched in Scheme 1, the Fc junctions and the ethynyl linkers can be considered as rotating joints giving access to both structures, the deltoid and the rhomboid. In the precursor of the deltoid (Scheme 1, right side on the top), the two benzene rings are arranged parallel on top of each other stabilized by stacking interactions, as already reported in the solid state structures of 1,1'-bis(phenylethynyl)ferrocene¹⁷ and further decorated derivatives thereof.^{9,18} However, potential substituents (R in Scheme 1) come in close proximity in the deltoid precursor, and the steric repulsion probably disfavors this conformer when large enough substituents are involved. Instead, the rotational motions around the ferrocene and ethynyl joints might favor a conformer enabling the ring-closing reaction on the opposed side, resulting in the desired rhomboid. The equilibrium between both precursors should depend on the balance between attractive stacking interactions and steric repulsion, which should be adjustable by the choice of the substituent R.

The assembly of the macrocycles and their precursors is based on a combination of acetylene scaffolding strategies¹⁹ and

Scheme 1. Equilibrium between Two Conformers during the Ring-Closing Reaction a



"The two conformers are expected to yield each in another welldefined structure, namely, either the deltoid or the rhomboid. The bulkiness of the substituent R might serve as trigger to favor one conformer over the other and consequently also direct the resulting macrocycle.

the well-developed Sonogashira-type coupling chemistry with ferrocene building blocks.^{16,18,20–22} As the substituent R is selected at an early stage of the stepwise assembly strategy, each macrocycle has to be synthesized from scratch.

To scrutinize the hypothesis presented in Scheme 1, we focused on two model compounds each favoring one of the two precursor conformers. In order to favor the deltoid conformation, the steric interaction between both R groups has to be minimized and we thus decided to get rid of the substituent (R = H in 1). To steer the precursor equilibrium toward the rhomboid conformation, the bulky *tert*-butylsulfanyl group has been selected (R = St-Bu in 2). The bulkiness of the substituent was not the only selection criteria; the *tert*-butylsulfanyl substituent can also be considered as a masked thiol anchor group which might become interesting to integrate the macrocycle in future single-molecule junction experiments.

RESULTS AND DISCUSSION

Synthesis. As already mentioned above, the macrocycles were synthesized in a stepwise assembling strategy consisting of repetitive reaction sequences consecutively closing one linker after the other. As a key building block, the properly masked 1,2-diethynylbenzene derivative was required. To optimize both chemical control and synthetic flexibility, an orthogonal pair of ethynyl protection groups was desired. The combination triisopropylsilyl (TIPS) and 2-hydroxy-propyl (HOP) as ethynyl masking groups reported by Kukula et al.²³ was ideally suited for the purpose. The synthesis of deltoid 1 is displayed in Scheme 2. Monoprotected 1,2-diethynylbenzene derivative 5 was prepared by successive Pd-catalyzed coupling of 1-bromo-2-iodobenzene with 2-methyl-3-butyn-2-ol and (triisopropylsilyl)acetylene profiting from the difference in reactivity of the two halogen substituents, followed by removal of the triisopropylsilyl protection group by treatment with a 1 M TBAF solution. We recently reported⁹ the high-yield experience we made in C-C coupling reactions between 1,1'diiodoferrocene (6) and acetylenes with the palladium/

Scheme 2. Linear Seven-Step Synthesis of the Deltoid Bis-ferrocene Metallacycle 1^a



"Reagents and conditions: (a) (i) Pd(PPh₃)₂Cl₂, CuJ, NEt₃, 2-methyl-3-butyne-2-ol, 50 °C, 3 h, (ii) TIPSA, 90 °C, 12 h; (b) TBAF, THF, 25 °C; (c) Pd(MeCN)₂Cl₂, [(*t*-Bu)₃PH]BF₄, CuJ, THF/DIPA, 60 °C, (d) TBAOH, toluene, 70 °C 1 h; (e) FcI₂, Pd(MeCN)₂Cl₂, [(*t*-Bu)₃PH]BF₄, CuJ, THF/DIPA, 60 °C, (f) TBAOH, toluene, 70 °C; (g) Pd(MeCN)₂Cl₂, [(*t*-Bu)₃PH]BF₄, CuJ, THF/DIPA, 1.5 mM in [11], 60 °C.

phosphine couple²⁴ elaborated by Inkpen et al.²¹ For the assembly of Fc-macrocycles reported here, we used the corresponding air-stable trialkylphosphonium salt,²⁵ since preliminary studies showed that the advantages in handling and storage outbalanced the moderate loss in yields. We thus treated 1,1'-diiodoferrocene 6 with 3 equiv of acetylene 5 in the presence of catalytic amounts of $Pd(MeCN)_2Cl_2$, $[(t-Bu)_3PH]$ -BF₄, and CuI in a THF/DIPA mixture at 60 °C for 12 h. After aqueous workup, the reaction products were isolated by flash column chromatography (FCC) on silica gel. As main product, 1,1'-diethynyl-substituted ferrocene derivative 8 was isolated in 47% yield, together with 23% of singly ethynyl-substituted compound 7. We were particularly interested in doubly HOP protected diacetylene 8, as considerable differences in the $R_{\rm f}$ values of the compounds as a function of the number of polar protection groups were expected. This enables the chromatographic separation of the differently protected compounds, an important feature when statistical deprotection reactions are considered. Indeed, treatment of doubly HOP protected diacetylene 8 with a n-Bu₄NOH solution in degassed toluene for 1 h at 70 °C provided monoprotected derivative 9 in very good 60% isolated yield after FCC. In order to favor the decoration of the free ethynyl group of 9 with an additional 1iodo-1'-yl ferrocene unit, a 5-fold excess of the 1,1'diiodoferrocene was used for the coupling between 9 and 6. Apart from the ratio of the coupled reagents, reaction conditions similar to those described above for the coupling between 5 and 6 were applied. After workup, desired openchain bis-ferrocene derivative 10 was isolated in 39% yield by FCC. The major side product we observed was the oxidative acetylene coupling product providing diethynyl interlinked Fcdimer 12 in 12% yield. Despite extensive precautions to exclude oxygen and air from the reaction mixture, the formation of 12 could not be suppressed and might originate from the activation cycle forming the catalytically active Pd(0) species. The remaining HOP protection group in 10 was removed again by treatment with a *n*-Bu₄NOH solution in degassed toluene at

70 °C for 3 h, and free acetylene 11 was isolated as orange solid in 73% yield after FCC. With terminal acetylene and iodoferrocene functionalized bis-ferrocene derivative 11, the ideal precursor for the intramolecular Sonogashira reaction as cyclization step was available. To perform the cyclization step, a 1.5 mM solution of 11 in a THF/DIPA mixture was prepared and treated with the same reagents and conditions as those described above for the coupling between 5 and 6. After work up, we isolated as the only reaction product formed in reasonable yields deltoid bis-ferrocene metallacycle 1 as pale orange solid in 29% yield. The remaining material probably forms larger oligomers and polymers which were not isolated. Target structure 1 displayed very limited solubility features in all organic solvents investigated, and we were initially afraid of facing challenging boundary conditions for its characterization. However, we were pleased to realize that its poor solubility is reflected in its pronounced tendency to crystallize, and single crystals suitable for X-ray analysis were obtained by slow evaporation of a solution of 1 in dichloromethane. X-ray crystallography unambiguously corroborated the identity of compound 1 and displayed its conformation (Figure 2). Bisferrocene 1 has C₂ symmetry and resembles the expected deltoidal shaped geometry, with small deviations from the



Figure 2. Solid-state structure of the deltoid 1. ORTEP plots with ellipsoids plotted at the 50% probability level (hydrogen atoms are omitted for clarity).

Scheme 3. Synthesis of Rhomboidal Bis-ferrocene Metallacycle 2 Consisting of 11 Consecutive Steps^a



"Reagents and conditions: (a) NH₄SCN, Oxone, MeOH, 25 °C; (b) CuBr₂, *t*-BuONO, MeCN/DCM, 65 °C; (c) (i) LAH, THF, 25 °C (ii) 2-chloro-2-methylpropane, AlCl₃, 25 °C; (d) (i) Pd(PPh₃)₂Cl₂, CuI, 2-methyl-3-butyn-2-ol, THF/NEt₃, 25 °C., 5 h, (ii) TIPSA, 80 °C, 16 h; (e) TBAF, THF, 25 °C; (f) TBAOH, toluene, 70 °C, 3 h; (g) Pd(MeCN)₂Cl₂, $[(t-Bu)_3PH]BF_4$, CuI, THF/DIPA, 60 °C, (h) Pd(dppf)Cl₂, CuI, 18, THF/DIPA, 70 °C; (i) TBAF, THF, 25 °C; (j) 5 equiv of 6, Pd(dppf)Cl₂, CuI, THF/DIPA, 50 °C, 2 h; (k) TBAOH, toluene, 70 °C; (l) Pd(PPh₃)₄, DIPA, toluene 0.1 mM in [24], 90 °C.

geometrical ideal arrangement of an isosceles triangle, with enclosed angles of 61.01 and 66.13°, respectively. The deviation is caused by one ferrocene unit, which is inclined with respect to the aryl plane by ~7°, while the other ferrocene is almost in plane. The iron centers are almost coplanar, based on Cp centroid–Fe1–Fe2 enclosed angle of 89.32°, and separated by only 7.116 Å. The interplanar phenyl distance is with 3.577 Å slightly longer than the Cp–Cp distance (3.311 Å), and both phenyl rings are sitting on top of each other. In addition, the two Fe atoms and the center between the phenyl rings share a plane of symmetry due to their parallel arrangement and fixation in the bis-metallacyclic framework. Deltoid 1 was further characterized by ¹H and HMBC NMR spectra and MALDI-ToF mass spectrometry. Due to the poor solubility of 1, we were not able to record meaningful ¹³C NMR spectra.

The exclusive formation of the syn conformation supports the first part of our working hypothesis, namely, that in the absence of steric restriction the deltoid bis-metallacycle is favored. Bulky substituents (*tert*-butyl and *tert*-pentyl) are known to restrict the revolving motion of the Cp rings in ferrocene model compounds.²⁶ The comparable spacing between both phenyl rings and the Cp rings in the solid-state structure of **1** suggested that substituents of comparable dimensions should be bulky enough to handicap the syn arrangement and steer the ring-closing reaction toward the rhomboidal anti conformation. As already discussed in the "Cyclization Strategy" section above, we chose *tert*-butylsulfanyl groups as R substituents combining the required bulkiness with promising features as potential anchor groups. It is noteworthy that our initial approach considering even bulkier triphenylmethylsufanyl groups failed, due to severe deactivation of the triphenylmethylsufanyl decorated aryl system in the subsequent C–C coupling reactions.

The synthesis of rhomboid **2** is displayed in Scheme 3. The assembly of the *ortho*-diethynylbenzene building block started with the regioselective oxidative thiocyanation of 2-iodoaniline in para position, using Oxone and ammonium thiocyanate, which provided 2-iodo-4-thiocyanato-aniline **13** in excellent yield.²⁷ Aniline **13** was readily sublimed in batch scales of up to 15 g and was converted to bromo derivate **14**, using Cu(II) bromide and *tert*-butyl nitrite²⁸ in a 5:1 ratio of acetonitrile/ methylene chloride. Reduction of thiocyanate using LAH to provide the free thiol which was alkylated with 2-chloro-2-methylpropane in the presence of catalytic amounts of aluminum chloride to yield **15** in 76% over both steps. With bromo-iodo-aryl derivative **15** in hands, the different reactivity of both halides in Pd-catalyzed Sonogashira coupling allows for the subsequent coupling with two differently protected



Figure 3. (a) Equilibrium between the different conformers of rhomboid 2 accessible via rotational motion of a ferrocene subunit within the macrocycle's framework. Exclusively the α and β ferrocenyl protons are labeled for visibility. The helical chirality descriptors *P* and *M* refer exclusively to the arrangement of the macrocycle and ignore the peripheral *t*-BuS substituent. (b) Region of the ferrocene signals of the recorded ¹H NMR spectra of **2** in CD₂Cl₂ in a temperature range from 298 to 173 K. The signals of the β ferrocene protons were used for LSA and are highlighted in light blue.

acetylene derivatives in a single reaction step. Thus, 15 together with both catalysts (Pd(PPh₃)₂Cl₂ and CuI were dissolved in a degassed 3:1 THF/NEt₃ mixture and 2-methyl-3-butyn-2-ol was added at 25 °C. After 3 h, the monitoring of the reaction mixture by thin layer chromatography (TLC) displayed the complete consumption of the acetylene and (triisopropylsilyl)acetylene was added, and the reaction mixture was heated at 80 °C overnight (16 h). FCC of the concentrated crude reaction mixture provided differently protected diethynyl 16 in 81% yield. The orthogonal protection groups enable either the removal of triisopropylsilane or the hydroxypropyl and thus the perfect control over the demasking of the ethynyl groups in para and meta position, respectively. Doubly protected diethynyl 16 was either treated with fluoride ions in wet THF to give singly HOP protected diethynyl 17 in good yield, or it was exposed to *n*-Bu₄NOH in degassed toluene at 70 °C for 3 h to provide singly TIPS protected diethynyl 18 in good yields. Either one of the iodine atoms of 1,1'-diiodoferrocene had to be substituted consecutively by one of two monoprotected diethynyls 17 and 18. This is particularly important to control the symmetry of the targeted rhomboid bis-ferrocene metallacycle, as the substitution of both iodines of 6 with the same monoprotected diethynyl would yield after ring closure in a rhomboid metallacycle with C_2 symmetry instead of the here desired C_i symmetry. To favor monosubstitution, HOP-masked diethynyl 17 was treated with a 3-fold excess of 1,1'-diiodoferrocene using the already described Sonogashira coupling conditions, providing monosubstituted iodoferrocene 19 in moderate isolated yields of 37%.

In contrast to our prior experience with this catalytic system, the reaction progress was slower, and we observed notable quantities of dehalogenated ferrocene derivatives. We thus altered the catalytic system to $Pd(dppf)Cl_2$ with copper(I) iodide for the next coupling and added TIPS-masked diethynyl **18** in a slight excess to the preheated mixture of **19** dissolved in

DIPA/THF. After keeping the reaction mixture at 70 °C for 4 h, desired doubly substituted Fc derivative 20 was isolated also in moderate yields of 35% by FCC. Ferrocene 20 is again an orthogonally HOP and TIPS protected diethynyl, and the TIPS group was efficiently removed by treatment with TBAF in wet THF at 25 °C giving monodeprotected diethynylferrocene moiety 21 almost quantitatively. To favor the formation of open-chain bis-ferrocene 22, the Sonogashira reaction was performed with a 5-fold excess of diiodoferrocene 6. The excess of **6** and the catalysts (Pd(dppf)Cl₂ and CuI were dissolved in a degassed THF/DIPA (2:1) mixture to which acetylene 21 dissolved in degassed THF was added. After keeping the reaction mixture for 2 h at 50 °C, the reaction products were isolated by FCC. Besides desired open-chain bis-ferrocene 22, which was isolated in 38% yield, again oxidative acetylene coupling product 23 was obtained in 23% despite of all attempts to avoid the presence of oxygen. For the final deprotection, HOP-ethynyl derivative 22 was treated with n-Bu₄NOH in degassed toluene at 70 °C for 3 h to provide openchain precursor 24 with an acetylene at one end and an iodoferrocene subunit at the other end.

With open-chain precursor 24 in hand, we were striving for exploring suitable cyclization conditions. To our surprise, all attempts using typical Sonogashira reaction conditions like all the variations used during the assembly of the linkers also failed. Independent of the initial concentration of 24, the desired intramolecular cyclization product was not detected, but instead, exclusively intermolecular reaction products were found by mass-spectrometric analysis of the reaction mixtures, pointing at oxidative acetylene coupling as main competing reaction. After numerous unsuccessful attempts, we investigated copper-free reaction conditions and were delighted to observe the mass signal pointing at the formation of the macrocycle by an intramolecular C-C coupling reaction. By far the best result was achieved with $Pd(PPh_3)_4$ and DIPA in toluene without an additional copper salt.

A 0.1 mM solution of 24 in degassed toluene together with the Pd catalyst and DIPA was kept at 70 °C for 4 h. FCC of the concentrated crude reaction mixture provided desired rhomboid bis-ferrocenemetallacycle 2 as orange solid in 54% isolated yield. Rhomboid 2 was fully characterized by high-resolution mass spectrometry and ¹H and ¹³C NMR spectra, supplemented by advanced NMR experiments (NOESY, HMBC, HMQC, and VT NMR experiments) to determine the spatial arrangement of the subunits.

Spectroscopic Evidence of the Rhomboid Macrocycle. The two peripheral *tert*-butylsulfanyl groups of bis-ferrocene 2 considerably increased its solubility in polar aprotic solvents (e.g., acetone, DCM, THF, EtOAc, and DMF) but also reduced its tendency to crystallize, and so far, all attempts to grow single crystals suitable for X-ray analysis failed. It thus remained a spectroscopic challenge to prove its identity, in particular the rhomboid macrocyclic structure of bis-ferrocene 2. Molecular model analyses displayed an interesting feature of the rhomboidal arrangement which might be observed by variable temperature NMR (VT NMR) experiments. While the rhomboid macrocyclic arrangement of 2 is shape-persistent and cannot interconvert to the deltoid arrangement observed for 1, an additional motion of the macrocyclic framework was expected for 2.

The freely suspended ferrocene subunits between both phenyl rings mounted with revolving ethynyl joints should enable a rotary motion of each Fc subunit within the macrocyclic framework as sketched in Figure 3a. Thereby, the rotation of a single ferrocene unit by 180° should result in a helical arrangement of the macrocycle with a pseudo C_2 symmetry. It is noteworthy that the term "pseudo" for the symmetry description is only correct if exclusively the macrocyclic structure is considered and the two peripheral tert-butylsulfanyl substituents are ignored. Subsequent rotation of the second ferrocene unit renders the initial conformer. Such a rotation is only possible in the rhomboid anti arrangement and should allow its differentiation from the more rigid stacked deltoid arrangement, which does not allow for such motions. Also, the frequency of the rotation is expected to depend on the sample's temperature and might alter the differentiation of the NMR signals of the involved Fc subunits. We thus recorded the ¹H NMR spectra of 2 at 25 °C and successively cooled the sample to -100 °C (Figure 3b). At 25 °C, we observe two overlapping high-order multiplets, one for the 4 Cp α -protons (Cp-ring in para-position) and the 4 Cp α' -protons (Cp-ring in meta-position) that resonate at $\delta = 4.59$ ppm and a further high-order multiplet for 8 Cp β -protons at δ = 4.39 ppm. The observed spectrum reflects the averaged conformation in fast exchange at the NMR time scale.

Gradual lowering of the temperature forces the revolving motion of the ferrocene joints to match the NMR time scale and hence differentiate the protons from interior and exterior position, in which all α -protons become anisochronous δ ($\alpha_{int} \neq \alpha_{ext} \neq \alpha'_{int} \neq \alpha'_{ext}$). Likewise, β -protons diverge into two signals with different chemical shifts $\delta(\beta_{int} = \beta'_{int}) \neq \delta(\beta_{ext} = \beta'_{ext})$. This splitting can be explained by the magnetic inequivalence of the two Cp rings due to the different substitution at the unsymmetric phenyl ring and the spatial variance of protons facing the exterior or interior of the macrocycle. The coalescence temperature ($T_c = 186.7 \pm 0.5$ K) was identified by line shape analysis (LSA) of β -protons and used to determine the rate constant of interconversion $k_{eT_c} \approx$ 71.0 s⁻¹ with an activation energy of $\Delta G_{eT_c}^{\ddagger} = 38.5 \pm 2.2$ kJ mol⁻¹, $\Delta H_e^{\ddagger} = 44.8 \pm 2.0$ kJ mol⁻¹, and $\Delta S_e^{\ddagger} = 34.0 \pm 1.6$ J K⁻¹ mol⁻¹ (see Figure S77). The positive entropy term suggests a transition state with reduced symmetry (see Figure S10).

It is noteworthy that similar dangling motions of ferrocene subunits heteroannularly integrated in macrocycles have already been reported (e.g., the helical ferrocene porphyrinoids reported by Stępień et al.).²⁹

DFT Calculations. To get a better insight into the energies involved in the revolving motion of the Fc subunits analyzed by the VT NMR experiment discussed above, the rotational barrier was estimated by calculating the energy content of three extreme conformers (see Figure 4), namely, the starting point



Figure 4. Relative energy diagram of the calculated conformers of the macrocycle 2 together with the Gibbs free energy of the transition state obtained by the VT NMR experiment in red.

of coplanar rhomboid 2 with C_i symmetry, the "helical" macrocycle with pseudo- C_2 symmetry as end point of a single Fc subunit 180° rotation, and the transition state with a rotation of the moving Fc subunit of about 90°, which was considered as proxy for the highest point in the energetic landscape between both conformers. The geometries of the coplanar and the helical conformer of rhomboid 2 were optimized. Calculations were carried out using the Gaussian09 suite of codes,³⁰ on the B3LYP level of theory using a mixed basis set. C, H, and S atoms were treated with 6-31G**, whereas Fe was treated with the LANL2DZ basis set.^{31,32} The transition state with one Fc subunit perpendicular to the second one was located using the Synchronous Transit Guided Quasi-Newton (STQN) method.³³ As already expected from the VT NMR experiment, very comparable energy contents were obtained for the two conformers, with the relaxed helical ground state conformer being 3.6 kJ mol⁻¹ above the coplanar ground state structure. With $\Delta E^{\ddagger} = 70.1$ kJ mol⁻¹, the calculated activation energy of the Fc revolving motion is of comparable dimension as the Gibbs free energy value ΔG^{\ddagger} = 38.5 kJ mol⁻¹ obtained by the VT NMR experiment. The lower value obtained experimentally might be explained by the solvation of the transition state in the NMR experiment, which is not considered in the DFT calculation.

In conclusion, the analysis of the VT NMR spectra and their comparison with calculated values fully corroborated not only the rhomboidal arrangement of macrocycle 2 but also the second part of our starting hypothesis, namely, that the bulkiness of the peripheral substituents steers the conformational equilibrium and thereby determines the product formed in the ring closing C–C coupling reaction (see Scheme 1).

Electrochemical Analysis. Both bis-ferrocene metallacycles, deltoid 1 and rhomboid 2, consist of two ferrocene subunits which are each interlinked with both Cp units by *ortho*-diethynylbenzene connections. While the separation of both Fc subunits is comparable in both structures, the mobility of each Fc subunit within the framework of the metallacycle alters considerably, as already discussed in the section before. As the Fc joints are at the same time the redox-active subunits of both structures, their electrochemical investigation was of particular interest.

The redox properties of 1 and 2 were first studied using cyclic voltammetry (CV) and square wave voltammetry (SWV) in CH_2Cl_2 using *n*-Bu₄NPF₆ as the supporting electrolyte. The results are displayed in Figure 5 and summarized in Table 1.



Figure 5. CV and SWV (dashed lines) curves of 1 (a) and 2 (c) with n-Bu₄NPF₆ as supporting electrolyte in DCM at 25 °C. The curve in panel b further displays the irreversible behavior of 2 when a wide potential window is exploited.

Table 1. Half-Wave Potentials $(E_{1/2}) = (E_{pa} - E_{pc})/2$, SWV Potentials in Parentheses for Complexes 1 and 2 in CH₂Cl₂ + *n*-Bu₄NPF₆ 0.1 M or NaBARF 0.005 M^{*a*}

complex	$E_{1/2}$ n-Bu ₄ NPF ₆	$E_{1/2}$ NaBARF	$E_{1/2}$ NaBARF
1	0.63 (0.67)	0.54 (0.56)	
2	0.63 (0.66)	0.13 (0.18)	0.41 (0.46)
^a Glassy carbo	on WE $Ø = 2 \text{ mm}, \nu$	$= 0.1 \text{ V s}^{-1}$, <i>E</i> vs	SCE in CH ₂ Cl ₂ at

25 °C with the respective electrolyte.

For compound 1, a single, reversible oxidation wave $(i_{pa}/i_{pc} \approx 1, i_p \propto v_s^{1/2}$ see Figure S4) at $E_{1/2} = 0.63$ V vs SCE is observed (Figure 5a) and formally attributed to the overlapping but sequential oxidation of both Fe^{II} centers to Fe^{III}. In the case of bis-ferrocene 2, two irreversible oxidation waves were observed at $E_{1 Pa} = 0.63$ V and $E_{2 Pa} = 1.68$ V vs SCE when scanning up to 1.8 V (Figure 5b).

Such reversibility challenges are well-known from studies on multiferrocenyl compounds when *n*-Bu₄NPF₆ in CH₂Cl₂ is used.^{34,35} When scanning up to 1.4 V vs SCE, only a single, reversible $(i_{\rm pa}/i_{\rm pc} \approx 1, i_{\rm p} \propto v_{\rm s}^{1/2}$, see Figure S5) two-electron oxidation wave was detected (Figure 5c). In literature, single-step multiple-electron transfers are common for multiferrocene complexes when a [PF₆]⁻ salt is employed.^{36–41} Diallo et al. deduced thereof that strong ion pairing as facilitated by nucleophilic [PF₆]⁻ ions, shield the electrostatic interaction

between two redox centers; hence, low electronic coupling between those redox centers leads to independent response.

Consequently, if a single redox wave is observed, then low electronic through-bond communication between the redox centers can be assumed. This is in accordance with the single redox wave recorded for fully conjugated 1,2-bis-(ferrocenylethynyl)-benzene, when n-Bu₄NPF₆ in CH₂Cl₂ is used.¹⁶

Barrière and Geiger reported that using a perfluorinated electrolytes such as BARF (*tetrakis*[3,5-bis(trifluoromethyl)-phenyl]-borate) weakens ion-pairing effects and favors the observation of electrostatic through-space communication.⁴² Consequently, we recorded CV and SWV voltammograms of bis-ferrocene 1 and 2 with NaBARF as supporting electrolyte in CH_2Cl_2 (Figure 6). In the case of compound 2, a well-resolved



Figure 6. CV and SWV (dashed lines) curves of 1 (a) and 2 (b) with NaBARF as supporting electrolyte in CH_2Cl_2 vs SCE at 25 °C.

two one-electron redox curve was recorded with half-wave potentials at $E_{1/2} = 0.13$ V and $E_{1/2} = 0.41$ V vs SCE (Figure 6b). Each redox event exhibits reversible behavior ($i_{pa}/i_{pc} \approx 1$, $i_p \propto v_s^{1/2}$, see Figures S5 and S6, respectively), and voltammograms of bis-ferreocene 1 displays a broad wave, with a lowered half-wave potential at $E_{1/2} = 0.53$ V vs SCE (Figure 6a). This seemingly complementary characteristic can be explained with the structure of the compounds. In the neutral form, the ferrocenes in 1 are relaxed and have no motivation to obtain opposing sides.

When the redox centers are oxidized, the Coulomb repulsion between the two Fe^{III} atoms forces them to turn out of plane. Obviously, the rigid structure of 1 does not facilitate free rotation along the Cp-sp single bonds. Twisting comes along with high conformational stress, which slows down the electron transfer rate and consequently broadens the redox wave. In contrast, bis-ferrocene 2 was shown to have highly flexible ferrocene joints that can freely twist, thereby reducing electrostatic repulsion which permits fast and sequential oxidation. These results allow to tentatively conclude the following: (i) The electronic through-bond communication between the two ferrocenes in 1 and 2 is insignificant, which consequently provides a framework capable of supporting charge localization, evident by absent wave splitting in a $[PF_6]^$ electrolyte media. (ii) The large half-wave potential split in compound **2** of $\Delta E_{1/2}$ = 280 mV and the broadened redox wave in bis-ferrocene 1 suggest considerable through-space communication when BARF is employed as electrolyte. These characteristics deliver the essentials for field-coupled applications in material science.^{37,43,44}

CONCLUSION

Two new bis-ferrocene macrocycles are presented, namely, rigid C_2 symmetric deltoid molecule 1 and rhomboidal shaped bis-ferrocene 2. Both are assembled by very similar Sonogashira-type coupling chemistry with tuned steric interactions in the ring closing step as decider whether the deltoid or the rhomboid structure is formed. While the identity of 1 is corroborated by its solid-state structure, only rhomboid 2 is able to allow for revolving motions of the ferrocene-subunits observed by VT NMR studies. Electrochemical investigations of 1 and 2 display through-space electrostatic interaction between both ferrocene subunits for both macrocycles. We are currently investigating the potential of such rhomboid bis-ferrocene macrocycles as electrochemically triggered single molecule mechanical transformers.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.6b00909.

General details, synthesis and spectroscopic data and copies of ¹H and ¹³C NMR spectra of new compounds. Experimental details on electrochemical measurements. Further details on theoretical calculations. Copies of VT NMR, 2D NMR and HRMS spectra of new compounds. (PDF)

Cartesian coordinates of computed structure of rhomboid coplanar 2 (XYZ)

Cartesian coordinates of computed structure of rhomboid helical 2 (XYZ)

Cartesian coordinates of computed transition state structure of rhomboid 2 (XYZ)

Crystallographic information file of compound 1 (CIF)

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Notes

The authors declare no competing financial interest.

Crystal data of compound 1 (CCDC 1515120) are also deposited with the Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk, e-mail: structures@ccdc.cam.ac.uk, fax: +44 (0)1223 336033).

ACKNOWLEDGMENTS

The authors thank the Swiss National Science Foundation (SNF) (grant number 200020-159730) for continuous and generous financial support.

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