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[1.1]Ferrocenophane-1,12-dione as a Precursor of 1,12-Di(cyclopenta-2,4-dienylidene)-[1.1]ferrocenophane, a Doubly Bridged Difulvene

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Dedicated to Armin de Meijere on the occasion of his 70th birthday.

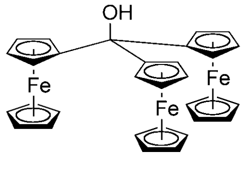
Abstract: An improved synthesis of [1.1]ferrocenophane-1,12-dione (**2**) by oxidation of [1.1]ferrocenophane with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) is presented. The *syn* conformer of dione **2** is structurally characterized. The compound undergoes various addition reactions at the bridging carbonyl groups. Attempts to add 1,1′-dilithioferrocene result, however, in the diadduct **9**, not in the symmetric trinuclear diol **8**. Reaction of **2** with sodium cyclopentadienide in the presence of aluminium trichloride ($AlCl_3$) gives the respective difulvene **11** in excellent yield. The dynamic behavior of **11** is investigated by variable temperature ^1H NMR measurements (VT-NMR). The cyclovoltammogram of **11** indicates two reversible oxidation steps. Reduction of difulvene **11** with lithium aluminium hydride ($LiAlH_4$) results in the formation of [1.1]ferrocenophane **12** with cyclopentadienyl anion substituents at either one of the two bridges. While attempts to generate a third ferrocene moiety by reaction with iron(II) choride ($FeCl_2$) have failed so far, the formation of **12** is established by protonolysis and methylation reactions.

Keywords: conformation; ferrocene; ferrocenophane; fulvenes; variable temperature NMR

Introduction

More than 50 years after its discovery by Pauson[1,2] and Miller[3] ferrocene still is the subject of research in numerous fields of chemistry.[4] These include important areas such as asymmetric catalysis,[5–10] bioorganometallic chemistry,[11,12] the construction of novel organometallic architectures,[13] molecular electronics,[14,15] redox active entities,[16] and material sciences.[17–19]

In contrast to compounds with one ferrocene unit, those incorporating more ferrocene moieties have been investigated to a lesser extent.[20–23] Our interest in the chemistry of systems with more than one ferrocene unit includes compounds with a triferrocenylmethyl moiety[24,25] as well as conceptually new molecular wires with ferrocene hinges thereby adding limited conformational flexibility to otherwise rigid molcular wires.[26,27] While ferrocenes, which are connected by one bridge, are still conformationally rather flexible, this is usually not the case with multibridged ferrocenophanes.[28,29] Here we report on an improved synthesis of [1.1]ferrocenophane-1,12-dione (**2**), its structural characterization and dynamic behavior in solution as well as on some reactions of this compound. The incentive for this research was the possibility of an introduction of a third ferrocene unit in order to get an access to the symmetrical trinuclear ferrocenophane with two tris(cyclopentadienyl)methane ligands, a gallium analogue of which had earlier been prepared by Jutzi.[30,31]



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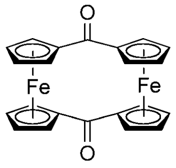

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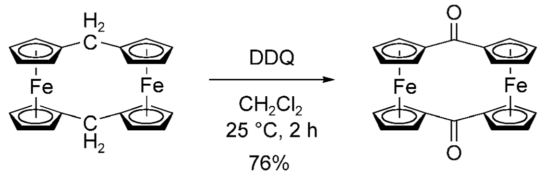
Results and Discussion

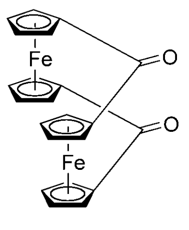
Compound **2** was first prepared by Watts et al. by double Friedel–Crafts alkanoylation of ferrocene with 1,1′-di(chlorocarbonyl)ferrocene or by self-condensation of (chlorocarbonyl)ferrocene.[32] However, the yields achieved did not exceed 7%. Kasahara et al. obtained **2** by carbonylation of 1,1′di(chloromercuri)ferrocene in the presence of lithium tetrachloropalladate in methanol at 50 atm pressure of CO in addition to significant amounts of biferrocenyl and methyl ferrocenecarboxylate.[33] Cowan et al. obtained **2** in only 13% yield by reacting 1,1′-bromoferrocene with 2 equivalents of butyllithium followed dimethylcarbamoyl chloride.[34] Watts et al. described the oxidation of [1.1]ferrocenophane (**3**) with MnO_2 in boiling benzene to result in the formation of [1.1]ferrocenophane-1,12-dione (**2**) in up to 89% yield.[35,36] However, in our hands the reaction never went to completion, often the starting material was consumed, presumably by adsorption on the metal oxide without adequate product formation. As MnO_2 oxidations are known to frequently give varying results depending on the specific MnO_2 used, we tried to perform the oxidation of **3** with dichlorodicyanoquinone (DDQ) in dichloromethane at 25 °C, and it was found that this reagent effected the double oxidation of **3** in a good and reproducible yield of 76%. No overoxidation to Fe(III) species was observed. The product **2** was identified by comparison of its NMR data with those published.[34]



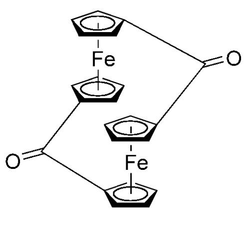
3 **2**

[1.1]Ferrocenophanes are expected to exist in two different conformations, a *syn* conformation with the two bridges standing on the same side and an *anti* conformation with the bridges standing on opposite sides. With respect to **2** the conformers *syn*-**2** and *anti*-**2** have to be considered.

Models show the *anti* conformers to be quite rigid systems, which have no way to escape a steric interaction of the α hydrogen atoms pointing to the other ferrocene unit. In contrast, the *syn* conformers are considered to be much more flexible with a coupled rotation of the ferrocene units allowing for the adoption of a twisted conformation with minimized steric repulsion of the respective α hydrogen atoms. By way of such a twisted conformation a degenerate conformational change has been formulated, which converts a *syn* conformation into its mirror image with a formal exchange of the α hydrogen atoms.[28] VT-NMR studies are in accord with this assumption.[37] However, the discovery of Ahlberg et al. that a 1,12-dimethyl[1.1]ferrocenophane adopts an *anti* conformation does not allow a simple conformational assignment for [1.1]ferrocenophanes.[38] While the mixed [1.1]ferrocenoruthenocenophane-1,12-dione adopts the *syn* conformation in the solid state,[37] the structure of **2** has so far not been reported. However, the similarities in the NMR spectra made the authors suggest a *syn* conformation of **2** in solution; however, no structural information has become available so far.[37] Recrystallization of **2** from chloroform/hexane afforded crystals suitable for an X-ray crystal structure analysis (Figure 1).



syn-**2**



anti-**2**

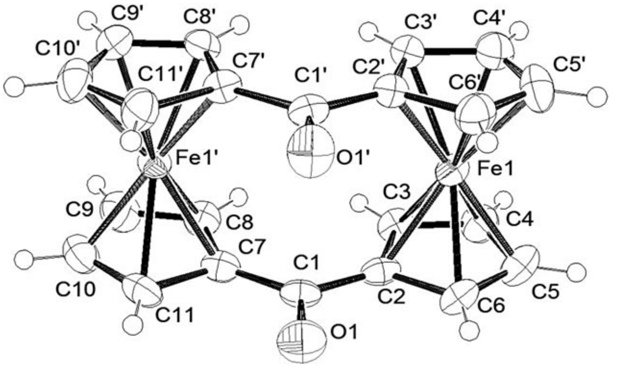
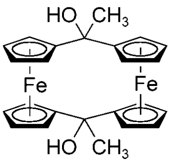


Figure 1. Structure of **2** in the crystal.[39] Selected bond lengths [pm], angles [°] and dihedral angles [°]: O1−C1 123.6(9), O1′−C1′ 121.4(8), C1−C7 148.0(10), C1−C2 148.5(10), C1′−C2′ 148.1(9), C1′−C7′ 149.0(9), O1−C1−C7 118.8(7), O1−C1−C2 117.5(6), C7−C1−C2 123.6(7), O1′−C1′−C2′ 118.7(6), O1′−C1′−C7′ 118.7(7), C2′−C1′−C7′ 122.5(7), C3−C2−C1−C7 −0.5, C8−C7−C1−C2 −1.4, C11−C7−C1−O1 1.9, C5−C6−C2−C1 −178.8, C3′−C2′−C1′−C7′ −0.4, C8′−C7′−C1′−C2′ −0.5, C11′−C7′−C1′−O1′ −1.4, C5′−C6′−C2′−C1′ −179.6.

While in many [1.1]ferrocenophanes the ferrocenyl units are twisted in order to alleviate the steric repulsion between the inner protons,[40] **2** adopts an almost perfect coplanar *syn* conformation with the cyclopentadienyl ligands of the ferrocene moieties being eclipsed and parallel to one another. The distance between the inner α protons can be calculated to be 208.4 and 211.1 pm, which are significantly shorter than the sum of the van der Waals radii of two hydrogen atoms (240 pm). The solid state structure obviously differs from that in solution, as the ^{1}H NMR spectrum shows only two signals at 298 K and above ($\delta =$ 4.5, 5.27 ppm in $CDCl_3$) indicating equivalence of all α and all β hydrogen atoms, respectively, as a result of an exchange due to the molecular dynamics being rapid relative to the NMR time scale. However, coalescence leading to eight different signals at 220 K has been observed by Watanabe et al.[37]

Presumably due to its low-yielding synthesis and poor solubility in most solvents the chemistry of [1.1]ferrocenophane-1,12-dione (**2**) has only marginally been investigated. Compounds obtained from **2** by Barr et al. include **3**, which was obtained by reduction with $LiAlH_4/AlCl_3$ in 87% yield, the 1,12-dimethyl-1,12-diol **4** obtained by reaction with MeMgI, which was reported to be unstable and was reduced with $LiAlH_4/AlCl_3$ to the 1,12-dimethyl derivative **5**.[36]



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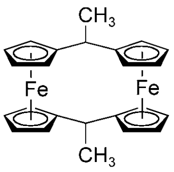

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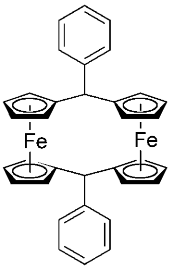

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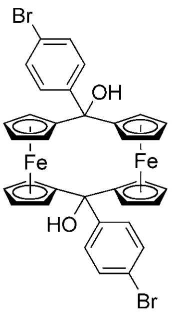

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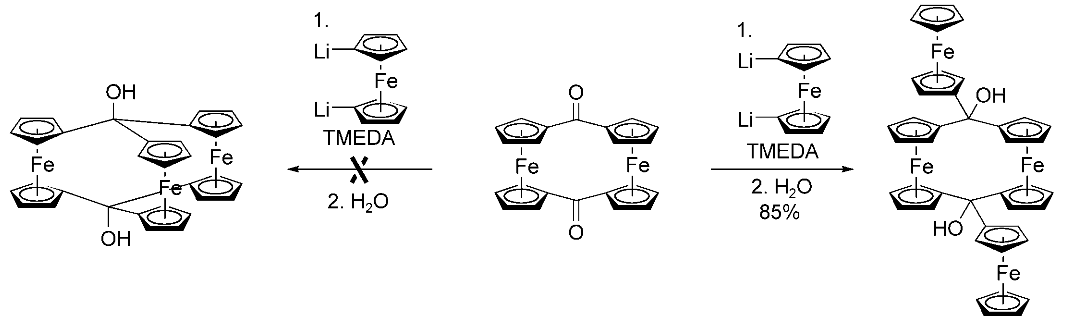
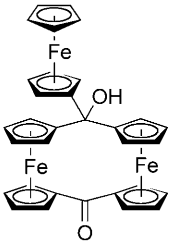
In order to test the implementation of unsaturated substituents, the diaddition of phenyllithium followed by reduction with $LiAlH_4/AlCl_3$ was tried and led to **6** in 39% yield. The compound had earlier been prepared by a different route and was identified by comparison of the ^{1}H NMR data with those published.[36] Similarly, **7** was obtained in 98% yield by reaction of **2** with (4-bromophenyl)lithium in the presence of an excess of $AlCl_3$. Compound **7** was identified by its IR, ^{1}H, ^{13}C NMR and mass spectra. An attempt directed to get access to the multibridged ferrocenophane **8** by a diaddition of 1,1′-dilithioferrocene was tried under dilution conditions ($c = 5 \times 10^{-4}$ mol/L) in order to facilitate the monoaddition. In the ESI mass spectrum peaks at $m/z = 796$ and 610 were particularly interesting. While the peak at $m/z = 796$ corresponds to diadduct **9**, the peak at $m/z = 610$ either corresponds to the desired diol **8** or to the isomeric keto alcohol **10**. To differentiate between these possibilities the mixture was treated with HBF_4 causing a dehydration and formation of the respective cations. Inspection of the ESI MS taken from this mixture clearly showed signals in accord with the monocation derived from **10** ($m/z = 593$) and not of the dication expected from **8** ($m/z = 288$). Diadduct **9** was obtained in 85% yield, the complex was identified on the basis of its spectroscopic data.

6-Ferrocenylfulvenes have proven to be suitable starting materials for ferrocenophanes.[28,36,41,42] In an attempt to access the multibridged framework of **8** it was reasoned that the difulvene **11** might be a suitable



8 **2** **9**



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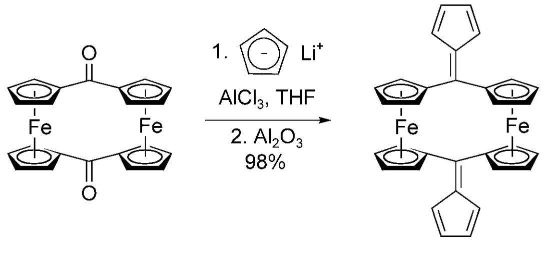
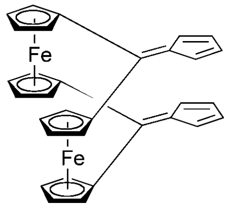
precursor. Although **11** has been mentioned in a review article by Mueller-Westerhoff, no synthesis or characterization has been published.[28] Reaction of lithium cyclopentadienide in the presence of $AlCl_3$ to [1.1]ferrocenophane-1,12-dione (**2**) gave a mixture from which the desired difulvene **11** was isolated in 98% yield by column chromatography on basic alumina as a red-black liquid and was characterized spectroscopically.

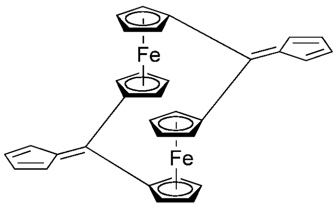


2 **11**

Just as for **2**, also for **11** two different conformations have to be considered, *syn*-**11** and *anti*-**11**. Like for **2** the *anti* conformation is considered to be rigid while the *syn* conformation might undergo a degenerate conformational change to its mirror image. In order to elucidate this possibility, variable temperature ^{1}H NMR measurements were performed. While the "inner" and the "outer" α and β protons of the cyclopentadienyl ligands are different in *syn*-**11** the degenerate interconversion process should make them equivalent on the NMR time scale at fast exchange.



syn-**11**



anti-**11**

Indeed, the signals assigned to the cyclopentadienyl ligand protons showed coalescence in VT-NMR spectra in toluene-d_8 at 500.1 MHz (Figure 2). While there are two signals (AA′BB′ pattern) for the cyclopentadienyl protons at room temperature, lowering of the temperature caused a broadening of these signals. Below the coalescence temperature of $T_c = 192$ K the signal at lower field, which is assigned to the α protons, split into two signals, which appeared at $\delta = 4.6$ and 4.9 ppm ($\nu = 1853.37$ and 1977.21 Hz). Re-heating to 198 K gave the original signal. These data correspond to an activation energy for the process of $\Delta G^{\neq} = 38\ \mathrm{kJ\,mol^{-1}}$, which is somewhat smaller than that determined for the corresponding process in [1.1]ferrocenophane-1,12-dione ($\Delta G^{\neq} = 60\ \mathrm{kJ\,mol^{-1}}$, $T_c = 285$ K, 400 MHz).

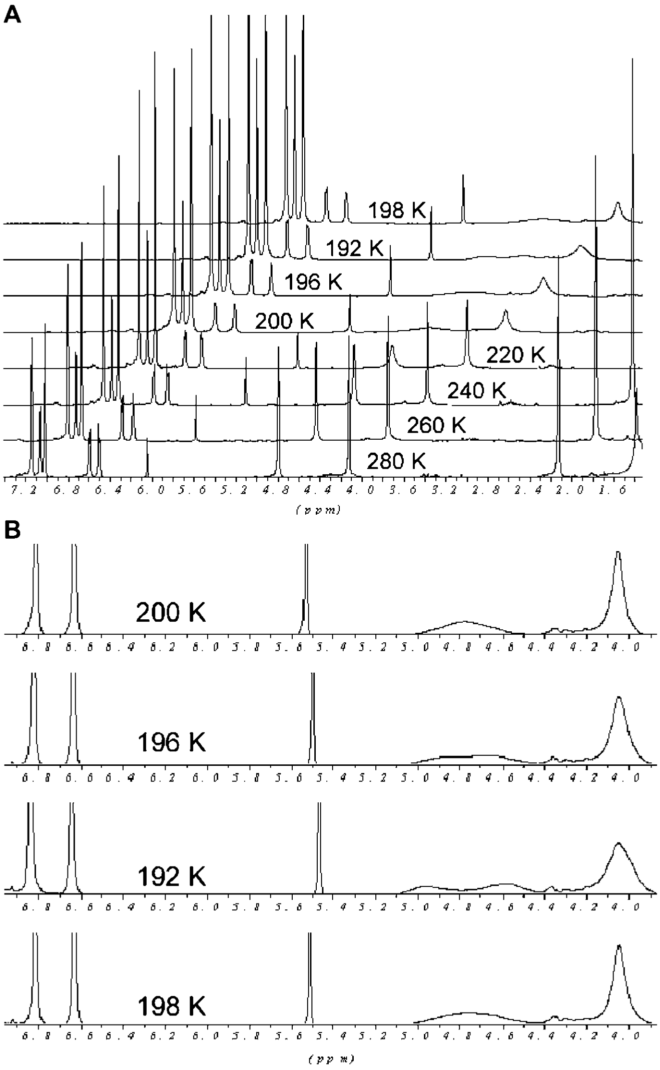


Figure 2. Variable temperature ^{1}H NMR spectra of **11** in toluene-d_8 at 500.1 MHz. **A**: spectra obtained between 280 K and 192 K with re-heating to 198 K. **B**: expansion of spectra obtained between 200 K and 192 K with re-heating to 198 K.

Compound **11** was also characterized by cyclic voltammetry. The measurements show two reversible redox processes at $E_{1/2} = 56.5$ and 308 mV, presumably corresponding to the reversible oxidation to the Fe(II)-Fe(III) and further to the Fe(III)-Fe(III) species (Figure 3, Table 1).

In order to obtain a ligand system suitable for generation of a third ferrocene unit,[43] difulvene **11** was reduced with an excess of $LiAlH_4$. We expected that the di(cyclopentadienyl) ligand system **12** would be well suited for the insertion of the third iron atom. The reduction led after hydrolysis in 90% yield to an

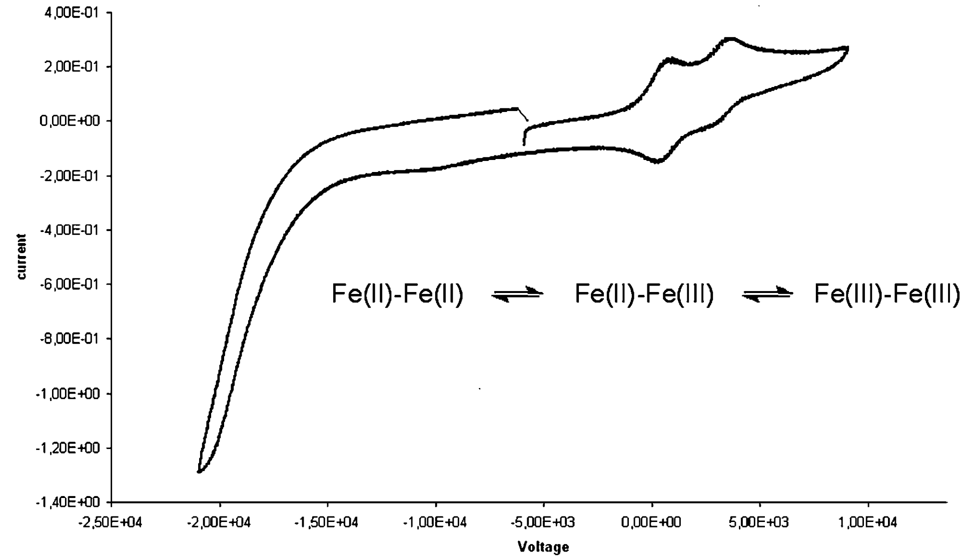
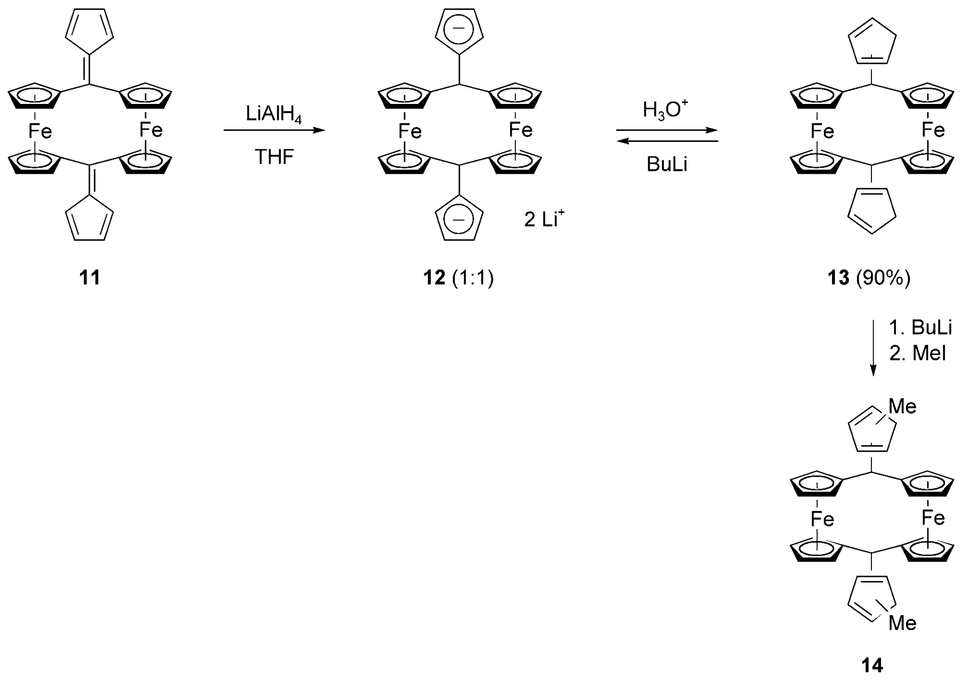


Figure 3. Cyclic voltammogram of **11**. Potential in mV *vs.* FcH/FcH$^+$, $v=2$ V/s, $T=25\,°C$, $c=0.5$ mmol L,$^{-1}$ $c_{TBAHFP}=0.2$ mol/L (TBAHFP $=Bu_4N^+$ PF_6^-) in acetonitrile; current in μA.

Table 1. Cyclic voltammetry data of **11**. For conditions see Figure 3.

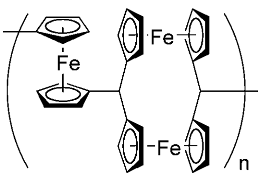
E_a [mV]	i_a [μA]	E_k [mV]	i_k [μA]	ΔE [mV]	$E_{1/2}$ [mV]	i_a/i_k	$i_k/v^{1/2}$ [μAs$^{1/2}$ V$^{-1/2}$]
94.5	0.232	32.5	−0.153	63.5	56.5	−1.5	0.108
357.5	0.306	258.5	−0.027	99	308	−13.3	0.019

approximately 1:1 *endo-exo/exo-exo* diastereomeric mixture of **13**, which was characterized spectroscopically. The NMR spectra were further complicated by the cyclopentadienyl substituents bonded at C-1(4), C-2(3), or C-5. However, this is not of much concern as a deprotonation would lift this issue. In order to test this, a sample of **13** was deprotonated with butyllithium followed by addition of iodomethane. The im-



plementation of two methyl groups was then confirmed by mass spectrometry.

All attempts to trap dianion **12** with $FeCl_2 \cdot 2THF$ under dilution unfortunately led to insoluble, presumably polymeric material, which we so far were unable to characterize. We suggest that the material was the result of intermolecular reaction instead of the desired intramolecular reaction and propose, based on the synthesis, constitution **15**.



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Conclusions

In conclusion, we have found a reliable synthesis of [1.1]ferrocenophane-1,12-dione (**2**), making amounts of this compound accessible that allow investigations of its chemistry. Compound **2** exists as the *syn* conformer in the solid state. Reaction of **2** with 1,1′-dilithioferrocene yields diadduct **9** instead of the desired trinuclear monoadduct **8**. Reaction of **2** with lithium cyclopentadienide/$AlCl_3$ affords difulvene **11** in almost quantitative yield. Compound **11** can be reduced to the dicyclopentadienyl dianion **12** in high yield as demonstrated by hydrolysis resulting in **13** in 90% yield. In addition, **12** has been dimethylated with MeI further confirming its dianionic nature. Attempts to trap dianion **12** with $FeCl_2 \cdot 2THF$ at high dilution gave insoluble polymeric material only, for which we propose constitution **15**.

Future attempts to realize the trapping of dianion **12** in a way allowing the formation of trimetallic derivatives will include the use of metal halides of other metals such as ruthenium and zirconium. While ruthenium might facilitate the desired reaction due to its larger size thereby reducing steric constraints in the target molecule, the bent nature of zirconocene derivatives might be beneficial.

Experimental Section

General Remarks

All operations involving air-sensitive materials were performed under argon using standard Schlenk techniques. Diethyl ether (EE) and THF were dried over Na/K-benzophenone; petroleum ether (PE) was distilled from calcium chloride. Dichloromethane was dried over CaH_2 and distilled under Ar prior to use. Starting materials were either purchased or prepared according to literature procedures. IR: Perkin–Elmer 2000, FT 1170 (ATR). ^1H NMR: Bruker AM 500 (500 MHz), AVS 400 (400.1 MHz). Chemical shifts refer to $\delta_{TMS}=0$ ppm or to residual solvent peaks. br: broad, unresolved signal. ^{13}C NMR: Bruker AVS 400 (100 MHz). Chemical shifts refer to $\delta_{TMS}=0$ ppm or to residual solvent peaks. MS (EI, ESI-MS): AMD 604 Inectra, Finnigan MAT 112, MAT 312, 70 eV. HR-MS: Finnigan MAT 312, VG Autospec. Melting points: Electrothermal IA 9200. CV: Potentiostat Heka PG 285, reference electrode Ag/AgCl (Alfa), counter electrode Pt wire, 0.1 M tetrabutylmmonium hexafluorophosphate (Fluka, electrochemical grade), dichloromethane, potential normalized to ferrocene/ferrocenium ion ($E_0=0.35$ V *vs.* Ag/AgCl).

[1.1]Ferrocenophane-1,12-dione (2)[36]

At 25 °C, to a well stirred solution of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ, 2.900 g, 12.7 mmol) in 1 L of CH_2Cl_2, [1.1]ferrocenophane (**3**)[35,42] (0.598 g, 1.5 mmol) in 200 mL CH_2Cl_2 was added dropwise, and the solution immediately darkened. The reaction mixture was stirred at 25 °C for 2 h before hydrolysis was performed by addition of 200 mL of MeOH. The reaction mixture was washed with 200 mL of a 1.0 M aqueous solution of NaOH until the aqueous layer was colorless, washed with 200 mL of H_2O, dried over $MgSO_4$, and the solvent was removed under reduced pressure. Column chromatography (neutral alumina, 25 × 4 cm, CH_2Cl_2/EE 9:1) gave pure [1.1]-ferrocenophane-1,12-dione (**2**), identified by comparison of the ^1H NMR data with the published values;[35,36] yield: 0.490 g (1.2 mmol, 76%). Recrystallization from $CHCl_3$/hexane gave pure crystals suitable for an X-ray structure analysis. ^1H NMR (200 MHz, $CDCl_3$): $\delta=4.5+5.27$ (AA′BB′ line system, 2 × 8H, CpR); MS (70 eV, 240 °C): *m/z* = 425 (50) $[M^+ + H]$, 330 (41) $[M^+ - COCp]$, 304 (53) $[M^+ - CpFe]$, 243 (100) $[M^+ - Fc + 3H]$.

Crystal Structure Analysis of 2[39]

$C_{22}H_{16}Fe_2O_2$, molecular weight 424.05 $g\,mol^{-1}$, temperature 300(2) K, wavelength 0.71073 Å, crystal system triclinic, space group P-1, $a=6.053(1)$, $b=14.224(2)$, $c=14.703(2)$ Å, $\alpha=71.12(2)°$, $\beta=87.26(2)°$, $\gamma=89.66(2)°$, $V=1196.4(3)$ Å^3, $Z=3$, $\rho_{calcd.}=1.766\ g\,cm^{-3}$, $F(000)=648$, absorption coefficient = 1.833 mm^{-1}, crystal size 0.96 × 0.04 × 0.03 mm, Stoe IPDS area detector diffractometer, θ-range = 2.42 to 26.20°, limiting indices $-7 \leq h \leq 7$, $-17 \leq k \leq 17$, $-18 \leq l \leq 18$, reflections collected/unique 17203/4404 [R(int) = 0.0623], completeness of data (θ = 26.20): 91.4%, no absorption correction, no extinction correction, refinement method full-matrix least-squares on F^2, goodness-of-fit on $F^2=1.070$, $R_1=0.0637$, $wR_2=0.1322$ ($I>2\ \sigma(I)$), R-indices[all data]: $R_I=0.1044$, $wR_2=0.1415$, minimal and maximal residual electron density $-0.631/0.589$ e Å^{-3}.

exo,exo-1,12-Diphenyl[1.1]ferrocenophane (6)[36]

At 25 °C phenyllithium (1 mL, 1.8 M in cyclohexane, 1.8 mmol) was added to a well stirred solution of [1.1]ferrocenophane-1,12-dione (**2**, 0.121 g, 0.3 mmol) in 100 mL of anhydrous THF. After 1 h at 25 °C, $AlCl_3$ (0.90 g, 0.7 mmol) and $LiAlH_4$ (0.098 g, 2.5 mmol) were added, and the suspension was stirred for 1 h. Hydrolysis was performed by slow addition of 10 mL of H_2O. The reaction mixture was diluted with 50 mL of PE, and the organic layer was washed with 3×25 mL of H_2O, dried over $MgSO_4$, and the solvent was removed at reduced pressure. Column chromatography (neutral aluminum oxide, 25×2 cm, PE/CH_2Cl_2, 3:1), gave pure *exo,exo*-1,12-diphenyl[1.1]ferrocenophane (**6**), identified by ^{1}H NMR comparison;[36] yield: 0.065 g (0.2 mmol, 39%).^{1}H NMR (200 MHz, $CDCl_3$): δ=4.20 (m, 4H, CpR), 4.35 (m, 4H, CpR), 4.42 (m, 4H, CpR), 4.75 (m, 4H, CpR), 5.20 [s, 2H, 11(11′)-H], 7.00–7.20 (m, 10H, Ph) ppm.

exo,exo-1,12-Di(4-bromophenyl)-[1.1]ferrocenophane-1,12-diol (7)

At 25 °C 4-bromo-1-lithiobenzene [from 1,4-dibromobenzene (0.500 g, 2.1 mmol), *tert*-BuLi (2.35 mL, 1.7 M in pentane, 4.0 mmol) in 20 mL of anhydrous THF] was added to a well stirred solution of [1.1]ferrocenophane-1,12-dione (**2**, 0.070 g, 0.2 mmol) and $AlCl_3$ (0.105 g, 0.8 mmol) in 50 mL of anhydrous THF. After 1 h at 25 °C, $LiAlH_4$ (0.300 g, 8.0 mmol) was added, and the suspension was stirred for 1 h. Hydrolysis was performed by slow addition of 10 mL of H_2O. The reaction mixture was diluted with 50 mL of PE, and the organic layer was washed with 3×25 mL of H_2O, dried over $MgSO_4$, and the solvent was removed at reduced pressure. Column chromatography (neutral alumina, 25×2 cm, PE/CH_2Cl_2, 3:1), gave pure *exo,exo*-1,12-di(4-bromophenyl)-[1.1]ferrocenophane (**7**) as a yellow solid; yield: 0.120 g (0.2 mmol, 98%); mp > 200 °C, dec.). IR (ATR): $\tilde{\nu}$=3450 (w, OH), 3318 (w, OH), 2963 (w), 2924 (w), 2853 cm^{-1} (w); ^{1}H NMR (400 MHz, $CDCl_3$): δ=4.20 (m, 4H, CpR), 4.37 (m, 8H, CpR), 4.71 (m, 4H, CpR), 4.91 (s, 2H, OH), 7.02 (d, ^3J=6.8 Hz, 4H, Ph), 7.19 (d, ^3J=6.8 Hz, 4H, Ph); ^{13}C NMR (100 MHz, BB, HMQC, HMBC, $CDCl_3$): δ=66.1 (C_{Fc}H), 68.3 (C_{Fc}H), 68.7 (C_{Fc}H), 70.2 (C_{Fc}H), 73.4 (C_{Fc}R), 98.1 (COH), 120.1 (HOCC_{Ph}), 126.6 (BrCC*C*H), 130.7 (BrC*C*H), 149.6 (CBr); MS (ESI, ES$^+$): *m/z*=738 [M+H$^+$], 658 [M+H$^+$–Br]; HR-MS (ESI): *m/z*=735.9000 [M], calcd. for $C_{34}H_{26}Br_2Fe_2O_2$: 735.8998.

exo,exo-1,12-Diferrocenyl-[1.1]ferrocenophane-1,12-diol (9)

At 25 °C 1,1′-dilithioferrocene [from ferrocene (**14**) (1.00 g, 5.4 mmol), TMEDA (2.20 mL, 14.6 mmol), BuLi (9.00 mL, 1.6 M in hexane, 14.4 mmol)[44]] in 12.5 mL of anhydrous hexane was added to a well stirred solution of [1.1]ferrocenophane-1,12-dione (**5**, 0.050 g, 0.1 mmol) in 25 mL of anhydrous THF. After 1 h at 25 °C, hydrolysis was performed by addition of 10 mL of H_2O. The reaction mixture was diluted with 50 mL of CH_2Cl_2, and the organic layer was washed with 3×25 mL of H_2O, dried over $MgSO_4$, and the solvent was removed under reduced pressure. Column chromatography (SiO_2 deactivated with Et_3N 5% in PE, 25×4 cm, PE/CH_2Cl_2, 7:3), gave pure *exo,exo*-1,12-diferrocenyl-[1.1]ferrocenophane-1,12-diol (**9**); yield: 0.068 g (0.1 mmol, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=3.83 (m, 4H, CpR), 3.94 (m, 4H, CpR), 4.05 (s, 10H, CpH), 4.27 (m, 8H, CpR), 4.58 (m, 4H, CpR), 4.67 (m, 4H, CpR), 4.90 (s, 2H, OH); ^{13}C NMR (100 MHz, BB, HMQC, HMBC, 297 K, $CDCl_3$): δ=66.1 (C_{CpR}H), 67.0 (C_{CpR}H), 67.1 (C_{CpR}H), 67.3 (C_{CpR}H), 67.7 (C_{CpR}H), 68.7 (C_{CpH}H), 70.2 (C_{CpR}H), 70.7 (C_{CpR}R), 97.1 (C_{CpR}R), 103.0 [COH]; MS (ESI, ES$^+$): *m/z*=796 [M$^+$], 779 [M$^+$–OH]; HR-MS (ESI): *m/z*=786.0103 [M], calcd. for $C_{42}H_{36}Fe_2O_2$: 796.0113.

1,12-Di(cyclopentadienylidenyl)-[1.1]ferrocenophane (11)

At 25 °C lithium cyclopentadienide [from cyclopentadiene (0.28 mL, 3.4 mmol), *n*-BuLi (2.10 mL, 1.6 M in hexane, 3.4 mmol) in 10 mL of anhydrous DEE] was added to a well stirred solution of [1.1]ferrocenophane-1,12-dione (**2**) (0.144 g, 0.3 mmol) and $AlCl_3$ (0.180 g, 1.4 mmol) in 50 mL of anhydrous THF. After 1 h at 25 °C an excess of $AlCl_3$ was added (0.60 g, 4.6 mmol) and the reaction mixture was stirred for 1 h at 25 °C. Hydrolysis was performed by addition of 10 mL of H_2O, the organic layer was washed with 3×25 mL of H_2O, dried over $MgSO_4$, and the solvent was removed at reduced pressure. Column chromatography (basic alumina grade IV, 25×4 cm, PE/CH_2Cl_2, 7:3), gave pure 1,12-di(cyclopentadienylidene)-[1.1]ferrocenophane (**11**), as a red-black liquid; yield: 0.174 g (0.3 mmol, 98%). IR (ATR): $\tilde{\nu}$=2956 (s), 2925 (s), 2857 (s, CH); 1725 (s), 1261 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): δ=4.54 + 4.99 (AA′BB’ line system, 2×8H, CpR), 6.31–6.34 [m, 4H, C=CCH or C=CCHC*H*], 6.44–6.45 [m, 4H, C=CCH or C=CCHC*H*]; ^{13}C NMR (100 MHz, BB, HMQC, HMBC, $CDCl_3$): δ=70.4 (C_{CpR}H), 75.9 (C_{CpR}H), 86.0 (C_{CpR}R), 123.9 [=CH], 129.8 [=CH], 144.9 [*C*=CCH or C=*C*CH], 147.9 [*C*=CCH or C=*C*CH]; MS (ESI, ES$^+$): *m/z*=521 [M+H$^+$]; HR-MS (ESI): *m/z*=521.0641 [M+H], calcd. for $C_{32}H_{25}Fe_2$: 521.0655.

endo,exo- and *exo,exo*-1,12-Di(cyclopenta-1,3-dienyl)-[1.1]ferrocenophane (13)

At 25 °C $LiAlH_4$ (0.060 g, 1.6 mmol) was added to a well stirred solution of 1,12-di(cyclopentadienylidenyl)-[1.1]ferrocenophane (**11**) (0.050 g, 0.1 mmol) in 10 mL of anhydrous THF and was allowed to react over 3 d at 25 °C. Hydrolysis was performed by addition of 10 mL of H_2O, and the organic layer was diluted with 50 mL of diethyl ether, washed with 3×25 mL of H_2O, dried over $MgSO_4$, and the solvent was removed under reduced pressure. The yellow-orange solid was washed with cold diethyl ether to give a 1:1 mixture of *endo,exo*- and *exo,exo*-1,12-di(5-cyclopenta-1,3-dienyl)-[1.1]ferrocenophane (**13**); yield: 0.045 g (0.085 mmol, 90%). ^{1}H NMR (400 MHz, 297 K, $CDCl_3$): δ= 2.48 (s, 4H, C_5H_5), 2.77 (s, 4H, C_5H_5), 4.13 (m, 16H, CpR), 4.25 (s, 8H, CpR), 4.39 (s, 4H, CpR), 4.42 (s, 4H, CpR), 4.61 (s, 2H, C*H*C_5H_5), 4.65 (s, 2H, C*H*C_5H_5), 5.73 (s, 2H, C_5H_5), 5.98 (s, 2H, C_5H_5), 6.05 (m, 2H, C_5H_5), 6.15–6.2 (m, 6H, C_5H_5); ^{13}C NMR (100 MHz, BB, HMQC, HMBC, $CDCl_3$): δ=40.8 (C_5H_5 or *C*HC_5H_5), 40.9 (C_5H_5 or *C*HC_5H_5), 41.12 (C_5H_5 or *C*HC_5H_5), 41.15 (C_5H_5 or *C*HC_5H_5), 41.9 (C_5H_5 or *C*HC_5H_5), 66.88 (C_{CpR}H), 66.91 (C_{CpR}H), 67.0 (C_{CpR}H), 68.89 (C_{CpR}H), 68.91 (C_{CpR}H), 69.9 (C_{CpR}H), 70.0 (C_{CpR}H), 91.8 (C_{CpR}R), 92.5 (C_{CpR}R), 124.26 (C_5H_5), 124.27 (C_5H_5), 131.1 (C_5H_5), 131.8 (C_5H_5), 133.17 (C_5H_5), 133.19 (C_5H_5), 133.5 (C_5H_5), 153.1 (C_5H_5), 156.0 (C_5H_5); MS (ESI, ES$^+$): *m/z*=524 [M$^+$], 459 [M$^+$–C_5H_5]; HR-MS (ESI): *m/z*=524.0897 [M], calcd. for $C_{32}H_{28}Fe_2$:

524.0890; $m/z = 459.0514$ $[M-C_5H_5]$, calcd. for $C_{27}H_{23}Fe_2$: 459.0499.

Detection of *endo,exo*- and *exo,exo*-1,12-Di(methylcyclopenta-1,3-dienyl)-[1.1]ferrocenophane (14)

At 25 °C BuLi (0.25 mL, 1.6 M in hexane, 0.4 mmol) was added to a well stirred solution of *endo,exo*- and *exo,exo*-1,12-di(5-cyclopenta-1,3-dienyl)-[1.1]ferrocenophane (**13**) (0.097 g, 0.2 mmol) in 200 mL of anhydrous THF and was allowed to react for 1 h. A sample of the reaction mixture was taken and added to an excess of MeI. Hydrolysis was performed by addition of H_2O, and the organic layer was investigated by mass spectrometry. MS (ESI, ES^+): $m/z = 552$ $[M^+]$; HR-MS (ESI): $m/z = 552.1199$ [M], calcd. for $C_{34}H_{32}Fe_2$): 552.1203.

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