Synthesis and Reactions of Ferrocenyl-capped Long-chain Alkynes

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Dedicated to Professor Gerhard Maas on the occasion of his 60th birthday

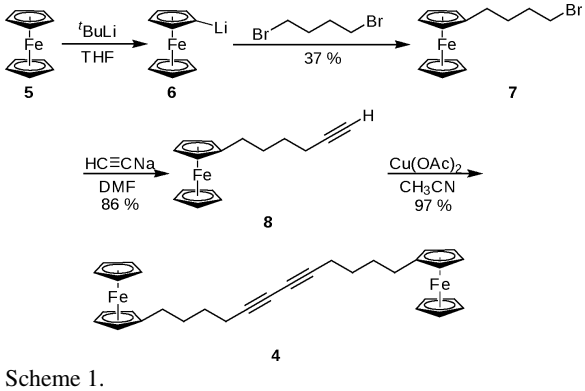
Alkyl-substituted acetylenes and diacetylenes with terminal ferrocenyl groups were synthesised starting from ferrocene. The reactivity of the triple bonds in the resulting compounds was used to prepare cobalt-alkyne complexes. Cyclotrimerisation of the monoacetylene resulted in a hexa-substituted benzene derivative with six pending ferrocenyl groups.

Key words: Ferrocene, Diacetylene, Alkyne-Cobalt Complex, Hexa-substituted Benzene

Introduction

We had recently used a series of ferrocenyl-capped linear oligomethylene systems Fc-$(CH_2)_n$-Fc (**1**; with n = 4, 8, 14, 18) to form self-assembled highly ordered monolayers on "Highly Ordered Pyrolytic Graphite" (HOPG) [1]. The assemblies were all characterised by structures where the polar organometallic "head groups" were found close to each other and the long oligomethylene chains oriented parallel. It was found that the individual patterns showed a structural dependency of the length of the bridging chain and that they resembled specific planar cuts through the three-dimensional structures of these compounds as they were determined by X-ray diffraction. There seemed to be a relationship between the three-dimensional crystal structures and the two-dimensional surface structure of these specific compounds. The systems **1** were either prepared by the straight forward reaction of the α,ω-dibromoalkanes with ferrocenyllithium or by olefin-metathesis routes followed by hydrogenation. The respective mono-unsaturated analogues **2** (Fc-$(CH_2)_x$–CH=CH–$(CH_2)_x$-Fc) were also investigated with regard to their surface assembly behaviour.

We have now prepared the corresponding mono- and di-acetylene compounds (**3**, **4**). We used them for the preparation of examples of **1** (hydrogenation) and have begun to investigate their specific surface chemistry. In this account we wish to report on the preparation of these ferrocenyl-capped acetylenes and diacetylenes, show their structural and coordination chemistry properties, and describe the catalytic trimerisation of one of these systems (**3**) to yield the respective hexa-substituted benzene derivative.



Scheme 1.

Results and Discussion

Synthesis

We prepared the compounds **3** and **4** along the lines depicted in Schemes 1 and 2. Ferrocene was mono-deprotonated by treatment with *tert*-butyllithium [2]. Subsequent reaction with 1,4-dibromobutane followed by chromatographic work-up gave (4-bromobutyl)ferrocene (**7**) [3] in 37 % yield. Compound **7** shows a ^{1}H NMR Cp singlet (5H) at δ = 3.99 (in [D$_6$]benzene) and an AA′BB′ pattern of the η^5-C$_5$H$_4$ unit (δ = 3.93, 3.88). The signals of the tetramethylene chain are observed at δ = 2.04, 1.38, 1.52, and 2.94 (CH_2-Br). The bromide **7** was then converted to the terminal acetylene **8** by reacting it with sodium acetylide

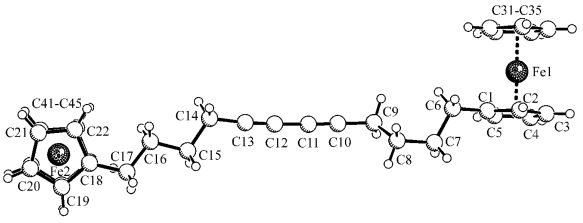
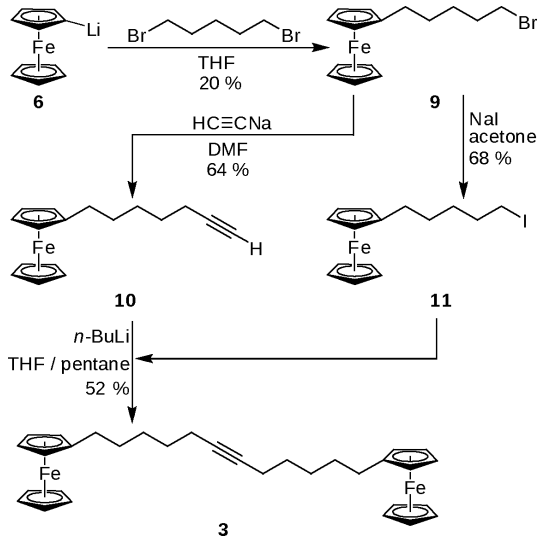


Fig. 1. A projection of the molecular geometry of compound **4**. Selected bond lengths (Å) and angles (deg): Fe–C_{Cp} 2.036(2) – 2.056(1), C9–C10 1.465(2), C10–C11 1.199(2), C11–C12 1.380(2), C12–C13 1.203(2), C13–C14 1.460(2); C9–C10–C11 178.5(2), C10–C11–C12 178.5(2), C11–C12–C13 177.9(2), C12–C13–C14 175.9(2).

in DMF [4]. Compound **8** was isolated from the reaction mixture in $> 80\,\%$ yield. It is characterised by ^{13}C NMR signals of the terminal -C≡CH unit at δ = 84.3 and 69.0 (^{1}H: δ = 1.78, t, ^4J = 2.6 Hz). Compound **8** features a weak IR (-C≡C-) stretching band at $\nu = 2115\ cm^{-1}$.

Glaser coupling [5] of **8** ($Cu(OAc)_2$ / acetonitrile) then gave the diacetylene product **4** in close to quantitative yield (97 % isolated). Compound **4** features ^{13}C NMR signals of the central -C≡C–C≡C- unit at δ = 77.0 and 66.8. It was further characterised by X-ray diffraction (single crystals were obtained from dichloromethane). The structure of **4** features a linear conjugated diacetylene C_4 core in the centre of the C_{12} chain that is connecting the pair of ferrocenyl units (Fig. 1). In the crystal the molecule attains a conformation that features the ferrocene moieties oriented almost perpendicularly. One of the connecting tetramethylene subunits is oriented in an extended all-antiperiplanar arrangement, whereas the other -$(CH_2)_4$- building block contains a *gauche* conformation.

The synthesis of the internal monoacetylene compound **3** starts similary: treatment of lithioferrocene (**6**) in this case with 1,5-dibromopentane under carefully controlled reaction conditions gave the ω-bromopentylferrocene derivative **9** [6]. It was isolated in *ca.* 20 % yield after chromatographic separation and purification. Treatment with sodium acetylide gave the terminal acetylene building block **10** that was then coupled with the ω-iodopentylferrocene reagent **11** under basic reaction conditions to yield **3** (52 %). The coupling component **11**, in turn, was prepared from **9** by Finkelstein halide exchange [7] (Scheme 2). Compound **3** was obtained as an orange solid. It features a ^{1}H NMR ferrocene singlet of 10 H relative intensity at

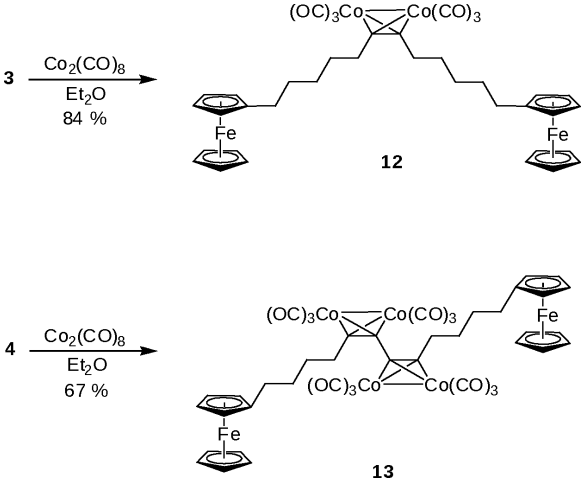


Scheme 2.

δ = 4.01 (in [D_6]benzene) and only one broad singlet for the isochronic protons of the η^5-C_5H_4 units of the ferrocenyl end groups at δ = 3.96 (relative intensity 8 H). The ^{13}C NMR resonance of the central acetylene unit was observed at δ = 80.5. The ^{13}C NMR spectrum of compound **3** also features five CH_2 resonances at δ = 31.2, 29.8, 29.4, 29.1, and 19.2.

Cobalt complexes

We have prepared the (acetylene)cobalt carbonyl complexes from the ferrocenyl-capped long-chain acetylenes **3** and **4**. Treatment of **3** with dicobaltoctacarbonyl [8] (1.5 equiv.) in ether (overnight at r. t.)



Scheme 3.

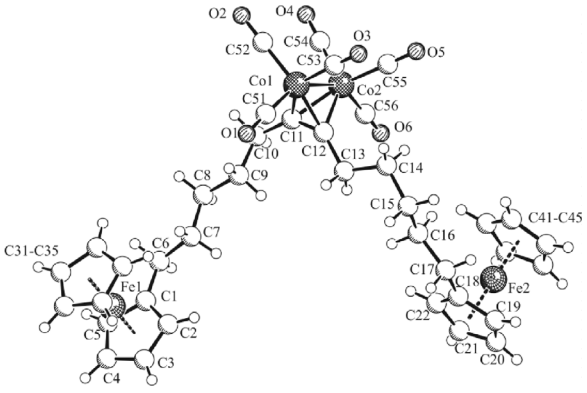


Fig. 2. A view of the molecular geometry of the cobalt complex **12**. Selected bond lengths (Å), angles and dihedral angles (deg): Fe–C_{Cp} 2.026(3) – 2.052(2), C10–C11 1.497(3), C11–C12 1.330(3), C12–C13 1.491(3), Co1–C11 1.971(2), Co1–C12 1.966(2), Co2–C11 1.975(2), Co2–C12 1.972(2), Co1–Co2 2.466(1), Co–C_{CO} 1.776(3) – 1.822(3); C10–C11–C12 140.0(2), C11–C12–C13 141.3(2), C10–C11–Co1 134.8(2), C10–C11–Co2 136.0(2), C13–C12–Co1 135.2(2), C13–C12–Co2 134.0(2), C11–Co1–C12 39.5(1), C11–Co2–C12 39.4(1), C11–Co1–Co2 51.4(1), C11–Co2–Co1 51.3(1), C12–Co1–Co2 51.4(1), C12–Co2–Co1 51.1(1); C10–C11–C12–C13 2.4(6).

gave the (acetylene)$Co_2(CO)_6$ complex **12**. It was obtained as a dark solid in > 80 % yield (Scheme 3). In solution complex **12** features the typical ^{1}H NMR signals of the terminal ferrocenyl units [δ = 4.03 (s, 10H), 3.99/3.97 (AA′BB′, 8H)]. The ^{13}C NMR resonance of the central acetylene C_2 ligand moiety appears at δ = 100.2, and we observe a typical single ^{13}C NMR carbonyl signal of the $Co_2(CO)_6$ unit at δ = 200.8. The IR spectrum of **12** features the typical strong (overlapping) ν(CO) bands between ν = 2085 and 1983 cm^{-1}.

Single crystals of **12** suitable for the X-ray crystal structure analysis were obtained from a saturated pentane solution. In the crystal we see the central pseudo-tetragonal arrangement of the C_2Co_2 unit with each cobalt atom featuring a pseudo-octahedral coordination geometry (Fig. 2). Again, the connecting pair of pentamethylene chains shows slightly different conformational characteristics: one moiety is close to an all-antiperiplanar orientation whereas the other features a *gauche* conformation.

We prepared the cobalt carbonyl complex **13** of the bis-ferrocenyl-diacetylene ligand by treatment of **4** with $Co_2(CO)_8$ in a similar way. The hexa-metallic (Co_4Fe_2) complex was obtained as a dark brown solid in 67 % yield (Scheme 3). The ^{13}C NMR spectrum of complex **13** exhibits a single carbonyl resonance at δ = 199.7 and the signals of the central -C_4- unit at δ = 106.7 and 91.9.

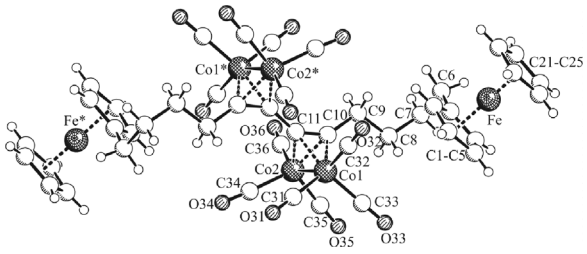


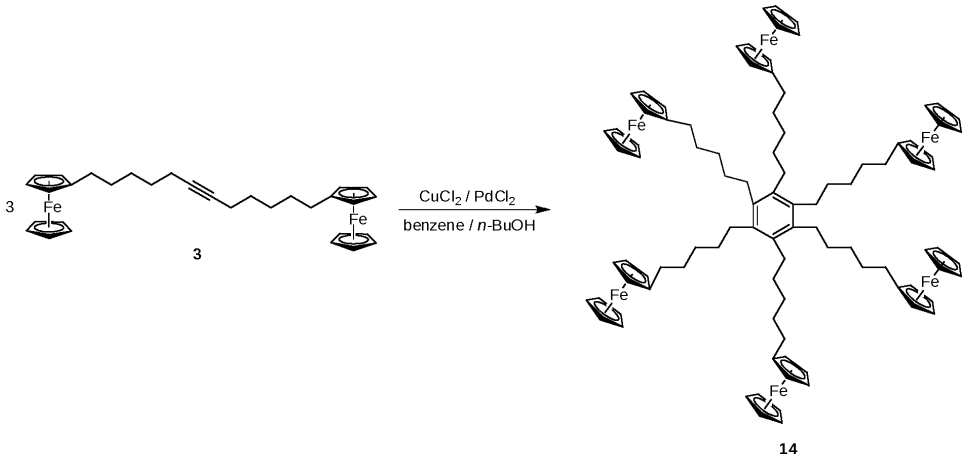
Fig. 3. A projection of the molecular geometry of the hexa-metallic complex **13**. Selected bond lengths (Å), angles and dihedral angles (deg): Fe–C_{Cp} 2.027(3) – 2.047(3), C9–C10 1.489(3), C10–C11 1.344(3), C11–C11* 1.427(5), Co1–C10 1.964(2), Co1–C11 1.970(2), Co2–C10 1.965(2), Co2–C11 1.977(2), Co1–Co2 2.471(1), Co–C_{CO} 1.792(3) – 1.822(3); C9–C10–C11 143.0(2), C10–C11–C11* 145.4(3), C9–C10–Co1 133.8(2), C9–C10–Co2 133.5(2), C11*–C11–Co1 132.6(2), C11*–C11–Co2 133.4(2), C10–Co1–C11 40.0(1), C10–Co2–C11 39.9(1), C10–Co1–Co2 51.1(1), C10–Co2–Co1 51.0(1), C11–Co1–Co2 51.4(1), C11–Co2–Co1 51.1(1); C9–C10–C11–C11* −0.7(8).

Single crystals of complex **13** were obtained from dichloromethane. The X-ray crystal structure analysis shows a -$C_2[Co_2(CO)_6]$–$C_2[Co_2(CO_6)]$- core. The $C_2[Co_2(CO)_6]$ subunits are symmetry-equivalent in the crystal. They are arranged *anti* to each other (Fig. 3). Both of the connecting tetramethylene linkers feature conformational arrangements that include *gauche* orientations. The ferrocenyl units are also arranged anti-oriented relative to each other.

Catalytic acetylene trimerization

Astruc *et al.* had previously prepared a hexa-[-$(CH_2)_5$-Fc]-substituted benzene by coupling Fc-$(CH_2)_4$–I with $CpFe^+$-activated hexamethylbenzene under basic conditions followed by a photochemical de-metallation reaction to remove the product **14** from iron [9]. Having the bis-pentamethylene-ferrocenyl-substituted acetylene system **3** at hand it was tempting to prepare the interesting compound **14** by a simple catalytic alkyne trimerisation reaction. This proved to be successful.

For the cyclotrimerisation of **3** we adapted a procedure by H. Jiang *et al.* using a $CuCl_2$/$PdCl_2$ catalyst [10]. Treatment of the mixture for 4 h at 60 °C in a benzene / *n*-butanol mixture gave the hexa-substituted benzene derivative **14** as a yellow solid in 37 % yield (Scheme 4). Complex **14** features the typical ^{1}H NMR signals of the six peripheral symmetry-equivalent fer-



Scheme 4.

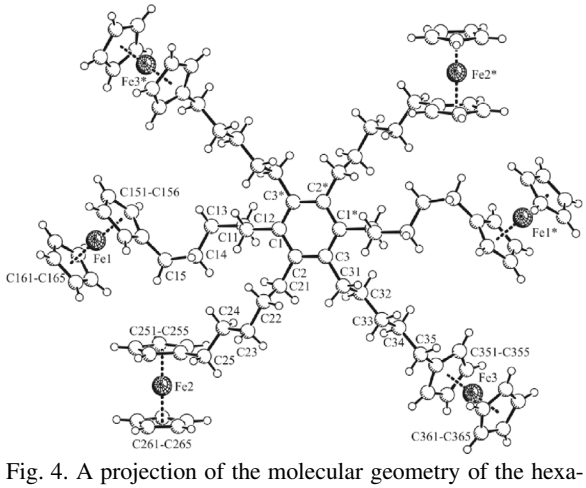


Fig. 4. A projection of the molecular geometry of the hexa-substituted benzene derivative **14**.

rocenyl substituents at δ = 4.03 (s, 30H) and 4.02/3.99 (broad, 24H). The ^{13}C NMR resonance of the central aromatic C_6 ring occurs at δ = 137.0.

Single crystals of compound **14** suitable for the X-ray crystal structure analysis were obtained from pentane/dichloromethane. In the crystal, two halves of the central benzene core are symmetry-equivalent. Two of the pending ferrocenyl groups are oriented above respectively below the benzene plane. The pentamethylene linkers of these units are in an all-antiperiplanar configuration. The other four ferrocene units are close to the plane of the central benzene core, and their alkyl linkers feature *gauche* conformations (Fig. 4).

Experimental Section

All reactions with air- and moisture-sensitive compounds were carried out under dry argon (Argon 5.0; Westfalen) in Schlenk-type glassware. Tetrahydrofuran, diethyl ether, dichloromethane, pentane, and toluene were dried using a Grubbs-type system [11], with activated alumina (basic) or molecular sieves as drying agents. *N,N*-Dimethylformamide was refluxed over P_2O_5 and distilled prior to use. [D_6]Benzene was dried over Na/K alloy and distilled under vacuum. Commercially available reagents were used as received. NMR spectra were recorded with a Varian 500 MHz INOVA (^{1}H: 499.8 MHz, ^{13}C: 125.7 MHz) and a Varian UNITYplus 600 (^{1}H: 599.6 MHz, ^{13}C: 150.8 MHz) instrument. IR spectra were recorded for solids in pure form on an ATR unit using a Varian 3100 FT-IR (Excalibur Series) spectrometer. For the determination of melting points a DSC Q 20 and a DSC 2910 CE (both of TA Instruments) were employed. Mass spectra were obtained using a MAT8200 (Thermo-Finnigan-MAT) for ESI spectra or a LAZARUS IIIDE (Institute of Organic Chemistry, Münster) for MALDI measurements. Elemental analyses were performed using a CHNO-Rapid (Foss-Heraeus). Lithioferrocene (**6**) was prepared as reported in the literature [2].

*(4-Bromobutyl)ferrocene (**7**)* [12]

A suspension of 2.60 g (13.7 mmol, 1.5 eq.) lithioferrocene in thf (20 mL) and toluene (10 mL) was cooled to −78 °C. 1,4-Dibromobutane (1.10 mL, 1.97 g, 9.12 mmol) was added dropwise. The mixture was stirred for 12 h while warming to r. t. The reaction mixture was poured into water (100 mL), and the aqueous layer was extracted three times with toluene (20 mL). After drying over $MgSO_4$ the crude product was purified by column chromatography (pentane / toluene, 95 / 5 → 90 / 10). Compound **7** was obtained as an orange oil (1.07 g, 37 %). – ^{1}H NMR (499.8 MHz, 298 K, [D_6]benzene): δ = 3.99 (s, 5H, Cp), 3.93 (pt, 2H, (3-H, 4-H)), 3.88 (pt, 2H, (2-H, 5-H)), 2.94 (t, $^3J_{H,H}$ = 6.7 Hz, 2H, 9-H), 2.04 (m, 2H, 6-H), 1.52 (m, 2H, 8-H), 1.38 (m, 2H, 7-H). –

^{13}C $\{^1H\}$ NMR (125.7 MHz, 298 K, [D_6]benzene): δ = 88.6 (C1), 68.8 (Cp), 68.3 (C2, C5), 67.6 (C3, C4), 33.5 (C9), 32.7 (C8), 29.8 (C7), 28.9 (C6). – MS (MALDI): *m/z* (%) = 319.8 (100) $[C_{14}H_{17}BrFe]^+$. – IR (film): ν = 3090 (w), 2930 (m), 2856 (w), 1437 (w), 1104 (m), 1000 (m), 813 (s), 646 (w) cm^{-1}. – $C_{14}H_{17}BrFe$ (321.03): calcd. C 52.38, H 5.34; found C 52.64, H 5.49.

*(5-Bromopentyl)ferrocene (**9**)* [13]

At 0 °C a 1.6 M solution of *tert*-butyllithium in pentane (13.0 mL, 21.0 mmol, 1.1 eq.) was slowly added to a solution of ferrocene (3.50 g, 18.8 mmol, 1 eq.) in 50 mL thf. After 1 h the reaction mixture was cooled to −78 °C. A solution of 1,5-dibromopentane (3.40 mL, 25.0 mmol, 1.3 eq.) in thf (20 mL) / toluene (5 mL) was added. Under continuous stirring overnight the mixture was slowly warmed to r. t. To quench the reaction, the mixture was poured into water (150 mL), and the aqueous layer was extracted three times with pentane (50 mL). After drying over $MgSO_4$ the crude product was purified by column chromatography (pentane/dichloromethane, 95/5). The product was obtained as an orange oil (1.29 g, 20 %). – ^1H NMR (599.6 MHz, 298 K, [D_6]benzene): δ = 3.99 (s, 5H, Cp), 3.94 (pt, 2H, (3-H, 4-H)), 3.91 (pt, 2H, (2-H, 5-H)), 2.96 (t, $^3J_{HH}$ = 6.9 Hz, 2H, 10-H), 2.10 (pt, 2H, 6-H), 1.48 (m, 2H, 9-H), 1.26 (m, 2H, 7-H), 1.17 (m, 2H, 8-H). – $^{13}C\{^1H\}$ NMR (150.8 MHz, 298 K, [D_6]benzene): δ = 89.0 (C1), 68.8 (Cp), 68.3 (C2, C5), 67.5 (C3, C4), 33.7 (C10), 32.9 (C9), 30.6 (C7), 29.6 (C6), 28.2 (C8). – HRMS ((+)-ESI): *m/z* = 334.0013 (calcd. 334.0014 for $C_{15}H_{19}BrFe$, $[M]^+$). – IR (film): ν = 2944 (w), 2854 (w), 2362 (w), 1410 (m), 1284 (m), 1213 (m), 1103 (m), 1040 (m), 996 (m), 923 (w), 828 (s), 803 (s), 768 (w) cm^{-1}. – $C_{15}H_{19}BrFe$ (335.06): calcd. C 53.77, H 5.72; found C 53.95, H 5.70.

*(5-Iodopentyl)ferrocene (**11**)*

(5-Bromopentyl)ferrocene (**9**) (793 mg, 2.37 mmol) was dissolved in acetone (30 mL), and subsequently sodium iodide (2.13 g, 14.2 mmol, 6 eq.) was added. After stirring overnight the solvent was removed *in vacuo*. The residual solid was dissolved in water and pentane (100 mL each). The layers were separated, and the aqueous layer was extracted three times with pentane (50 mL). The combined organic layers were dried using $MgSO_4$, and the solvent was removed *in vacuo*. The crude product was filtered through silica gel (eluent: pentane). Finally, **11** was obtained as an orange oil after evaporation of the solvent (621 mg, 68 %). – ^1H NMR (599.6 MHz, 298 K, [D_6]benzene): δ = 4.00 (s, 5H, Cp), 3.95 (m, 2H, (3-H, 4-H)), 3.92 (m, 2H, (2-H, 5-H)), 2.70 (t, $^3J_{HH}$ = 7.0 Hz, 2H, 10-H), 2.10 (pt, 2H, 6-H), 1.42 (m, 2H, 9-H), 1.25 (m, 2H, 7-H), 1.12 (m, 2H, 8-H). – ^{13}C $\{^1H\}$ NMR (150.8 MHz, 298 K, [D_6]benzene): δ = 89.0 (C1), 68.8 (Cp), 68.3 (C2, C5), 67.5 (C3, C4), 33.6 (C9), 30.5 (C8), 30.4 (C7), 29.6 (C6), 6.8 (C10). – HRMS ((+)-ESI): *m/z* = 381.9872 (calcd. 381.9875 for $C_{15}H_{19}FeI$, $[M]^+$). – IR (film): ν = 3092 (m), 2929 (m), 2854 (s), 2360 (s), 2342 (s), 1458 (s), 1193 (s), 1105 (s), 999 (s), 816 (vs) cm^{-1}. – $C_{15}H_{19}FeI$ (382.06): calcd. C 47.15, H 5.01; found C 47.40, H 5.34.

*(Hex-5-ynyl)ferrocene (**8**)*

(4-Bromopentyl)ferrocene (**7**) (600 mg, 1.88 mmol) was dissolved in 10 mL dimethylformamide. At 0 °C sodium acetylide (649 mg (18 weight-% slurry in xylene), 2.43 mmol, 1.3 eq.) was slowly added, and the mixture was stirred for 1 h. After complete conversion, monitored by TLC, 2.00 mL water was added. The solvent was removed *in vacuo*, and the residue was dissolved in water (40 mL) and pentane (30 mL). Layers were separated, and the aqueous layer was extracted three times with pentane (20 mL). After drying the solution over $MgSO_4$, filtration through silica gel (pentane/toluene, 9/1) and evaporation of the solvent, the product was obtained as an orange oil (430 mg, 86 %). – ^1H NMR (599.6 MHz, 298 K, [D_6]benzene): δ = 3.99 (s, 5H, Cp), 3.93 (pt, 2H, (3-H, 4-H)), 3.91 (pt, 2H, (2-H, 5-H)), 2.11 (m, 2H, 6-H), 1.95 (td, $^3J_{H,H}$ = 7.1 Hz, $^4J_{H,H}$ = 2.6 Hz, 2H, 9-H), 1.78 (t, $^4J_{H,H}$ = 2.6 Hz, 2H, 11-H), 1.49 (m, 2H, 7-H), 1.36 (m, 2H, 8-H). – ^{13}C $\{^1H\}$ NMR (150.8 MHz, 298 K, [D_6]benzene): δ = 89.0 (C1), 84.3 (C10), 69.0 (C11), 68.8 (Cp), 68.3 (C2, C5), 67.5 (C3, C4), 30.3 (C7), 29.2 (C6), 28.5 (C8), 18.4 (C9). – MS (MALDI): *m/z* (%) = 265.8 (100) $[C_{16}H_{18}Fe]^+$. – IR (film): ν = 3301 (m), 3090 (w), 3027 (w), 2935 (m), 2860 (m), 2115 (w), 1459 (m), 1105 (m), 1000 (m), 815 (s), 730 (s), 695 (s), 630 (s) cm^{-1}. – $C_{16}H_{18}Fe$ (266.16): calcd. C 72.20, H 6.82; found C 72.14, H 6.98.

*(Hept-6-ynyl)ferrocene (**10**)*

(5-Bromopentyl)ferrocene (**9**) (547 mg, 1.63 mmol) was dissolved in 20 mL dimethylformamide. At 0 °C sodium acetylide (610 mg (18 weight-% slurry in xylene), 2.29 mmol, 1.4 eq.) was slowly added, and the mixture was stirred for 1 h. After complete conversion, monitored by TLC, 20 mL of water and pentane were added. The layers were separated, and the aqueous layer was extracted three times with pentane (60 mL). After drying the combined solutions over $MgSO_4$, filtration through silica gel (pentane/toluene, 9/1), and evaporation of the solvent, the product was obtained as an orange oil (290 mg, 64 %). – ^1H NMR (499.8 MHz, 298 K, [D_6]benzene): δ = 4.00 (s, 5H, Cp), 3.95 (m, 2H, (3-H, 4-H)), 3.93 (m, 2H, (2-H, 5-H)), 2.15 (pt, 2H, 6-H), 1.95 (td, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 2.6 Hz, 2H, 10-H), 1.80 (t, $^4J_{HH}$ = 2.6 Hz, 1H, 12-H), 1.35 (m, 2H, 7-H), 1.34 (m, 2H, 9-H), 1.28 (m, 2H, 8-H). – ^{13}C $\{^1H\}$ NMR (125.7 MHz, 298 K, [D_6]benzene): δ = 89.2 (C1), 84.4 (C11), 68.9 (C12),

68.8 (Cp), 68.3 (C2, C5), 67.5 (C3, C4), 31.0 (C7), 29.7 (C6), 28.9 (C8), 28.6 (C9), 18.6 (C10). – HRMS ((+)-ESI): *m/z* = 280.0916 (calcd. 280.0909 for $C_{17}H_{20}Fe$, $[M]^+$). – IR (film): ν = 3303 (m), 3093 (w), 2933 (s), 2858 (m), 1457 (w), 1436 (w), 1105 (m), 1000 (m), 816 (s), 627 (vs) cm^{-1}. – $C_{17}H_{20}Fe$ (280.19): calcd. C 72.87, H 7.19; found C 72.78, H 7.33.

*1,12-Diferrocenyldodeca-5,7-diyne (**4**)*

The terminal acetylene **8** (300 mg, 1.13 mmol) was dissolved in acetonitrile (15 mL), and copper acetate (1.62 g, 8.12 mmol, 7.2 eq.) was added. After refluxing the reaction mixture for 7 h the solvent was removed *in vacuo*. The remaining solid was directly submitted to column chromatography (silica gel, eluent: pentane/toluene, 8/2) to yield the diyne **4** (294 mg, 97 %) as a yellow solid. Single crystals suitable for the X-ray crystal structure determination were obtained by slow evaporation of a saturated solution of **4** in dichloromethane. – ^{1}H NMR (499.8 MHz, 298 K, [D_6]benzene): δ = 4.00 (s, 10H, Cp), 3.93 (pt, 4H, (3-H, 4-H)), 3.89 (pt, 4H, (2-H, 5-H)), 2.07 (m, 4H, 6-H), 1.95 (t, $^3J_{H,H}$ = 7.0 Hz, 4H, 9-H), 1.45 (m, 4H, 7-H), 1.30 (m, 4H, 8-H). – ^{13}C {^{1}H} NMR (125.7 MHz, 298 K, [D_6]benzene): δ = 89.0 (C1), 77.0 (C10), 68.8 (Cp), 68.3 (C2, C5), 67.5 (C3, C4), 66.8 (C11), 30.4 (C7), 29.1 (C6), 28.3 (C8), 19.2 (C9). – MS (MALDI): *m/z* (%) = 529.8 (100) $[C_{32}H_{34}Fe_2]^+$. – M. p. 84.3 °C. – $C_{32}H_{34}Fe_2$ (530.30): calcd. C 72.48, H 6.46; found C 72.67, H 6.55.

*1,12-Diferrocenyldodec-6-yne (**3**)*

(6-Heptynyl)ferrocene (150 mg, 0.54 mmol) was dissolved in 15 mL thf at 0 °C and deprotonated by addition of *n*-butyllithium (0.37 mL of a 1.6 M solution in pentane, 0.54 mmol, 1 eq.). After 1 h a solution of **11** (205 mg, 0.54 mmol, 1 eq.) in 5 mL thf was added, and the mixture was stirred overnight while warming to r. t. The reaction was stopped by adding 50 mL water and 50 mL pentane. Layers were separated, and after extraction of the aqueous layer with pentane (2 × 50 mL) the combined organic layers were dried over $MgSO_4$. The crude product was purified by column chromatography at silica gel (eluent: pentane/dichloromethane, 95/5 → 80/20). Compound **3** was obtained as an orange solid (150 mg, 52 %). – ^{1}H NMR (599.6 MHz, 298 K, [D_6]benzene): δ = 4.01 (s, 10H, Cp), 3.96 (m, 8H, (2-H to 5-H)), 2.22 (pt, 4H, 6-H), 2.15 (t, $^3J_{HH}$ = 6.9 Hz, 4H, 10-H), 1.48 (m, 4H, 9-H), 1.45 (m, 4H, 7-H), 1.41 (m, 4H, 8-H). – ^{13}C {^{1}H} NMR (150.8 MHz, 298 K, [D_6]benzene): δ = 89.3 (C1), 80.5 (C11), 68.8 (Cp), 68.4 (C2, C5), 67.5 (C3, C4), 31.2 (C7), 29.8 (C6), 29.4 (C9), 29.1, (C8), 19.2 (C10). – HRMS ((+)-ESI): *m/z* = 534.1662 (calcd. 534.1668 for $C_{32}H_{38}Fe_2$, $[M]^+$). – IR (film): ν = 3101 (w), 2929 (m), 2855 (m), 2361 (w), 1466 (m), 1090 (s), 1044 (s), 1001 (s), 918 (m), 830 (vs), 821 (vs) cm^{-1}. – M. p. 57.7 °C. – $C_{32}H_{38}Fe_2$ (534.33): calcd. C 71.93, H 7.17; found C 71.58, H 7.06.

*[η^2-1,12-Diferrocenyldodec-6-yne]hexacarbonyldicobalt (**12**)*

The ferrocenylalkyne **3** (100 mg, 0.19 mmol) was dissolved in 15 mL diethyl ether. Subsequently, a solution of dicobaltoctacarbonyl (96.1 mg, 0.28 mmol, 1.5 eq.) in 10 mL ether was added. The reaction mixture was stirred overnight before the solvent was removed *in vacuo*. The crude product was dissolved again in 10 mL pentane and filtered through a short pack of silica gel (eluent: pentane/diethyl ether, 95/5). After removal of solvent **12** was obained as a dark solid (66.1 mg, 84 %). Single crystals suitable for the X-ray crystal structure determination were grown from a saturated solution of **12** in pentane at −30 °C. – ^{1}H NMR (599.6 MHz, 298 K, [D_6]benzene): δ = 4.03 (s, 10H, Cp), 3.99 (m, 4H, (2-H, 5-H)), 3.97 (m, 4H, (3-H, 4-H)), 2.64 (m, 4H, 10-H), 2.28 (pt, 4H, 6-H), 1.59 (m, 4H, 9-H), 1.47 (m, 4H, 7-H), 1.30 (m, 4H, 8-H). – ^{13}C {^{1}H} NMR (150.8 MHz, 298 K, [D_6]benzene): δ = 200.8 (CO), 100.2 (C11), 89.0 (C1), 68.8 (Cp), 68.5 (C2, C5), 67.6 (C3, C4), 34.2 (C10), 32.0 (C9), 31.4 (C7), 30.0 (C6), 29.5 (C8). – HRMS ((+)-ESI): *m/z* = 820.0013 (calcd. 820.0027 for $C_{38}H_{38}Co_2Fe_2O_6$, $[M]^+$). – IR (film): ν = 2936 (s), 2907 (w), 2085 (s), 2022 (sh), 2012 (vs), 1983 (vs), 1106 (s), 1002 (s), 829 (s) cm^{-1}. – M. p. 52.9 °C. – $C_{38}H_{38}Co_2Fe_2O_6$ (764.42): calcd. C 55.64, H 4.67; found C 55.40, H 4.26.

*[η^2, η^2-1,12-Diferrocenyldodeca-5,7-diyne]bis(hexacarbonyldicobalt)] (**13**)*

1,12-Diferrocenyldodeca-5,7-diyne (**4**) (100 mg, 0.21 mmol) was dissolved in 20 mL diethyl ether and treated with dicobaltoctacarbonyl (160 mg, 0.46 mmol, 2.2 eq.). The reaction mixture was stirred overnight before the solvent was removed *in vacuo*. The crude product was submitted to column chromatography (silica gel, eluent: pentane/diethyl ether 95/5). After removing the solvent **13** (150 mg, 67 %) was obtained as a dark brown solid. Crystals suitable for the X-ray crystal structure determination were grown from a saturated solution of **13** in dichloromethane by slow evaporation of the solvent. – ^{1}H NMR (599.6 MHz, 298 K, [D_6]benzene): δ = 4.01 (s, 10H, Cp), 3.98 (m, 4H, (2-H, 5-H)), 3.97 (m, 4H, (3-H, 4-H)), 2.87 (m, 4H, 9-H), 2.32 (pt, 4H, 6-H), 1.79 (m, 4H, 8-H), 1.59 (m, 4H, 7-H). – ^{13}C {^{1}H} NMR (150.8 MHz, 298 K, [D_6]benzene): δ = 199.7 (CO), 106.7 (C10), 91.9 (C11), 88.5 (C1), 68.9 (Cp), 68.4 (C2, C5), 67.7 (C3, C4), 33.8 (C9), 32.0 (C8), 31.5 (C7), 29.8 (C6). – HRMS ((+)-ESI): *m/z* = 1101.8078 (calcd. 1101.8074 for $C_{44}H_{34}Co_4Fe_2O_{12}$, $[M]^+$). – M. p. 111.9 °C. –

$C_{44}H_{34}Co_4Fe_2O_{12}$ (1102.16): calcd. C 47.95, H 3.11; found C 47.94, H 3.01.

*Hexa(5-ferrocenylpentyl)benzene (**14**)*

Alkyne **3** (100 mg, 0.19 mmol) was dissolved in 10 mL benzene and 0.8 mL *n*-butanol. After $PdCl_2$ (1.66 mg, 5 mol%) and anhydrous $CuCl_2$ (50.4 mg, 0.38 mmol, 2 eq.) had been added the mixture was heated for 4 h at 60 °C. The solvent was removed *in vacuo*, and the residue was filtered through silica gel (eluent: pentane/dichloromethane, 80/20). Compound **14** was obtained as a yellow powder (35 mg, 37 %). Single crystals suitable for the X-ray crystal structure determination were obtained by slow evaporation of a saturated solution of **14** in pentane/dichloromethane. – ^{1}H NMR (599.6 MHz, 298 K, [D$_6$]benzene): δ = 4.03 (s, 30H, Cp), 4.02 (m, 12H, (2-H, 5-H)), 3.99 (m, 12H, (3-H, 4-H)), 2.85 (br, 12H, 10-H), 2.32 (pt, 12H, 6-H), 1.76 (m, 12H, 9-H), 1.63 (m, 12H, 7-H), 1.59 (m, 12H, 8-H). – ^{13}C {^{1}H} NMR (150.8 MHz, 298 K, [D$_6$]benzene): δ = 137.0 (C11), 89.3 (C1), 68.9 (Cp), 68.4 (C2, C5), 67.5 (C3, C4), 32.4 (C9), 31.6 (C7), 30.9 (C8), 30.5 (C10), 29.9 (C6). – MS (MALDI): *m/z* (%) = 1602.8 (100) $[C_{96}H_{114}Fe_6]^+$. – M. p. 57.7 °C. – $C_{96}H_{114}Fe_6$ (1603.0): calcd. C 71.93, H 7.17; found C 72.04, H 7.82.

X-Ray structure determinations

Data sets were collected with a Nonius KappaCCD diffractometer, equipped with a rotating anode generator. Programs used: data collection: COLLECT [14]; data reduction: DENZO-SMN [15]; absorption correction: SORTAV [16] and DENZO [17]; structure solution: SHELXS-97 [18]; structure refinement: SHELXL-97 [19]; graphics: SCHAKAL [20].

*X-Ray crystal structure analysis of **4***

Formula $C_{32}H_{34}Fe_2$, M = 530.29, yellow-orange crystal, 0.45 × 0.20 × 0.07 mm^3, triclinic, space group $P\bar{1}$ (no. 2), a = 7.541(1), b = 11.800(1), c = 14.326(5) Å, α = 92.69(1), β= 102.13(1), γ = 91.71(1)°, V = 1243.9(2) Å^3, Z = 2, ρ_{calc} = 1.416 g cm^{-3}, μ = 1.185 mm^{-1}, empirical absorption correction (0.618 ≤ T ≤ 0.922), λ = 0.71073 Å, T = 198(2) K, ω and φ scans, 12655 reflections collected (±h, ±k, ±l), $[(\sin\theta)/\lambda]$ = 0.67 Å^{-1}, 5990 independent (R_{int} = 0.040) and 5412 observed reflections [$I \geq 2\sigma(I)$], 307 refined parameters, R1 = 0.029, wR2 = 0.078, max. (min.) residual electron density 0.33 (−0.47) e Å^{-3}; hydrogen atoms calculated and refined as riding atoms.

*X-Ray crystal structure analysis of **12***

Formula $C_{38}H_{38}Co_2Fe_2O_6$, M = 820.24, red crystal, 0.60 × 0.15 × 0.10 mm^3, monoclinic, space group $P2_1/c$ (no. 14), a = 21.1886(4), b = 8.6830(1), c = 20.9177(2) Å, β = 112.280(1)°, V = 3561.13(9) Å^3, Z = 4, ρ_{calc} = 1.530 g cm^{-3}, μ = 1.759 mm^{-1}, empirical absorption correction (0.418 ≤ T ≤ 0.844), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 29839 reflections collected (±h, ±k, ±l), $[(\sin\theta)/\lambda]$ = 0.67 Å^{-1}, 8576 independent (R_{int} = 0.044) and 5852 observed reflections [$I \geq 2\sigma(I)$], 433 refined parameters, R1 = 0.040, wR2 = 0.088, max. (min.) residual electron density 0.51 (−0.44) e Å^{-3}; hydrogen atoms calculated and refined as riding atoms.

*X-Ray crystal structure analysis of **13***

Formula $C_{44}H_{34}Co_4Fe_2O_{12}$, M = 1102.13, red crystal, 0.40 × 0.30 × 0.05 mm^3, monoclinic, space group $P2_1/c$ (no. 14), a = 15.3737(3), b = 9.3595(2), c = 15.2458(2) Å, β = 100.603(1)°, V = 2156.26(7) Å^3, Z = 2, ρ_{calc} = 1.698 g cm^{-3}, μ = 2.220 mm^{-1}, empirical absorption correction (0.470 ≤ T ≤ 0.897), λ= 0.71073 Å, T = 223(2) K, ω and φ scans, 12711 reflections collected (±h, ±k, ±l), $[(\sin\theta)/\lambda]$ = 0.66 Å^{-1}, 5120 independent (R_{int} = 0.049) and 3790 observed reflections [$I \geq 2\sigma(I)$], 280 refined parameters, R1 = 0.041, wR2 = 0.103, max. (min.) residual electron density 0.48 (−0.67) e Å^{-3}; hydrogen atoms calculated and refined as riding atoms.

*X-Ray crystal structure analysis of **14***

Formula $C_{96}H_{114}Fe_6 \cdot 2\,C_5H_{12}$, M = 1747.26, yellow crystal, 0.60 × 0.05 × 0.03 mm^3, monoclinic, space group $P2_1/c$ (no. 14), a = 23.003(1), b = 5.907(1), c = 33.602(1) Å, β = 99.55(1)°, V = 4502.5(8) Å^3, Z = 2, ρ_{calc} = 1.289 g cm^{-3}, μ = 0.988 mm^{-1}, empirical absorption correction (0.589 ≤ T ≤ 0.971), λ = 0.71073 Å, T = 198(2) K, ω and ϕ scans, 26044 reflections collected (±h, ±k, ±l), $[(\sin\theta)/\lambda]$ = 0.60 Å^{-1}, 7731 independent (R_{int} = 0.147) and 3617 observed reflections [$I \geq 2\sigma(I)$], 507 refined parameters, R1 = 0.079, wR2 = 0.211, max. (min.) residual electron density 0.46 (−0.46) e Å^{-3}; hydrogen atoms calculated and refined as riding atoms.

CCDC 728940 – 728943 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif.

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