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Triformylferrocenes, novel modules for organometallic scaffolds

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Dedicated to Professor M. Rosenblum on the occasion of his 75th birthday

Abstract

Protection of formylferrocene with propanediol under acidic conditions furnishes its acetal. Metalation of the acetal occurs mainly in the *ortho* position at the same ring. Reaction with *N*-formylpiperidine leads to the semiprotected 1,2-diformylferrocene, and the monoacetal of 1,1′,2-triformylferrocene, which can be obtained upon acidic deacetalization. Further protection of the semiprotected 1,2-diformylferrocene with propanediol results in the corresponding bisacetal, which is metalated to give the title compound 1,2,3-triformylferrocene after quenching of the anion with *N*-formylpiperidine and acidic deprotection. The 1,1′,2-triformylferrocene undergoes an interesting solid-state reaction at 170 °C under cross-linking to yield a novel organometallic polycondensate, while 1,2,3-triformylferrocene melts undecomposed. 1,2-Diformylferrocene was transformed into 1,2-bisbutadiynylferrocene by treatment with Taber's reagent, followed by coupling of 1,2-diethynylferrocene to bromo-triisopropylsilylethyne under Cadiot–Chodkiewicz conditions in an overall 40% yield starting from diformylferrocene. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Depending on one's view of the world, ferrocene is either a stable inorganic compound or an aromatic molecule, to which the encapsulated iron provides attractive optical, structural, and electrochemical properties. Ferrocene was the first dicyclopentadienyl complex and remains the prime representative of the whole class [1]. Ferrocene is stable, inexpensive, commercially available on a kg-scale, resulting in a well-developed organic chemistry with many functionalized ferrocene derivatives available [2]. Rosenblum was one of the pioneers, who skillfully applied chemistries developed for aromatic systems and transplanted them successfully to ferrocene. An instructive example is ferrocene–carbaldehyde [1], where Rosenblum and Pauson raced to make the ferrocene-based analog of benzaldehyde. Both succeeded and published their respective communications just weeks apart in Chemistry and Industry [3]. Rosenblum's subsequent full paper describes the synthesis of formylferrocene **1** [4] by Vilsmeier-formylation [5] of ferrocene. The very carefully worked-out and reliable preparation is still the best method to date to make this aldehyde. However, introduction of a second or third formyl group onto the ferrocene nucleus is impossible by this route due to the electronic deactivation of the sandwich by the aldehyde group. Carbonyl groups are synthons to access almost *any* conceivable structure and functionality, and for that reason it was of great fundamental and practical interest to obtain the two isomeric diformylferrocenes. The 1,1′-isomer was easily accessible via lithiation of ferrocene and subsequent electrophilic functionalization [6], whereas the 1,2-isomer (**5**) was synthesized first in a cumbersome multistep sequence, topped by a large-scale MnO_2-oxidation, from which the desired dialdehyde could never be obtained in yields $>25\%$ [7]. Due to the synthetic problems, the higher formylated ferrocenes are presently unknown, in contrast to the case of the ruthenocenes and osmocenes, where trilithiation in the 1,1′,2-positions is known [8]. In this contribution, we describe a general method to formylated ferrocenes via

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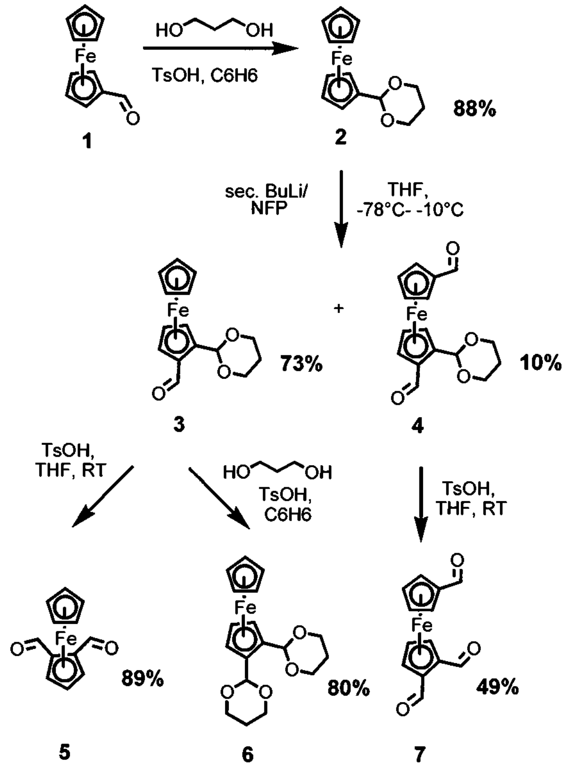
a metalation–functionalization route and discuss their structural and optical properties.

2. Results and discussion

2.1. Syntheses and structures

The dimetalation of ferrocene by organolithium reagents is known, and leads to 1,1′-lithiated derivatives [6]. In most cases even a stepwise metalation–functionalization scheme leads to this substitution pattern [6]. Exceptions are *ortho*-directing groups such as dimethylaminomethyl substituent, which furnishes 1,2-disubstituted ferrocenes [6]. We have a long-standing commitment to the synthesis of multiply alkynylated



Scheme 1.

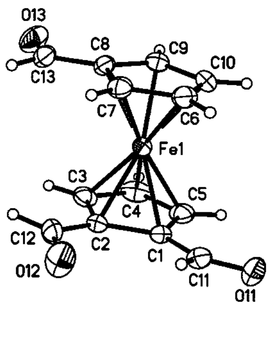
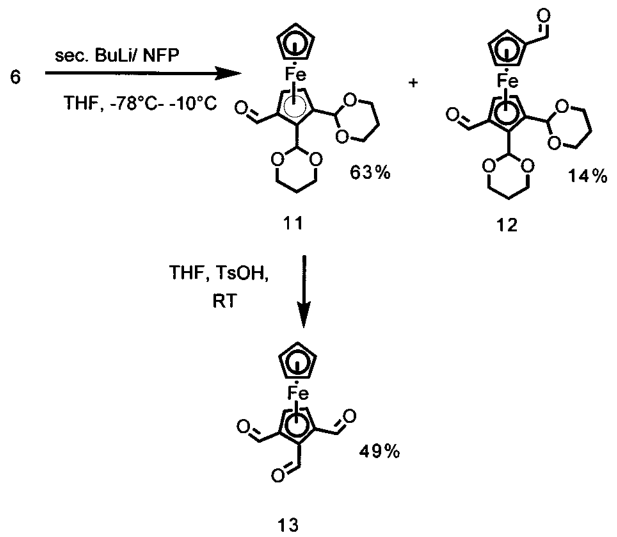


Fig. 1. ORTEP-plot of **13**.

π-complexes [9] and find that formyl-substituted iron-sandwiches are interesting in their own right, but likewise excellent precursors to alkynylated ferrocenes. We were interested in directing the metalation of **1** into the adjacent 2-position. Acid-catalyzed acetalization of **1** to **2** proceeds in 88%. Metalation of **2** at 0 °C resulted in the partial deprotection of the dioxane and the formation of two products, **3** and the 1,2′-diformylferrocene **4** after reaction with *N*-formylpiperidine (NFP) and hydrolysis (Scheme 1). Monitoring the reaction via TLC illustrated that the concentration of the monolithiated species increased with the reaction time at − 10 °C. Another experiment showed that substantial cleavage of the dioxane-ring occurs at ambient temperature. This cleavage was prevented by keeping the reaction temperature below − 10 °C. After careful optimization, the 1,2-substituted ferrocene **3** was reproducibly obtained in a 75% yield. Deprotection using *para*-toluenesulfonic acid in wet THF resulted in an overall 57% yield of dialdehyde **5** starting from **1**. The product of dilithiation of **2** reacts with NFP to afford **4**, deprotection of which gave rise to the isolation of 1,1′,2-triformylferrocene **7** in 50% yield (from **2**). The triformyl **7** was crystallized from dichloromethane and a single crystal X-ray structure was obtained to ultimately prove its molecular structure (Fig. 1). There are two molecules in the unit cell, and both adopt approximately the same eclipsed conformation of the two Cp-rings, in which the fully coplanar carbonyl groups are placed *gauche* to each other. Here the dihedral angles between the C=O groups and the Cp-ring vary from 7 to 11°. All of the bond lengths and bond angles are in excellent agreement with the expected values for ferrocene derivatives, and the C–C bond lengths in the Cp-rings are only slightly affected by the strong electron withdrawing nature of the formyl groups [11b,12]. To access 1,2,3-triformylferrocene (**13**), **3** was protected with 1,3-propanediol furnishing **6**, which was metalated under optimized (vide infra) conditions. Work-up of the reaction mixture gave **11** and **12** in a 4.5:1 ratio (Scheme 2). The desired triformylferrocene **13** could be obtained by the acidic deprotection of **11** by toluenesulfonic acid. Crystallization of **13** from CH_2Cl_2 led to a coffin-shaped specimen, which was used for single crystal X-ray structure determination (Fig. 2). In **13**, as in **4**, the Cp-rings are almost eclipsed with respect to each other (10.5°), and the formyl groups are almost coplanar featuring dihedral angles of 9.5–10.5° with respect to the cyclopentadienyl ligand. The C=O units are bent away from the rings. Again, the bond length and bond angles are in excellent agreement with literature values [11b,12]. The dialdehyde **5** is now conveniently available on a 10-g-scale by our route. It was efficiently converted by an optimized Ohira–Taber protocol (utilizing **8** [10]) into the 1,2-diethynylferrocene **9**, which could be transformed into **10** via a Cadiot–Chodciewcz



Scheme 2.

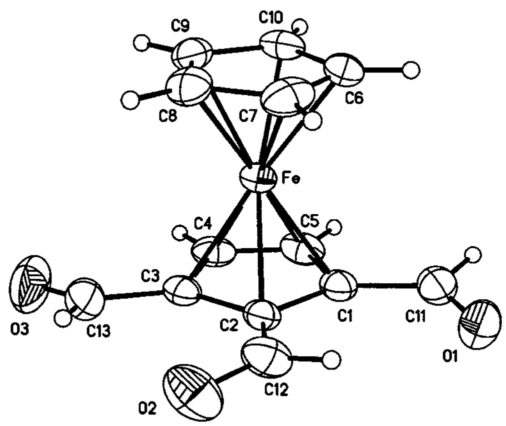
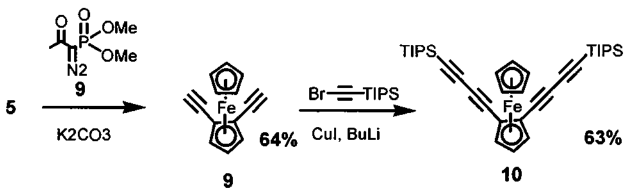


Fig. 2. ORTEP-plot of 7.



Scheme 3.

coupling (Scheme 3). Both the change from the cumbersome synthesis described by Marr and Rockett [7b], and the use of the Ohira Taber-methodology [10] make **9** readily available on the gram-scale. Its chemistry is being developed in our group. Compound **10** is the first reported bisbutadiynylated sandwich complex and may be an interesting substrate for a Bergman-type rearrangement by flash vacuum pyrolysis [11] and could furnish novel and unexpected conjugated organometallic products.

2.2. Spectral and thermal properties

While 1,2,3-triformylferrocene **13** melts undecomposed at 108 °C, its isomer **7** was stable up to 153 °C, at which temperature it reacted under evolution of gases into a dark and insoluble residue. To obtain more information about the optical properties of the cross-linked material formed, a thin film of **7** was drop-cast onto a quartz slide and heated in a vacuum oven to 170 °C for 1 h. An IR spectrum of this sample shows that the C=O stretch has completely disappeared, in accordance with the visible evolution of gas (probably CO). The UV–vis spectrum of the pristine films and the thermolyzed, dark material is shown in Fig. 3. The broad signature of the 1,1′,2-triformylferrocene has vanished and instead a shoulder at 430 nm has appeared. In addition, even thin films of the thermolyzed material become virtually black and highly absorbing between 285 and 350 nm. While we cannot assign a conclusive structure to the cross-linked material we intend to investigate its properties by transmission electron microscopy, X-ray powder diffraction, thin film cyclic voltammetry, spectroelectrochemistry, and magnetic SQUID measurements. An interesting question concerns the influence of the formyl groups on the electronic properties of ferrocene. In Fig. 4 the UV–vis spectra of **1**, **5**, **7**, and **13** are superimposed. In ferrocene there is an absorption at ca. 230 nm and a second very weak feature at 450 nm. In **1** there is a shoulder at 275 nm and an additional broad feature at 465 nm, which are likewise present in **5** and **7**; as a consequence, **1**,**5**, and **7** show similar electronic properties. Triformylferrocene **13** is different, because only one feature is visible at 400 nm for **13**, tailing to 550 nm. Consequently, all of the formylated ferrocenes show an increase in ε and bathochromic shifts to a varying degree. The spectrum of triformyl **13** shows some peculiarities, probably due to the extreme influence the formyl groups exert upon the ferrocene nucleus [13], leading to a slightly larger HOMO–LUMO gap.

In conclusion, we have shown that multiply formylated ferrocenes can conveniently be made by a repetitive metalation–formylation strategy utilizing NFP as an effective electrophile. The pinnacle of the synthetic success is the strong *ortho*-directing effect of the 1,3-dioxane ring in metalation reactions of ferrocenes. In future we will report upon reactions and materials, which stem from rearrangement, pyrolysis, and photolyses of multiply formylated ferrocenes and triformylferrocene **13** should be a valuable stepping stone for the synthesis of the hitherto unknown pentaethynylferrocene.

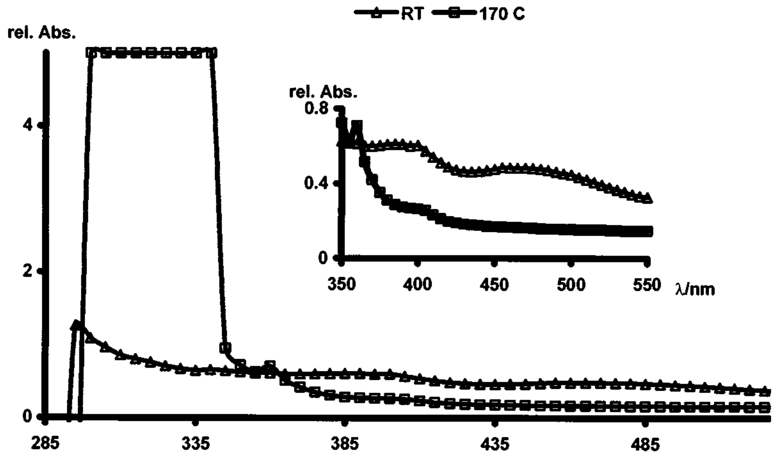


Fig. 3. UV–vis spectrum of **7** before ▲ and after ◆ thermolysis in thin films.

3. Experimental

3.1. Synthesis of **2**

Compound **1** (3.12 g, 14.6 mmol), 5.55 g (72.9 mmol) of 1,3-propandiol, and 0.222 g (1.16 mmol) of *p*-toluenesulfonic acid are placed into a 250 ml flask and dissolved in 150 ml of benzene. The reaction is refluxed for 8 h over a Dean–Stark-trap under the exclusion of light. After addition of 50 ml of deactivated silica gel (hexanes + 10% NEt_3) the solvent is removed in vacuo. Column chromatography (SiO_2–hexanes + 10% NEt_3) of the residue yields **2** (3.51 g, 88%, yellow crystals) in the first fraction, m.p.: 117 °C. IR (cm^{-1}): ν 3077, 2861, 1383, 1240, 1113, 999, 814. ^{1}H-NMR ($CDCl_3$): $\delta = 5.34$ (s, 1H, CH acetal), 4.30 (s, 2H, Cp–H), 4.20–4.16 (s, 5H, Cp–H unsubst. ring + m, 2H, CH_2 acetal), 4.10 (s, 2H, Cp–H), 3.89 (t, ^3J(H,H) = 11.0 Hz, 2H, CH_2 acetal), 2.16–2.10 (m, 1H, CH_2 acetal), 1.38–1.35 (m, 1H, CH_2 acetal). ^{13}C-NMR ($CDCl_3$): $\delta = 100.37$ (acetal-C), 86.06 (Cp–C), 68.72 (Cp–C unsubst. ring), 67.76 (Cp–C), 67.08 (Cp–C), 66.27 (Cp–C), 25.68 (acetal-C). UV–vis: (λ_{max} (ε)) ($CHCl_3$): 438 (99 000). MS (70 eV, EI): m/z (%): 272 (100).

3.2. Synthesis of **3**, **4**

Compound **2** (10.4 g, 38.3 mmol) are placed into an oven-dried 250 ml Schlenk flask and dissolved in 150 ml of abs. THF under an inert atmosphere. The solution is cooled to −78 °C for 10 min and 30.1 ml (42.0 mmol) *sec*-BuLi (1.4 m) were added. The solution turns dark-brown and cloudy after 5 min. After 20 min the temperature is raised to −10 °C for 1 h. To this solution are added 5.69 g (42.0 mmol) of NFP after the reaction was cooled to −78 °C. The mixture is warmed to room temperature (r.t.) and quenched with brine upon which the color of the solution turns deep red. The water layer is separated from the organic layer and extracted with 30 ml of hexanes. The combined organic layers are dried over magnesium sulfate and the solvent is removed in vacuo. Column chromatography (SiO_2–hexanes–CH_2Cl_2 4:1 + 10% NEt_3) yields **3** (8.38 g, 73% red crystals) as second fraction (m.p.: 87 °C) and **4** (1.26 g, 10%, red oil) as third fraction. **3**: IR (cm^{-1}): ν 2962, 2854, 1671, 1374, 1280, 1088, 998. ^{1}H-NMR ($CDCl_3$): $\delta = 10.16$ (s, 1H, CHO), 5.68 (s, 1H, CH acetal), 4.78–4.75 (m, 2H, Cp–H), 4.52 (t, ^3J(H,H) = 2.6 Hz, 1H, Cp–H), 4.26 (s, 5H, Cp–H unsubst. ring), 4.25–4.14 (m, 2H, CH_2 acetal), 4.00–3.91 (m, 2H, CH_2 acetal), 2.23–2.07 (m, 1H, CH_2 acetal), 1.44–1.37 (m, 1H, CH_2 acetal). ^{13}C-NMR ($CDCl_3$): $\delta = 193.84$ (CHO), 98.73 (acetal-C), 87.91 (Cp–C), 76.45 (Cp–C), 71.90 (Cp–C), 71.22 (Cp–C), 70.11 (Cp–C unsubst. ring), 69.43 (Cp–C), 66.88 (acetal-C), 25.28 (acetal-C). UV–vis: (λ_{max} (ε)) ($CHCl_3$): 456 (280), 340 (1011), 264 (8406). MS (70 eV, EI): m/z (%): 300 (100). **4**: IR (cm^{-1}): ν 3102, 2854, 1685, 1457, 1371, 1242. ^{1}H-NMR ($CDCl_3$): $\delta = 10.18$ (s, 1H, CHO), 9.89 (s, 1H, CHO), 5.54 (s, 1H, acetal), 4.88 (t, ^3J(H,H) = 1.3 Hz, 1H, Cp–H), 4.84–

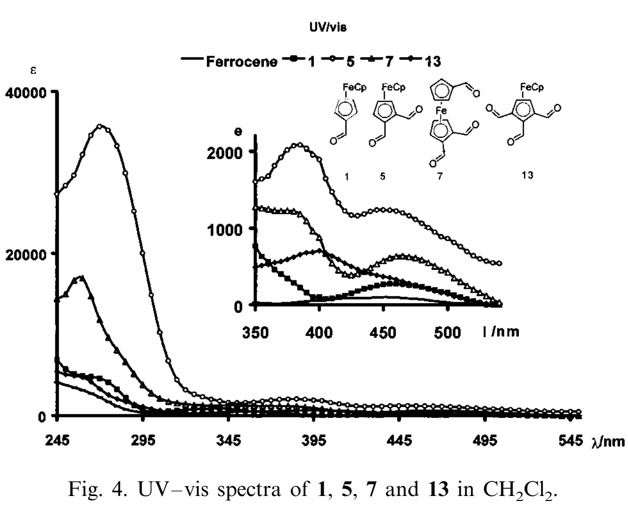


Fig. 4. UV–vis spectra of **1**, **5**, **7** and **13** in CH_2Cl_2.

4.83 (m, 2H, Cp–H), 4.82–4.81 (m, 1H, Cp–H), 4.65–4.64 (m, 2H, Cp–H), 4.57 (t, ^3J(H,H) = 2.5 Hz, 1H, Cp–H), 4.24–4.16 (m, 2H, CH_2 acetal), 3.96 (t, ^3J(H,H) = 11.7 Hz, 2H, CH_2 acetal), 2.19–2.13 (m, 1H, CH_2 acetal), 1.44–1.41 (m, 1H, CH_2 acetal). ^{13}C-NMR ($CDCl_3$): δ = 193.24 (CHO), 192.67 (CHO), 97.42 (acetal-C), 89.05 (Cp–C acetal), 80.30 (Cp–C), 77.31 (Cp–C), 74.32 (Cp–C), 74.28 (Cp–C), 72.77 (Cp–C), 71.87 (Cp–C), 71.02 (Cp–C), 70.63 (Cp–C), 69.91 (Cp–C), 66.68 (acetal-C), 66.60 (acetal-C), 24.96 (acetal-C). UV–vis: (λ_{max} (ε)) ($CHCl_3$): 465 (349), 261 (9896). MS (70 eV, EI): m/z (%): 328 (100).

3.3. Synthesis of **5**

Coumpound **3** (2.02 g, 6.73 mmol), and 1.28 g (6.73 mmol) p-toluenesulfonic acid are dissolved in 20 ml of THF containing 1 ml of water and stirred for 3 h under the exclusion of light. Aqueous workup and filtration through a silica gel plug with CH_2Cl_2 furnishes **5** (1.49 g, 89%, red crystals) m.p.: 172 °C. IR (cm^{-1}): ν 2953, 2861, 1669, 1438, 1038, 823. ^{1}H-NMR ($CDCl_3$): δ = 10.35 (s, 2H, CHO), 5.19 (d, ^3J(H,H) = 2.8 Hz, 2H, Cp–H), 4.92 (t, ^3J(H,H) = 2.8 Hz, 1H, Cp–H), 4.39 (s, 5H, Cp–H unsubst. ring). ^{13}C-NMR ($CDCl_3$): δ = 193.41 (CHO), 80.18 (Cp–C), 76.74 (Cp–C), 75.39 (Cp–C), 71.41 (Cp–C unsubst. ring). UV–vis: (λ_{max} (ε)) ($CHCl_3$): 450 (1238), 385 (2080), 268 (35 452).

3.4. Synthesis of **6**

Compound **4** (8.38 g, 27.9 mmol), 10.6 g (140 mmol) of 1,3-propandiol, and 0.424 g (2.23 mmol) of p-toluenesulfonic acid are placed into a 500 ml flask and dissolved in 250 ml of benzene. The reaction is refluxed for 8 h over a Dean–Stark-trap under the exclusion of light. After addition of 50 ml of deactivated silica gel (hexanes + 10% NEt_3) the solvent is removed in vacuo. Column chromatography (SiO_2–hexanes–CH_2Cl_2 4:1 + 10% NEt_3) of the residue yields **6** (8.00 g, 80%, yellow crystals) as first fraction, m.p.: 109 °C. IR (cm^{-1}): ν 2964, 2847, 1489, 1375, 1236, 1110, 998, 888, 817. ^{1}H-NMR ($CDCl_3$): δ = 5.46 (s, 1H, CH acetal), 4.29 (d, ^3J(H,H) = 2.7 Hz, 2H, Cp–H), 4.28–4.11 (s, 5H, Cp–H unsubst. ring + m, 4H, CH_2 acetal), 4.05 (t, ^3J(H,H) = 2.5 Hz, 1H, Cp–H), 3.96–3.80 (m, 4H, CH_2 acetal), 2.19–2.06 (m, 2H, CH_2 acetal), 1.59–1.32 (m, 2H, CH_2 acetal). ^{13}C-NMR ($CDCl_3$): δ = 99.88 (acetal-C), 83.88 (Cp–C), 69.65 (Cp–C unsubst. ring), 67.16 (acetal-C), 67.05 (Cp–C), 66.47 (Cp–C), 25.92 (acetal-C). UV–vis: (λ_{max} (ε)) ($CHCl_3$): 448 (76 000). UV–vis: (λ_{max} (ε)) ($CHCl_3$): 265 (4554). MS (70 eV, EI): m/z (%): 358 (100).

3.5. Synthesis of **7**

Compound **4** (0.901 g, 2.74 mmol), and 0.574 (3.02 mmol) of p-toluenesulfonic acid are dissolved in 10 ml of THF containing 1 ml of water and stirred for 12 h under the exclusion of light. Column chromatography (SiO_2–hexanes–CH_2Cl_2 4:1 + 10% NEt_3) furnishes **7** (0.370, 49%, red crystals) as second fraction; m.p. (dec.): 153 °C. IR (cm^{-1}): ν 3320, 3092, 2851, 1672, 1448, 1339, 1244, 1040. ^{1}H-NMR ($CDCl_3$): δ = 10.35 (s, 2H, CHO), 9.92 (s, 1H, CHO), 5.24 (d, ^3J(H,H) = 2.8 Hz, 2H, Cp–H), 4.99–4.97 (m, 3H, Cp–H), 4.74 (t, ^3J(H,H) = 1.7 Hz, 2H, Cp–H). ^{13}C-NMR ($CDCl_3$): δ = 192.73 (CHO), 192.00 (CHO), 81.19 (Cp–C), 76.15 (Cp–C), 75.99 (Cp–C), 75.21 (Cp–C), 71.86(Cp–C). UV–vis: (λ_{max} (ε)) ($CHCl_3$): 460 (630), 255 (16 800). MS (70 eV, EI): m/z (%): 270 (100).

3.6. Synthesis of **9**

To a solution of 1,2-bisformylferrocene (1.48 g, 6.11 mmol) in MeOH at 0 °C, are added dimethyl-(1-diazo-2-oxopropyl)phosphonate **8** (5.64 g, 29.4 mmol) and K_2CO_3 (3.80 g, 27.5 mmol) successively. The reaction mixture is stirred overnight and allowed to warm to r.t. Partitioning between saturated aqueous $NaHCO_3$ and CH_2Cl_2 leads after concentration and chromatography on silica gel (hexanes–CH_2Cl_2 4:1) to **9** (0.92 g, 64%, red crystalline solid) m.p.: 35 °C. IR (cm^{-1}): ν 3285, 3100, 2108, 1408, 1000. ^{1}H-NMR ($CDCl_3$): δ = 4.50–4.49 (d, ^3J(H,H) = 2.5 Hz, 2H, Cp–H), 4.24 (s, 5H, Cp–H unsubst. ring), 4.22–4.20 (t, ^3J(H,H) = 2.2 Hz, 1H, Cp–H), 2.92 (s, 2H, ethynyl-H). ^{13}C-NMR ($CDCl_3$): δ = 80.43 (ethynyl-C), 76.45 (ethynyl-C), 71.89 (Cp–C unsubst. ring), 71.86 (Cp–C), 68.60 (Cp–C), 67.21 (Cp–C). UV–vis (λ_{max} (ε)) ($CHCl_3$): 434 (553).

3.7. Synthesis of **10**

To a 100 ml oven-dried Schlenk flask is added **9** (0.200 g, 0.85 mmol) and THF (50 ml). The solution is cooled to −78 °C, then BuLi (0.94 ml, 2.0 M) is added drop-wise. After stirring for 30 min the temperature is increased to −10 °C and CuI (0.30 g, 1.58 mmol) is added. After stirring for 15 min, the temperature is decreased to −20 °C, upon which propylamine (5.0 ml) and 1-bromo-2-isopropylsilylacetylene (0.49 g, 1.88 mmol) were added and the solution was allowed to warm to r.t. Aqueous workup with hexanes was followed by removal of solvent in vacuo and chromatography on silica gel (hexanes) to give pure 10 (321 mg, 63%, red solid) m.p.: 95 °C. IR (cm^{-1}): ν 2944, 2856, 3221, 2188, 1461, 980. ^{1}H-NMR ($CDCl_3$): δ = 4.56–4.55 (d, ^3J(H,H) = 2.7 Hz, 2H), 4.32 (s, 5H), 4.29–4.27 (t, ^3J(H,H) = 2.6 Hz, 1H), 1.10 (s, 21H). ^{13}C-NMR

($CDCl_3$): $\delta = 90.29$ (ethynyl-C), 86.05 (ethynyl-C), 73.99 (ethynyl-C), 73.50 (ethynyl-C), 73.24 (Cp–C unsubst. ring), 72.29 (Cp–C), 69.87 (Cp–C), 67.22 (Cp–C), 18.59 (TIPS-C), 11.34 (TIPS-C). MS (EI): m/z: Found 594.2800 ($E = 2.2$ ppm). Calc. for M^+ ($C_{36}H_{50}FeSi_2$) 594.2813.

3.8. Synthesis of **11**, **12**

A 250 ml, oven-dried Schlenk flask is charged with 6.62 g (18.5 mmol) of **6** and 100 ml of abs. THF. Under an inert atmosphere the solution is cooled to −78 °C and stirred for 10 min. Then 14.0 ml (20.3 mmol) *sec*-BuLi (1.45 m) were added. The solution turned dark after 5 min. After 20 min the temperature was raised to −10 °C and stirred for 1 h, upon which 2.75 g (20.3 mmol) of NFP were added at −78 °C. The mixture is warmed to r.t. and quenched with brine, upon which the color turns deep red. The water layer is separated from the organic layer and extracted with 30 ml of hexanes. The combined organic layers are dried over magnesium sulfate and the solvent was removed in vacuo. Column chromatography (SiO_2–Hexanes–CH_2Cl_2 4/1 + 10%NEt_3) yields 11 (4.50 g, 63%) as second fraction (red crystals), m.p.: 106 °C, and 12 (0.995 g, 14%) as third fraction (red oil). **11**: IR (cm^{-1}): ν 2963, 2848, 1668, 1488, 1373, 1236, 1147, 1090. ^{1}H-NMR ($CDCl_3$): $\delta = 10.36$ (s, 1H, CHO), 5.74 (s, 1H, CH acetal), 5.52 (s, 1H, CH acetal), 4.77 (d, ^3J(H,H) = 3.0 Hz, 1H, Cp–H), 4.71 (d, ^3J(H,H) = 2.9 Hz, 1H, Cp–H), 4.30–4.15 (s, 5H, Cp–H unsubst. ring + m, 4H, CH_2 acetal), 3.99–3.84 (m, 4H, CH_2 acetal), 2.17–2.07 (m, 2H, CH_2 acetal), 1.40–1.36 (m, 2H, CH_2 acetal). ^{13}C-NMR ($CDCl_3$): $\delta = 196.05$ (CHO), 99.42 (acetal-C), 98.83 (acetal-C), 89.43 (Cp–C), 86.00 (Cp–C), 77.89 (Cp–C), 71.25 (Cp–C unsubst. ring), 70.73 (Cp–C), 67.46 (acetal-C), 67.41, 67.19 (acetal-C), 67.15 (acetal-C), 25.73 (acetal-C), 25.69 (acetal-C). UV–vis: (λ_{max} (ε)) ($CHCl_3$): 456 (513 000). UV–vis: (λ_{max} (ε)) ($CHCl_3$): 452 (272), 341 (1050), 264 (6100). MS (70 eV, EI): m/z (%): 386 (100). **12**: IR (cm^{-1}): ν 2964, 2853, 1686, 1458, 1372, 1238, 1001. ^{1}H-NMR ($CDCl_3$): $\delta = 10.38$ (s, 1H, CHO), 9.82 (s, 1H, CHO), 5.61 (s, 1H, CH acetal), 5.37 (s, 1H, CH acetal), 4.88–4.76 (m, 4H, Cp–H), 4.64–4.62 (m, 2H, Cp–H), 4.27–4.11 (m, 4H, CH_2 acetal), 3.99–3.82 (m, 4H, CH_2 acetal), 2.16–2.08 (m, 2H, CH_2 acetal), 1.41–1.37 (m, 2H, CH_2 acetal). ^{13}C-NMR ($CDCl_3$): $\delta = 194.79$ (CHO), 193.07 (CHO), 97.86 (acetal-C), 96.97 (acetal-C), 89.88 (Cp–C), 86.77 (Cp–C), 80.71 (Cp–C), 78.16 (Cp–C), 77.19 (Cp–C), 74.90 (Cp–C), 74.83 (Cp–C), 71.71 (Cp–C), 71.41 (Cp–C), 70.95 (Cp–C), 67.47 (acetal-C), 66.88 (acetal-C), 66.82 (acetal-C), 66.63 (acetal-C), 66.57 (acetal-C), 66.42 (acetal-C), 24.97 (acetal-C). UV–vis (λ_{max} (ε)) ($CHCl_3$): 464 (254), 263 (7390). MS (70 eV, EI): m/z: 414 (100).

3.9. Synthesis of **13**

Compound **11** (0.323 g, 0.889 mmol) and 0.507 (2.67 mmol) p-toluenesulfonic acid are dissolved in 5 ml of THF containing 1 ml of water. The mixture is stirred for 12 h under the exclusion of light. Column chromatography (SiO_2–hexanes–CH_2Cl_2 4/1 + 10%NEt_3) furnishes **13** (0.117, 49%) as third fraction (red crystals), m.p.: 108 °C. IR (cm^{-1}): ν 3092, 2872, 1668, 1442, 1295, 1150. ^{1}H-NMR ($CDCl_3$): $\delta = 10.69$ (s, 1H, CHO), 10.35 (s, 2H, CHO), 5.41 (s, 2H, Cp–H), 4.45 (s, 5H, Cp–H unsubst. ring). ^{13}C-NMR ($CDCl_3$): $\delta = 193.80$ (CHO), 192.74 (CHO), 84.74 (Cp–C), 77.21 (Cp–C), 76.81 (Cp–C), 73.15 (Cp–C unsubst. ring). UV–vis (λ_{max} (ε)) ($CHCl_3$): 400 (793). MS (70eV, EI): m/z (%): 270 (100).

3.10. X-ray single crystal structure determination of **7** and **13**

3.10.1. X-ray structure determination, $C_{13}H_{10}O_3Fe$ (7)

An irregular red crystal was coated in inert oil, mounted on the end of a thin glass fiber and quickly transferred to the cold stream of a Bruker SMART APEX CCD-based diffractometer system (Mo–K_α radiation, $\lambda = 0.71073$ Å). X-ray intensity data were measured at 173 K. After determining crystal quality and unit cell parameters based on reflections taken from a set of three scans measured in orthogonal regions of reciprocal space, a hemisphere of frame data was collected with a scan width of 0.3° in ω and an exposure time of **8** s per frame. The first 50 frames were re-collected at the end of the data set to monitor crystal decay. The raw data frames were integrated using SAINT+. Corrections for Lorentz and polarization effects were also applied by SAINT+. Analysis of the data showed negligible crystal decay during data collection. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied with the program SADABS. All non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were placed in idealized positions and refined using a riding model.

3.10.2. Crystal data for **7**

($C_{13}H_{10}O_3Fe$; 270.06 g mol^{-1}; dark-red coffin-shaped needles of $0.52 \times 0.38 \times 0.12$ mm^3 dimension): the triformyl crystallizes in the triclinic system ($P\bar{1}$) with the following unit cell: $a = 7.5164(5)$, $b = 11.9353(9)$, $c = 12.4466(9)$ Å, $\alpha = 97.416(2)$, $\beta = 102.030(1)$, $\gamma = 90.195(2)°$. The cell volume is 1082.40(14) Å^3 with $Z = 4$, $\rho_{calc} = 1.657$ g cm^{-3}, and an absorption coefficient of 1.383 mm^{-1}. The max and min transmission were in the range of 0.9622–0.7510. A semi-empirical absorption correction from equivalents was applied. $F(000) = 552 = 1.69 < \theta < 26.420$ with hkl:

$-8 < h < 9$, $-14 < k < 12$, $-15 < l < 15$; 7262 reflections were collected of which 4416 [$R_{int} = 0.0171$] were independent. Completeness to theta = 26.42° was 99.1%. The data were refined by a full-matrix least-squares on F^2. The ratio of data/restraints parameters was 4416/0/307, while the goodness-of-fit on F^2 1.019. R [$I > 2\sigma(I)$]: R_1 0.03164, $wR_2 = 0.0704$. R indices (all data) $R_1 = 0.0381$, $wR_2 = 0.0715$. The largest difference peak and hole: 0.498 and -0.415 e Å^{-3}.

*3.10.3. X-ray structure determination, $C_{13}H_{10}FeO_3$ (**13**)*

A red bar-shaped crystal was frozen onto the end of a thin glass fiber in the cold nitrogen stream of a Bruker SMART APEX CCD-based diffractometer system at 173(2) K utilizing the protocol described for **7**.

*3.10.4. Crystal data for **13***

($C_{13}H_{10}FeO_3$; 270.06 g mol^{-1}; dark-red coffin-shaped needles of $0.24 \times 0.12 \times 0.07$ mm^3 dimension): The triformyl crystallizes monoclinic ($P2(1)/n$) with the following unit cell: $a = 7.4060(5)$, $b = 12.0210(9)$, $c = 12.3728(9)$ Å, $\alpha = 90$, $\beta = 95.2030(10)$, $\gamma = 90°$. The cell volume is 1096.98(14) Å^3 with $Z = 4$, $\rho_{calc} = 1.635$ g cm^{-3}, and an absorption coefficient of 1.365 mm^{-1}. The max. and min. transmission were in the range of 0.9280–0.7843. A semi-empirical absorption correction from equivalents was applied. $F(000) = 552 = 2.37 < \theta < 26.390^0$ with hkl: $-9 \le h \le 6$, $-14 \le k \le 15$, $-15 \le l \le 15$; 7218 reflections were collected of which 2252 [$R_{int} = 0.0280$] were independent. Completeness to $\theta = 26.39°$ was 100.0%. The data were refined by a full-matrix least-squares on F^2. The ratio of data/restraints/parameters was 2252/0/154, while the goodness-of-fit on $F^2 = 1.008$. R [$I > 2\sigma(I)$]: $R_1 = 0.0334$, $wR_2 = 0.0778$. R indices (all data) $R_1 = 0.0397$, $wR_2 = 0.0795$.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 158531 and158532 for compounds **13** and **7**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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