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# Semimasked 1,1′-diethynylferrocenes: synthetic concepts, preparations, and reactions

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**Abstract**

Due to the inherent instability of 1,1′-diethynylferrocene, the respective coupling chemistry for the access of oligonuclear systems requires stepwise preparative sequences involving consecutive ethyne deprotection, or the conversion of latent ethyne precursor functionalities, respectively. The new derivatives 1-acetyl-1′-ethynylferrocene, **3**, and, preferably, 1-ethynyl-1′-formylferrocene, **9**, turned out to be the most favorable starting compounds. The subsequent synthetic chemistry, as well as the X-ray structures of selected starting and target derivatives are presented. A unique intramolecular coupling product, **12**, represents the first ladder-type tricyclic metallocenophane system exhibiting high ring strain. Supplementary novelties concerning monoacetylenic parent systems are also presented. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Ethynylferrocenes; Acetylene dicobalthexacarbonyl adducts; X-Ray structures

## 1. Introduction

The general chemistry of acetylenes [1], and even more of ferrocenylacetylenes exhibits high versatility and involves allene synthesis [2], triple bond additions [3,4], terminal substitutions [5], common or sophisticated [6] coupling reactions mediated by transition metal catalysts, as well as oligomerisations and polymerisations [7]. These chemical topics have, not surprisingly, an ongoing impact in the synthetic field for attaching ferrocene electrophores to various predesigned advanced materials like redox switchable ligands [8] and electrochromic molecular devices [9].

Furthermore, the convenience and versatility of the follow-up chemistry of unsubstituted, methoxylated [10] and aminomethylated [11] ethynylferrocenes offer a wide potential of applicability in basic research by giving access to illustrative models of metal–metal interaction processes [12], molecular wires [13], and special polymers [7,14–16]. The first application-relevant exploitation of acetylenic ferrocenes dealt with polymerisation studies of 4-ferrocenylphenyl-chloroacrolein and the elimination product thereof, 4-ferrocenylphenylacetylene [17,18]. The latter was used recently to modify porphyrins for the purpose of multibit information storage [19].

## 2. Results and discussion

### 2.1. General preparative aspects of ferrocene-based acetylenic chemistry

#### 2.1.1. Conversion of methyl ketones into terminal alkynes

For 4-ferrocenylphenylacetylene, as well as for the parent ethynylferrocene, most of the respective preparations reported earlier started from the corresponding

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acetophenones. This very reliable route [20] was adopted for ferrocenes by Schlögl [21] and, independently, by Rosenblum and coworkers [22].

In our experience, these known protocols, which have been further elaborated by Watts [23], showed some scale sensitivity, and several preparative runs failed completely. Therefore our sole intention was not to improve this important route, but to address critical reaction details in order to establish a more or less fool-proof procedure [24]. It curiously turned out that a key precondition is the use of purified dioxane, which is combined subsequently with aqueous sodium hydroxide in the final elimination step of ferrocenyl-chloroacrolein to form ethynylferrocene. Dioxane, predistilled from sodium benzophenone ketyl, is obviously free from any peroxides or antioxidant stabilizers, which may eventually also serve as radical sources, capable of inducing undesired polymerisation. Such redox-induced thermal radical polymerisations of similar 4-ferrocenylphenyl-chloroacrolein systems are reported to proceed efficiently [18].

However, for this final elimination step, DMSO was recently reintroduced [23] as an alternative reaction medium [25], thus avoiding the inherent problems of crude ethereal reaction media.

On the basis of commercial starting materials, the easiest and most direct way to combine a ferrocene with a terminal ethyne by a non-hydrolysable [26] covalently bonded connector, is a direct one-pot diazotization/arylation of ethynylanilines in the presence of ferrocene (Scheme 1). Thus, inert conditions as well as the use of expensive metallating or anion forming reagents can be avoided.

A more convenient, yet less economic approach would be the respective acetyl-dehydratation by Mukayamas reagent, 2-chloro-3-ethylbenzoxazolium tetrafluoroborate [27], which unfortunately gives only low yields with donor-substituted benzophenones. On the other hand, this represents a useful synthetic dehydration methodology for the partial conversion of doubly acetylated progenitors to semimasked ethynes [28]. In this context it is worth noting that for ferrocenylacetophenone the yields range around 30%, and the respective conversion of acetylferrocene only gives yields below 10% [29].

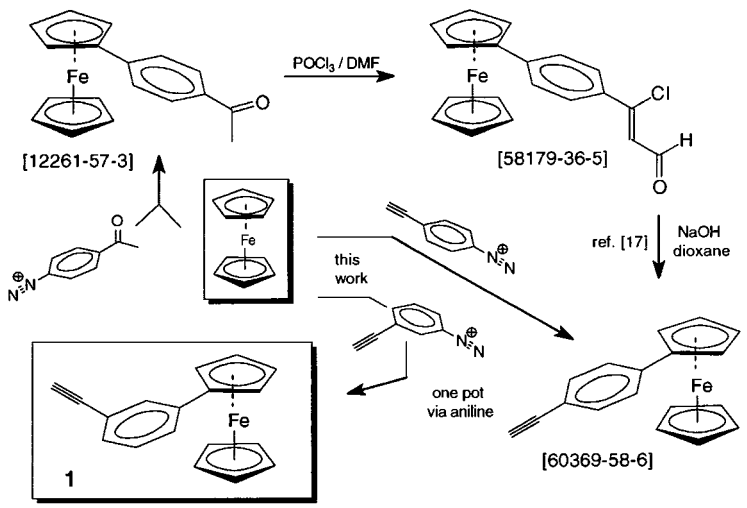
It can be concluded that attaching ethyne directly to ferrocenes definitely requires additional effort, and all methods introduced so far have both benefits and disadvantages.

A very valuable ethynylation starting from acetyl-substituted aromatics via formal dehydratation is the well established method [30] of Neghishi [31] which was successfully applied not only to mono- but also to disubstituted acetylferrocenes [32].

### 2.1.2. Conversion of aldehydes into terminal alkynes

Supplementarily, formylferrocene is also a highly recommendable and affordable starting material, since its preparation tolerates large-scale runs, and during the Vilsmeier formylation a cationic intermediate complex is formed, allowing the removal of all neutral impurities and traces of any unreacted ferrocene [33].

The conversion of aldehydes to acetylenes relies on haloolefinations by Wittig methodologies and subsequent dehydrohalogenations or dehalogenations, respectively. This approach was pioneered by Corey and Fuchs [34], and several groups have published similar procedures independently for the convenient access to ethynylferrocene [35,36], as well as for the preparation of 1,2-doubly ethynylated systems [37a]. In contrast to the 1,1′-diethynylated counterpart, 1,2-diethynylferrocene exhibits much higher stability, thus allowing the




Scheme 1. Synthetic concepts towards ferrocenylphenylacetylenes.

construction of various oligomeric ethyne-bridged *ortho*-ferrocenylenic arrays [37b][37c][37d] as well as Bunz polymers [37e][37f].

Very recently, the Appel reaction [38] was resumed, again for the synthesis of (monosubstituted) ethynylferrocene [39,40], which obviously represents a permanent preparative challenge.

### 2.2. General aspects of preparative chemistry towards diethynylferrocenes

As mentioned above, the unprotected parent compound 1,1′-diethynylferrocene was recognized to be unstable as early as 1965 [21], and found to form four-carbon bridged *ansa*-ferrocenes under conditions of caustic methanolysis of silylated diethynylferrocenes [41].

For the systematic preparative utilisation of 1,1′-diethynylferrocene, a core structure of high synthetic importance, two principal possibilities may be given realistic consideration.

The concept of terminally half-protected ethyne pairs requires a balanced reactivity of the differently protected ethyne termini with respect to adjustable deprotection conditions [42], or, in the case of statistical deprotection, sufficient separability of the desired monoprotected products. For this purpose, the polar mebynol-protecting group (3-hydroxy-3-methylbut-1-ynyl-), which is introducable by quenching acetylides, the primary products of the Neghishi phosphate elimination, with acetone, is a preferable candidate, since the polarity difference versus silanes significantly facilitates chromatographic workup [43].

A second possibility is to keep one acetylenic equivalent on hold by a stepwise conversion of the respective ethyne progenitor functionalities.

In this context, the concept of 1-halo-1′-ethynyl ferrocenes, by treating the halogen as a dormant functionality, has opened an early access to the legendary bimetallocenophane FDA (ferrocenylenediacetylene), an elongated dinuclear system, spaced by two parallel ethyne links [44]. However, this earlier research has found further applications only sparingly [43,45] until it was investigated in depth by the Butler group [46].

A key precondition for this breakthrough was the discovery that 1,1′-dibromoferrocene can be specifically monolithiated at low temperatures and appropriately quenched before warming [47,48]. In the meantime, even *ortho*-lithiations of dibromoferrocenes by means of LDA have been achieved, thus broadening the field towards trisubstituted ethynylferrocenes [49].

Since attempted direct ortholithiations of ferrocenylacetylenes with *tert*-butyllithium/potassium *tert*-butylate resulted in complex mixtures due to unspecific multiple lithiations [50], again the use of LDA according to Butler would be an inviting task.

Finally, also 1,1′-bis(tri-*n*-butylstannyl)ferrocene is capable of selective monotransmetallation, which gives, e.g. access to the stannylated monoaldehyde, a system fit for various couplings or ethynylations on both functionalities [51a].

Doubly stannylated diethynylferrocenes represent equivalently protected starting compounds, also suitable for bridge-incorporation towards heteronuclear organometallic oligomers [51b].

### 2.3. Results based on acetyl- and formylferrocenes

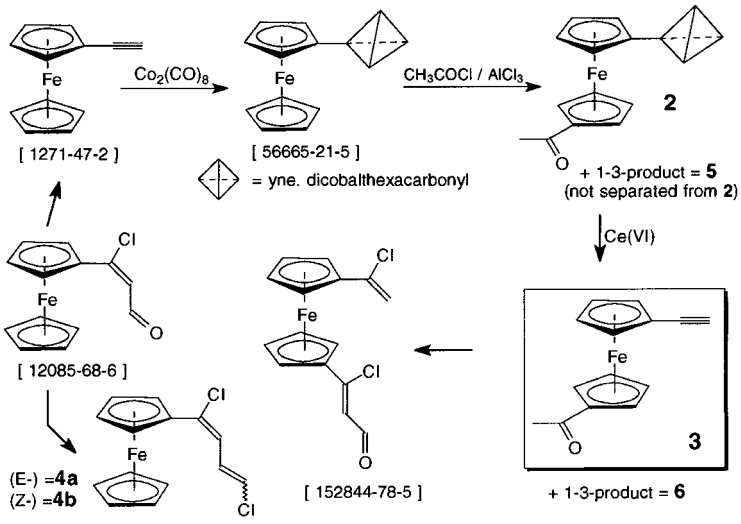
In contrast to halogen-substituted ethynylferrocenes, which are only accessible by preliminary lithiations of suitable ferrocenes, via the stoichiometric use of organometallic bases [53], the semimasked acetyl- or formylferrocenyl substituted acetylenes allow, in certain cases, a more convenient or affordable access to these interesting target compounds.

A paradigm for a masked acetyl-based ferrocenylethyne is of course 3-ferrocenyl-3-chloroacrolein [**12085**] (Scheme 2,Fig. 1), which is also accessible in very high purity in multigram quantities [24].

This key intermediate may not only be of value as a starting compound for the synthesis of ethynylferrocene, but is also a candidate for homologations via the isomers **4** (Scheme 2) to form, e.g. ferrocenylbutadiyne [52] by a twofold dehydrohalogenation, or as a versatile haloalkene-coupling synthon [53].

For Friedel–Crafts acylations, ferrocenylacetylenes have to be prepared by a protection-step of the ethyne-substituent. This is preferably achieved by the dicobalthexacarbonyl fragment [54], since it is stable under the reaction conditions required, and the acetylene is reconstituted very efficiently. The acetylation of ethynylferrocene dicobalthexacarbonyl [**56665-21-5**] proceeds to about 60% of theory, also forming the 1-3-product **5** in 10–15% yield. As expected, the isomers **2** and **7** have very similar retention behavior due to their almost equal polarity, and a separation is not possible by standard chromatography. As a further disadvantage it has to be stated that in contrast to Pauson–Khand reactions of ethynylferrocene dicobalthexacarbonyl [55], the simple protection/deprotection sequence with stoichiometric amounts of hardly affordable cobaltcarbonyl is justified only for special synthetic requirements. For example, 1-iodoethynylferrocene [56] dimerizes unexpectedly upon complexation with dicobalthexacarbonyl [57]. Of course, the resulting bis(dicobaltheaxcarbonyl)1,4-diferrocenylbutadiyne is prepared more conveniently by direct complexation of the already preformed 1,4-diferrocenylbutadiyne [58].

The attempted conversion of **3** to 3-(1′-ethynylferrocen-1-yl)-3-chloroacrolein works as intended on the acetylated site, but also addition of hydrochloric acid occurs under the classical conditions employed, and




Scheme 2. Synthetic routes related to 1-acetyl-1′-ethynylferrocene.

finally 3-(1′-chlorovinylferrocen-1-yl)-3-chloroacrolein, [**152844-78-5**], is formed.

This compound represents the interesting case of a differently masked diethynylferrocene. Fortunately, it can be prepared far more efficiently from 1,1′-diacetylferrocene [59]. The primarily formed bis(1-chlorovinyl)ferrocene undergoes predominantly (54%) [59] only a single Vilsmeier formylation in the next reaction step due to electronic deactivation of the second chloroolefinic moiety imposed by the 1-chloro-3-oxo-propen-1-yl substituent. Whether this compound is suitable for distinct unmasking sequences in a selective manner, remains to be investigated.

Therefore, for the synthetic rationale of the present communication some more affordable semimasked equivalents of 1,1′-ethynylferrocene than **3** are desirable, which implies syntheses with the avoidance of dicobaltoctacarbonyl as an unrecoverable reagent.

This can best be realized by the preparation of 1-ethynyl-1′-formylferrocene (**9**) (Scheme 3).

1-Acetyl-1′-formylferrocene [60] represents an ideal starting compound for this task, since it is prepared cleanly by a Friedel–Crafts acetylation of formylferrocene, and no homoannular 3-substitution takes place.

The subsequent conversion of acetyl- to chloroacrolein-systems (according to the standard route as discussed above for ethynylferrocene) leads to a remarkable by-product, when the reaction mixture is quenched with aqueous sodium acetate. The predominant formation of acylal **7** beside the expected product **8** is attributable to the well known ability of ferrocene to stabilize adjacent carbocations, which presumably facilitates the formation of an adduct of an oxophilic Lewis acid species [61]. This would be possible in the present reaction system in the form of a respective mesomer of an intermediate cationic Vilsmeier formyl-adduct, which is likely to be $S_{N1}$-substituted by acetate ion (see also Scheme 3).

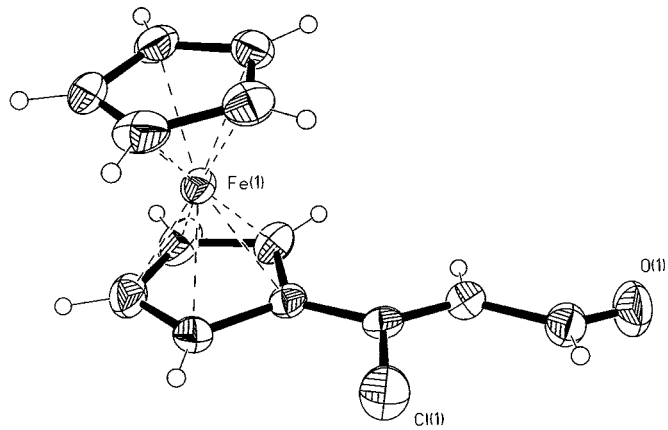



Fig. 1. X-Ray structure of [**12085-68-6**] (CCDC deposit no. 157907).

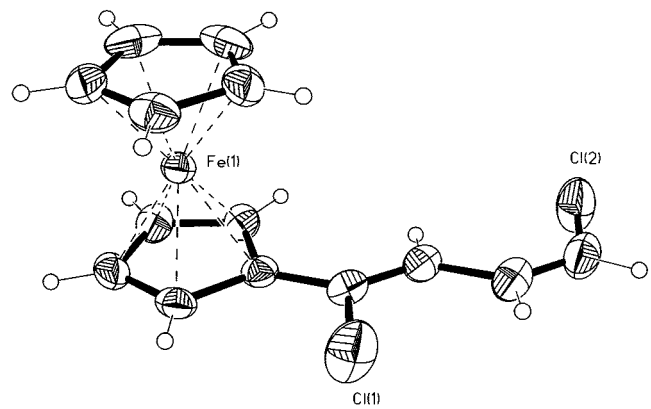



Fig. 2. X-Ray structure of **4a** (CCDC deposit no. 157908).

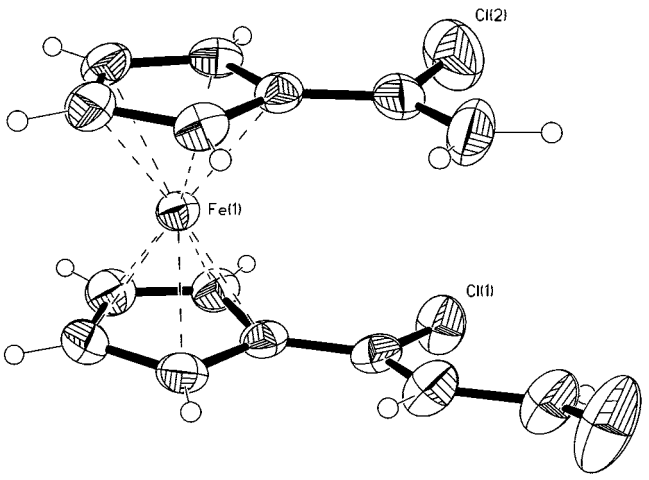
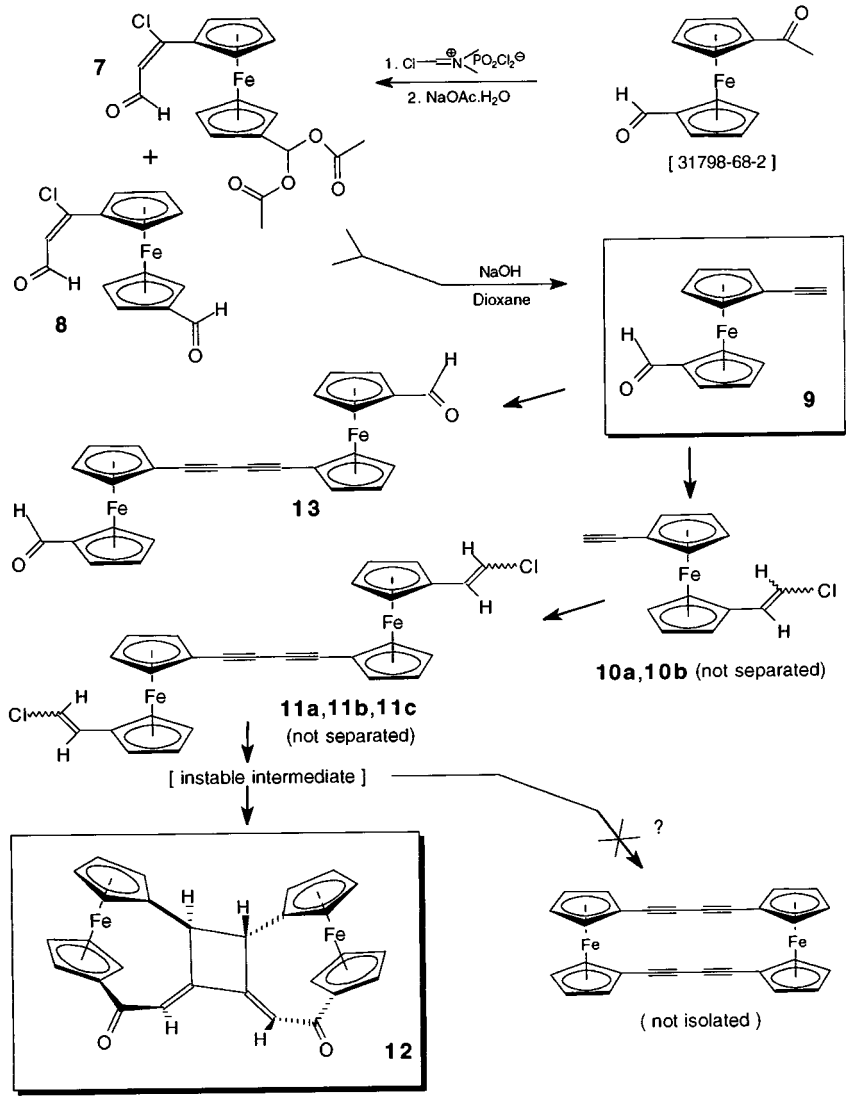



Fig. 3. X-Ray structure of [**152844-78-5**] (CCDC deposit no. 157909).

For the final elimination step to 1-ethynyl-1′-formylferrocene, **9**, no separation of the mixture of the progenitors **7** and **8** is necessary, since both compounds react cleanly to **9**.

With 1-formyl-1′-ethynyl ferrocene at hand, there exist two possibilities to proceed: either derivating the preformed acetylene by substitution steps, e.g. by a Glaser coupling to compound **13**, or to perform the Wittig-haloolefination first, to yield the respective ethynyl-chlorovinylferrocenes (**10a**, **10b**) as 1,1′-diethynylferrocene-equivalents, which can be considered ultimately close to the target compound.

The ultimate goal of this work was to make available a doubly butadiyne-linked biferrocenophane, thus representing a very rigid conjugated system with an even more extended spacer than embodied in ferrocenylene-diacetylene, FDA [44].




Scheme 3. Synthetic routes related to 1-ethynyl-1′-formylferrocene.

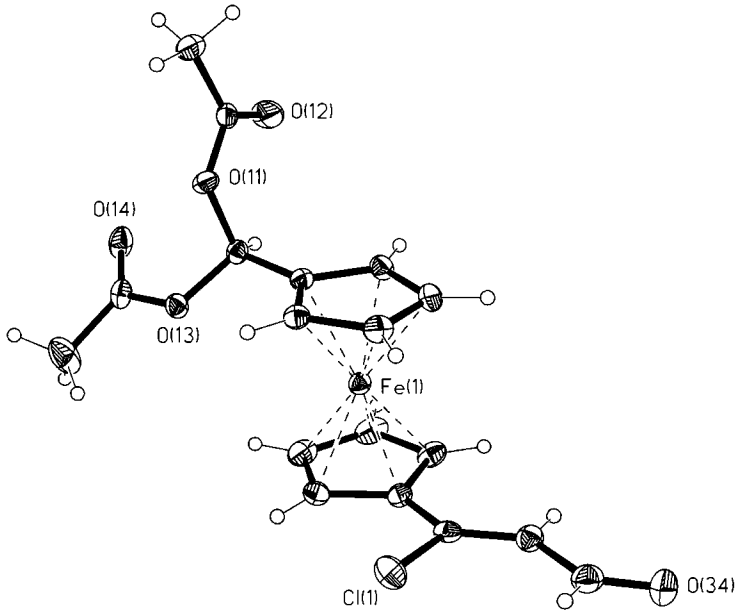



Fig. 4. X-Ray structure of acylal **7** (CCDC deposit no. 157910).

Surprisingly, in an attempted one-pot sequence (see Section 4) starting from the Glaser coupling product **11**, involving the reconstitution of terminal ethynes, followed by their intended intramolecular coupling, the somewhat exotic biferrocenophane **12** could be isolated in about 35% yield, thus posing a still unresolved challenge of mechanistic interpretation. Interestingly, a very specific intrusion of oxygen took place, resembling strikingly a (twofold) sequence analogous to the enol ether ansa-system reported by Pudelski and Callstrom (from bis(trimethylsilylethynyl-)ferrocene by alkaline methanolysis) [41a], which is likely to form a final ketone by protic cleavage of the enol ethers in the aqueous quenching step.

However, it is also possible that, in contrast to the postulated initial attack of methoxide onto liberated 1,1′-diethynylferrocene, a primary monoacetylide anion, (which is likely to be formed by fluoride-mediated desilylation from monoprotected 1,1′-diethynylferrocene) is the actual cyclisation intermediate. If this unstable diacetylenic species is capable of undergoing a type of metathetical ring closure, the respective mechanistic pathway would involve a (transient) species of bent cumulenic [41b] or ethynylcarbenoid [41c] ansa-systems, respectively. Any ring strain imposed by such a bridge formation could be partially relieved by a subsequent addition of methanol or water from the reaction medium.

Substituent alignments equivalent to the conformative preconditions of the Callstrom pathway would also be possible with one terminal and one butadiynic triple bond each. An alcoholate-like anion could eventually be generated from the known THF degradation by butyllithium, namely the enolate anion of acetaldehyde. The remaining carbon framework would still incorporate a (never-disconnected) original butadiyne chain (C21–C24–C23–C22) (Fig. 6). Whether the concomitant squarylene link eventually proceeds under assistance of radical sources from any (acetylenic) copper(I) species remains also a matter of speculation. Conclusively, the outcome of the reaction protocol disclosed herein should encourage the continuation and mechanistic elucidation of this intriguing area of ferrocenophane chemistry offering entirely new perspectives.

### *2.3.1. X-Ray structural results and conformational particularities of **12***

With its peripheric ferrocenediyl units, compound **12** forms a tricyclic system. Because of the conformational

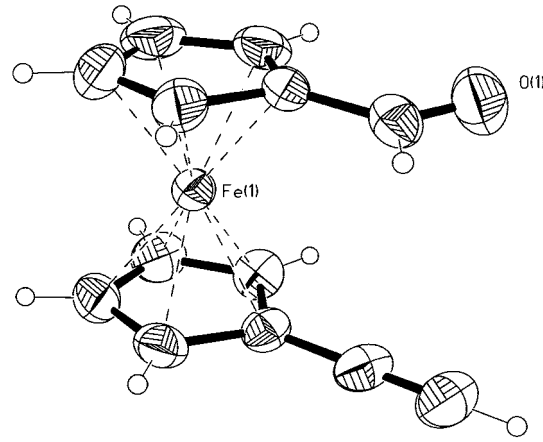
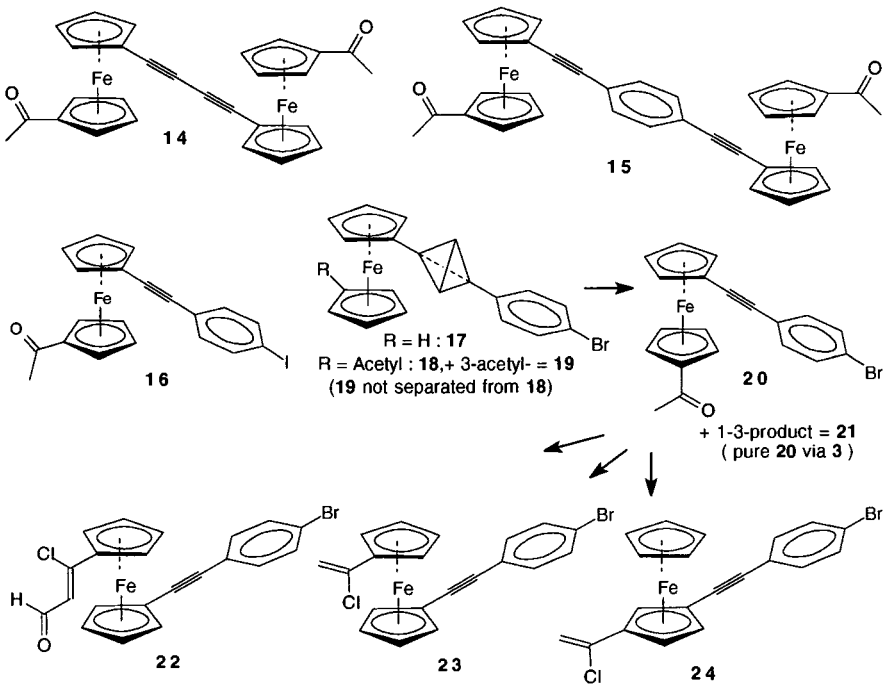



Fig. 5. X-Ray structure of 1-ethynyl-1′-formylferrocene **9** (CCDC deposit no. 157911).




Scheme 4. Synthetic concepts towards dimers and haloarylated ethynylferrocenes.

strain, the cyclopentadienyl rings of the ferrocenes are not planar and the interplanar angles of these rings are 9.4(3)° at Fe(1) and 14.7(2)° at Fe(2), respectively. Therefore the substituted carbon atoms of the cyclopentadienyl rings are nearer to the iron atoms. The ferrocene rings have no exact eclipsed conformation and are twisted by some degrees. As a further consequence of this strain, the central cyclobutane ring is not planar. The torsion angles of C(21)–C(24)–C(23)–C(22) and C(25)–C(24)–C(23)–C(27) are 17.0(3) and 35.0(6)°, respectively. On the other hand, the $C_{sp^2}$-atoms C(23) and C(24) have a nearly exact planar environment, the sum of angles with their substituents are 359.16 and 359.14°. Parts of single bond lengths with the different configurations of the carbon atoms can be compared with a cyclobutene ring ($C_{sp^3}$–$C_{sp^3}$: 1.573 Å and $C_{sp^3}$–$C_{sp^2}$: 1.513 Å), and the short $C_{sp^2}$–$C_{sp^2}$ bond with the attached double bonds can be compared with a butadiene system ($C_{sp^2}$–$C_{sp^2}$: 1.455 Å and $C_{sp^2}$=$C_{sp^2}$: 1.330 Å); all bond values were extracted from Bürgi and Dunitz [62]. The single bonds are C(21)–C(21), C(21)–C(24), C(22)–C(23) and C(23)–C(24) with 1.581(5), 1.532(5), 1.526(3) and 1.477(5) Å and the double bonds are C(23)–C(27) and C(24)–C25) with 1.338(5) and 1.340(5) Å.

### 2.4. Follow-up chemistry

#### 2.4.1. Monomasked terminally substituted ferrocenylacetylenes

The concept of a consecutive 1,1′-double elongation of ferrocenes is of course not limited to Glaser dimerisations, but bears a high potential in aryl couplings, since the linkage of halogenated systems switches the template-motifs again to formal diethynyl equivalents. This was exemplified on the basis of 1-acetyl-1′-ethynylferrocene (**3**) (Scheme 4). Related haloarylations based on 1-ethynyl-1′-formylferrocene (**9**) will be communicated in a dedicated paper.

Alternatively, acetylation/ethyne-introduction is also achievable by a preliminary protection of the already residing ethynes. However, this approach is of limited synthetic value as discussed in detail before.

In this context it is worth noting that, depending on scale and reaction time, again not only the (classical) formyl-chlorovinyl derivative (**24**) is formed exclusively, but the reaction partially ends up with the simple chlorovinyl-products **22** and **23** in a similar manner such as Toma's [59] conversion of 1,1′-diacetylferrocene to [**152844-78-5**] (see also Scheme 2).

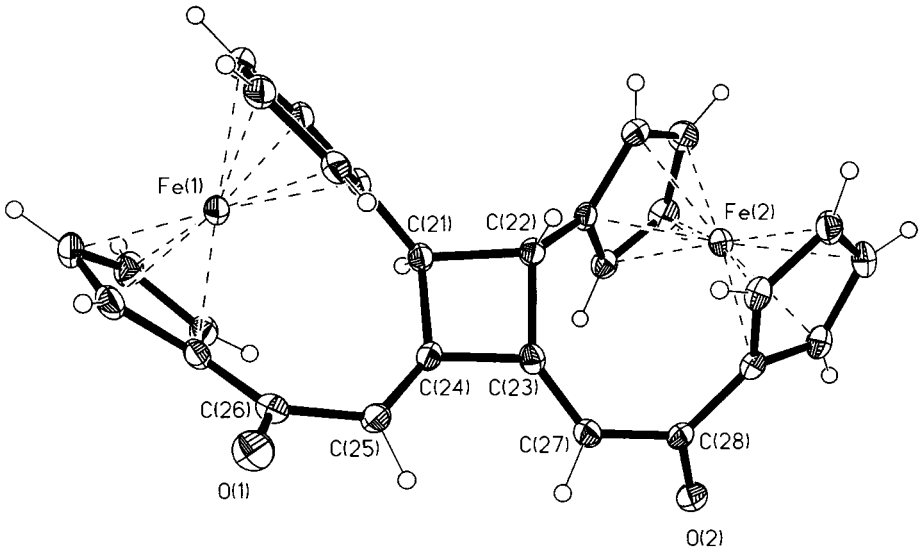



Fig. 6. X-Ray structure of **12** (CCDC deposit no. 157912).

## 3. Conclusions

The combination of reliable classical concepts of acetylenic as well as olefinic and aromatic ferrocene chemistry presented in this communication invite the preparation of sophisticated conjugates with a high diversity, thus facilitating straightforward specific syntheses on demand [63].

## 4. Experimental

All reactions were carried out in the absence of air using standard Schlenk techniques unless stated otherwise. Solvents were deoxygenated, purified and dried prior to use. Purchased starting materials were used without any further purification. Other reagents or starting compounds were prepared according to literature procedures. Improved syntheses of known compounds are also given below.

All starting compounds not referenced are commercially available.

### *4.1. Instrumentation*

$^1$H-NMR: and $^{13}$C-NMR: Bruker AC 200 (200 MHz); IR: Nicolet 510 FT-IR; MS: Varian CH-7 (EI, 70 eV); MAT 95 (FAB); melting points (uncorrected): Kofler hot-plate apparatus.

### *4.2. X-Ray measurement and structure determination of compounds [12085-68-6], 4a, [152844-78-5], 7, 9, 12, [56665-21-5], and [31798-68-2]*

For compounds [**31798-68-2**], **7**, **9**, and **12**, a Bruker P4 diffractometer with graphite-monochromatized Mo–$K_\alpha$ radiation ($\lambda = 0.71.073$ Å) was used for data collection. Intensities were measured via ω-scans and corrected for Lorentz and polarisation effects and an absorption correction, based on φ-scans, was applied to the data. Compounds [**12085-68-6**], **4a**, [**152844-78-5**], and [**56665-21-5**] were measured on a Nonius Kappa CCD area-detector diffractometer ($\lambda = 0.71.073$ Å) with the CCD detector placed 36 mm from the crystal via a mixture of 2° ϕ and ω-scans. The raw data were processed with the program DENZO-SMN [64] to obtain conventional data.

The structures were solved by direct methods (SHELXS-86) [65] and refined by full matrix least-squares against $F^2$ (SHELXL-93) [66]. The function minimized was $\Sigma[w(F_o^2 - F_c^2)^2]$ with the weight defined as $w^{-1} = [\sigma^2(F_o^2) + (xP)^2 + yP]$ and $P = (F_o^2 + 2F_c^2)/3$. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located by difference Fourier methods, but in the refinement they were generated geometrically and refined with isotropic displacement parameters 1.2 times and 1.5 (for the methyl-group) higher than $U$(eq) of the attached carbon atoms.

Further tabulated crystallographic data are included with the supplementary material.

## 5. Synthetic procedures

### *5.1. Preparative section of compounds depicted in Scheme 1*

#### *5.1.1. General diazotization procedure for 3-(Ferrocenyl)-phenylacetylene (1) and 4-(Ferrocenyl)-phenylacetylene [60369-58-6]*

3-Ethynylaniline or 4-ethynylaniline, respectively (1.17 g, 10.0 mmol), was dissolved in a mixture of water

and 3 ml concentrated hydrochloric acid (12 M). The resulting solution was cooled by means of an external ice bath, and afterwards a solution of sodium nitrite (760 mg, 11 mmol) in 50 ml water was added drop-wise through a dropping funnel at a rate so that a temperature of 5 °C was not exceeded. Subsequently, the reaction mixture was stirred for another 30 min under external ice cooling. Then a solution of ferrocene (1.86 g, 10.0 mmol) in 100 ml toluene containing 3 ml acetonitrile was added via a dropping funnel over a period of 15 min. After the removal of the cooling bath, the reaction mixture was stirred for 12 h at ambient temperature. Afterwards the organic layer was separated with a separatory funnel and removed with a rotary evaporator. The residue was dissolved in hexane and subjected to a bed filtration (alumina, 30 g) with a total of 400 ml of hexane. The filtrate was again evaporated to dryness. Residual traces of unconverted ferrocene were sublimed off at 75 °C on a vacuum line equipped with an oil pump. The remainder was recrystallized from *n*-hexane.

*5.1.1.1. 3-(Ferrocenyl)-phenylacetylene (**1**).* Yield: 580 mg (20.3% of theory), yellow solid, m.p.: 110–112 °C; $^1$H-NMR ($CDCl_3$, TMS): $\delta$ 3.10 (s, 1H, ethyne); 4.05 (s, 5H, fec); 4.33 (m, 2 H, fec), 4.64 (m, 2H, fec), 7.22–7.61 (m, 4H, phenylene); $^{13}$C-NMR ($CDCl_3$, TMS): $\delta$ 66.45 (fec), 69.14 (fec), 69.61 (fec), 76.92 (ethyne), 83.84 (ethyne), 84.06 (fec), 121.97, 126.54, 128.33, 129.43, 129.51, 139.73 (phenylene); IR: 3282 $cm^{-1}$, m($\nu$ ≡C–H); 2109 $cm^{-1}$, w($\nu$ ≡C–C).

*5.1.1.2. 4-(Ferrocenyl)-phenylacetylene **[60369-58-6]**.* Yield: 1.258 g (of theory), red solid, m.p.: 63–65 °C; $^1$H-NMR ($CDCl_3$, TMS): $\delta$ 3.09 (s, 1H, ethyne); 4.02 (s, 5H, fec), 4.33(m, 2 H, fec), 4.63(m, 2H, fec), 7.40 (s, 4H, phenylene); $^{13}$C-NMR ($CDCl_3$, TMS): $\delta$ 66.52 (fec), 69.36 (fec), 69.62 (fec), 77.24 (ethyne), 83.98 (ethyne), 84.01 (fec), 119.10, 125.74, 132.12, 140.44 (phenylene); IR: 3294 $cm^{-1}$, m($\nu$ ≡C–H); 2107 $cm^{-1}$, w($\nu$ ≡C–C).

## *5.2. Preparative section of compounds depicted in Scheme 2*

### *5.2.1. Ethynylferrocene.dicobalthexacarbonyl complex **[56665-21-5]***

Since yield improvements have been achieved by modifying the protocol given in the literature [67]; procedural details are given below.

In a Schlenk tube, carefully dried and purged with argon, was placed a solution of ethynylferrocene (3.90 g, 18.5 mmol) in 100 ml of anhydrous THF. To this solution was added in small portions a total of 6.35 g (18.5 mmol) $Co_2(CO)_8$. Spontaneous effervescence of carbon monoxide was accompanied by a color change from orange to black–green. After stirring for about 6 h at room temperature under inert conditions, the complex had formed quantitatively. After filtration of the dark green solution through a glass sintered Schlenk frit and removal of the THF on a vacuum line, ethynylferrocene.hexacarbonyldicobalt was obtained as greenish-black powder (9.00 g, 98% of theory), which was used in the following steps without further purification. For the growth of single crystals, the product was recrystallized from pentane.

Analytical data are in accordance with the literature [63]. MS (EI, 70 eV): $m/z = 496$ $M^+$. IR (KBr) ($cm^{-1}$): 3114m, 2088vs, 2026vs.

$^1$H-NMR ($CDCl_3$, TMS): $\delta$ 4.03 s 5H (unsubst. Cp), 4.24 m 4H, 6.13 s1H(–X–H) m.p.: 79–81 °C.

### *5.2.2. Acetylation of ethynylferrocene.hexacarbonyldicobalt to **(2)** and **(5)***

In contrast to reported procedures [54], the acetylation mixture was added to the substrate (reverse addition mode), since excess $AlCl_3$/acetyl chloride leads to undesired overacetylation. In a Schlenk flask (250 ml), carefully dried and purged with argon, was placed a solution of ethynylferrocene.hexacarbonyldicobalt (640 mg, 1.29 mmol) in 50 ml of anhydrous $CH_2Cl_2$. To this solution was added drop-wise, by means of a dropping funnel (100 ml), a solution of acetyl chloride (110 mg, 0.10 ml; 1.42 mmol = 1.1 equiv.) in 50 ml of anhydrous $CH_2Cl_2$, containing a suspension of $AlCl_3$ (380 mg, 2.85 mmol = 2.2 equiv.), which was separately preprepared in a separate Schlenk tube under stirring for 10–15 min at ambient temperature. After addition of the acetyl chloride/aluminum chloride-complex (within 15–20 min) the color had changed from green to brown and the evolution of hydrogen chloride had ceased (use of excess acetyl chloride/aluminum chloride-complex has to be strictly avoided. The end-point of the reaction can be monitored efficiently by means of TLC ($SiO_2$; pentane/ether 2:1).

After evaporation of $CH_2Cl_2$, a saturated aqueous solution of $NH_4Cl$ was added to the remainder and extracted with diethyl ether. The dark brown ethereal phase was washed thoroughly with water, dried with $Na_2SO_4$ and worked up as usual, yielding a dark, very viscous oil (400 mg, ca. 60% of theory).

The crude product mixture could not be separated by means of column chromatography, and the ethyne-protecting group was removed with $(NH_4)_2Ce(NO_3)_6$ afterwards without further purification. (For analytical purposes a recomplexation of pure target acetylenes is necessary.)

*5.2.2.1. Analytical data for crude mixture.* MS (EI, 70 eV): $m/z = 538$ $M^+$.

IR (KBr): 3089w; 2964w; 2929w; 2856w; 2093vs; 2053b,vs; 2020b,vs; 1675vs; 1455s; 1277vs; 517vs.

*5.2.2.2. Analytical data for 1′-Acetyl-1-ethynylferrocene.hexacarbonyldicobalt (**2**).* MS (EI, 70 eV): $m/z =$ 538 $M^+$.

IR (KBr) ($cm^{-1}$): 3089w; 2964w; 2929w; 2856w; 2093vs; 2053b,vs; 2020b,vs; 1675vs ($\nu$ C=O); 1455s; 1277vs; 517vs.

$^1$H-NMR ($CDCl_3$, TMS): $\delta$ 2.39 (s, 3H, $CH_3$–), 4.31 (s, 5H, unsubst. Cp), 4.44 (pst, 2H), 4.71 (pst, 2H), 6.28 (s, 1H,-ethyne adduct) (broad signals due to instantaneous formation of paramagnetic degradation products).

$^{13}$C-NMR ($CDCl_3$, TMS): $\delta$ 27.40 ($CH_3$–), 69.70, 70.86, 70.99, 71.38, 73.84, 74.41, 79.79, 88.21, 199.11(–$Co_2(CO)_6$–); m.p.: $>$155 °C decomp.

*5.2.3. 1′-Acetyl-1-ethynylferrocene (**3**) and 3-Acetyl-1-ethynylferrocene (**6**)*

Starting from ethynylferrocene.hexacarbonyldicobalt (8.0 g, 16.1 mmol) about 5.35 g of a **2**/**5** mixture was obtained (ca. 60% of theory) as a dark viscous oil. This crude mixture was dissolved in 100 ml acetone (not anhydrous), and $(NH_4)_2Ce(NO_3)_6$ g (16.2 g, 29.5 mmol) was subsequently added in powdered form, causing spontaneous effervescence of carbon monoxide and color change from brownish black to orange. The completion of the reaction can be monitored efficiently by means of TLC ($SiO_2$; pentane/ether 3:1). After evaporation of acetone, the remainder was distributed between water/diethyl ether and extracted with diethyl ether (reducing the aqueous phase with $Na_2S_2O_4$ in order to recover any ferricinium salts caused no improvement of yields). By the usual workup a total of 1.9 g crude **3**/**6** product mixture was obtained.

Afterwards, the product mixture was dissolved in 6 ml of diethyl ether and chromatographed ($SiO_2$ G-60 Fluka, 220–440 mesh; 40 × 4 cm, eluent pentane/ether 3:1). 3-Acetyl-1-ethynylferrocene (**6**) (260 mg, 1.04 mmol, 10% of theory) was eluted first, followed by 1′-acetyl-1-ethynylferrocene (700 mg, 2.78 mmol, 28% of theory).

*5.2.3.1. Analytical data for 1′-acetyl-1-ethynylferrocene (**3**).* MS (EI, 70 eV): $m/z = 252$ $M^+$.

IR (KBr) ($cm^{-1}$): 3236w($\nu$ ≡C–H); 2962m; 2927m; 2856w; 2111w($\nu$ –C≡C–); 1663vs($\nu$ C=O); 1461s; 1279s; 830s.

$^1$H-NMR ($CDCl_3$, TMS): $\delta$ 2.36 (s, 3H, –$CH_3$), 2.78 (s, 1H, –C≡C–H), 4.21 (pst, 2H), 4.42 (pst, 2H),4.51 (pst, 2H),4.75 (pst, 2H).

$^{13}$C-NMR ($CDCl_3$, TMS): $\delta$ 27.64 (–$CH_3$), 70.24, 71.27, 73.10, 73.87, 74.85; m.p.: 76–78 °C.

*5.2.3.2. Analytical data for 3-acetyl-1-ethynylferrocene (**6**).* MS (EI, 70 eV): $m/z = 252$ $M^+$.

IR (KBr): 3234s($\nu$ ≡C–H); 3095w; 2925w; 2856w; 2107w($\nu$ –C≡C–); 1667vs; 1461s; 1426s; 1358s; 1204s; 839s.

$^1$H-NMR ($CDCl_3$, TMS): $\delta$ 2.36 (s, 3H, –$CH_3$), 2.74 (s, 1H, –C≡C–H), 4.23 (s, 5H, unsubst. Cp), 4.74 (m, 2H), 5.01 (m, 1H).

$^{13}$C-NMR ($CDCl_3$, TMS): $\delta$ 27.30 (–$CH_3$), 69.80, 71.76, 72.28, 72.83, 74.87, 75.49; m.p.: 82–84 °C.

*5.2.4. 3-(1′-chlorovinylferrocen-1-yl)-3-chloroacrolein **[152844-78-5]***

1-Acetyl-1′-ethynylferrocene (**3**) (220 mg, 0.873 mmol) was suspended in 0.5 ml of DMF. The suspension was cooled down to 0 °C with an ice-water bath and then treated with the Vilsmeier-complex, which was preformed from 0.5 ml of $POCl_3$ and 0.5 ml of DMF. The resulting suspension turned deep blue after about 1 min. The reaction mixture was stirred for 1 h, while keeping the temperature at 0 °C by means of the ice-water bath. Afterwards, 3 ml of diethyl ether were added and the suspension was stirred for another 10 min in order to remove any unreacted ferrocene. The ethereal layer was removed by suction and replaced by 3 ml of fresh ether. Afterwards, the suspension was treated with 2.9 g of sodium acetate trihydrate (21.5 mmol, 4 equiv. based on $POCl_3$) The color changed from deep blue to burgundy-red within 5 min; stirring was continued for 12 h. To the red solution was added more water and ether, and the aqueous layer was extracted with four portions of ether (50 ml each). The combined organic layers were washed with three portions of saturated $NaHCO_3$ (50 ml each), and subsequently, with three portions of water (50 ml each). The ethereal phases were collected, dried over $Na_2SO_4$ and evaporated to dryness.

The crude product obtained was purified by column chromatography (ether/*n*-hexane 3:1, silica gel 60, Fluka 60741) yielding crystalline material (see also Fig. 3).

The spectroscopic data are in accordance with the literature [59].

*5.2.5. (E,Z-)1,4-Dichlorobut-1,3-dien-1-ylferrocene (**4a**, **4b**)*

A Schlenk vessel was charged with chloromethyl triphenylphosphonium chloride (1.518 g, 4.37 mmol) and 40 ml anhydrous THF. The suspension was cooled to −50 °C (ethanol/liquid nitrogen cooling bath). Afterwards, potassium *tert*-butylate (1.350 g, 12.0 mmol, 1.2 mequiv.) was added all at once. The cooling bath was replaced by an ice/water cooling bath and the deep red mixture was stirred for 30 min at 0 °C. Subsequently, 1-chloro-1-ferrocenylacroleine (1.00 g, 3.64 mmol) [**12085-68-6**] was added, and the mixture turned to red–blue. The cooling bath was removed, and after stirring for 1 h at room temperature, the mixture was quenched with 30 ml of saturated ammonium chloride solution, and most of the THF was removed on a

rotary evaporator. The resulting suspension was extracted with 100 ml $CH_2Cl_2$. The $CH_2Cl_2$ layer was washed with 50 ml water and 30 ml of brine. After drying with $Na_2SO_4$, the organic solvent was evaporated. The crude product was purified by column chromatography (silica, $3 \times 30$ cm, *n*-hexane). The (*E*-) isomer **4a** eluted first (separated (*Z*-) isomer **4b** see below). Total yield of isomer mixture: 0.835 g (75% of theory).

*5.2.5.1. Analytical data for **4a**.* $^1$H-NMR ($CDCl_3$, TMS): $\delta$ 4.21 (s, 5H, unsubst. Cp), 4.35 (pst, 2H, subst. Cp), 4.63 (pst, 2H, subst. Cp), 6.12 (d, 1H, $^3J = 6.27$, trans), 6.78 (m, 2H, olefinic) 6.32.

$^{13}$C-NMR ($CDCl_3$, TMS): $\delta$ 67.23, 69.95, 70.11, (fec), 117.40, 121.55, 129.79, 133.58 (olefinic); MS (FAB): $m/z$ 307 (100%) $C_{14}H_{12}FeCl_2$, M = 307.00 g/mol, red solid, air stable, m.p.: 95–97 °C (corrected with benzil); $R_f$-value(TLC): 0.83 (silica, *n*-hexane/ether = 1:1).

*5.2.5.2. Analytical data for **4b**.* $^1$H-NMR ($CDCl_3$, TMS): $\delta$ 4.21 (s, 5H, unsubst. Cp), 4.35 (pst, 2H, subst. Cp), 4.63 (pst, 2H subst. Cp) 6.32 (m, 2H, olefinic cis), 6.90(t, 1H, cis).

$^{13}$C-NMR ($CDCl_3$, TMS): $\delta$ 67.23, 69.95, 70.11, (fec), 117.40, 121.55, 129.79, 133.58 (olefinic), MS (FAB): $m/z$ 307 (100%).

### *5.3. Preparative section of compounds depicted in Scheme 3*

#### *5.3.1. 1-Acetyl-1′-formylferrocene [**31798-68-2**]*

In order to provide more details, slightly modified parameters of the protocol according to Sato [60] are given below.

Formylferrocene [33] is acetylated over a period of 4 h with $AlCl_3$/acetyl chloride at 0 °C (not at ambient temperature) in $CH_2Cl_2$. For large-scale syntheses (above 10 g formylferrocene) the purification is performed best by means of a silica-bed filtration ($20 \times 4$ cm): the reaction workup containing unconverted formylferrocene is loaded on the bed with a 1:1 mixture of pentane/diethyl ether (200 ml), where the product is retained, while formylferrocene can be eluted slowly. Afterwards, 1-acetyl-1′-formylferrocene is eluted with pure diethyl ether, (40% of formylferrocene can be recycled; the yield of 1-acetyl-1′-formylferrocene ranges between 40 and 45% of theory (reddish brown crystals).

#### *5.3.2. (1-Chloro-2-formylvin-1-yl)-1′-formylferrocene (**7**) and acylal **8***

In analogy to the procedural details according to Polin et al. [24]: The orange colored Vilsmeier complex formed from 10 ml (110 mmol = 2.5 equiv.) $POCl_3$ and 10 ml DMF (cooled to 0 °C) was added drop-wise within 15 min to a suspension (11.0 g, 43 mmol) of 1-acetyl-1′-formyl-ferrocene [60] in 10 ml DMF (no dried solvent required), precooled to 0 °C. Afterwards, the reaction mixture is stirred for another 15 min at 0 °C, and finally at room temperature for 2 h. During this time the color continuously changes from orange to brownish and finally to intensely deep blue. The Vilsmeier mixture was quenched with about 60 g (ca. 400 mmol) sodium acetate trihydrate. The aqueous phase was neutralized with sodium hydrogen carbonate. Afterwards, the deeply red product mixture, consisting of **7** and **8**, can easily be extracted with $CH_2Cl_2$.

Yield: ca. 12.4 g viscous red oil.

For analytical purposes, the mixture, consisting of about 50% **7** and **8**, was separated by means of silica-chromatography, with pentane/ether 1:1 as eluent.

Otherwise the mixture is converted without previous separation, since both compounds react cleanly to 1-ethynyl-1′-formylferrocene (**9**) in boiling KOH/dioxane as described below.

*5.3.2.1. Analytical data for **7**.* MS (EI, 70 eV): $m/z$ = 404.5 $M^+$.

IR (KBr): 1760vs + 1742s($\nu$ $CH_3$–C(=O)–), 1661vs($\nu$ –HC=O), 1602s + 1588s($\nu$ C=C), 1380s, 1250vs, 1218vs, 1208s, 1135s, 1079s, 1013s, 972s, 936s, 835s.

$^1$H-NMR ($CDCl_3$, TMS): $\delta$ 2.10 (s, 6H, $2 \times$ $CH_3$–), 4.29 (pst, 2H), 4.37 (pst, 2H), 4.54 (pst, 2H), 4.74 (pst, 2H), 6.35–6.39 (d, 1H, $J = 7.0$ Hz, –CH=), 7.55 (s, 1H, acetylal-H), 10.04–10.07 (d, 1H, $J = 7$ Hz, –CHO).

$^{13}$C-NMR ($CDCl_3$, TMS): $\delta$ 20.90($CH_3$–), 69.19, 69.58, 71.56, 72.96, 75.40, 87.46(–CH=), 121.07(=CCl–), 168.63(acetylal), 190.74(–CHO); m.p.: 96–99 °C.

*5.3.2.2. Analytical data for **8**.* MS (EI, 70 eV): $m/z$ = 302 $M^+$.

IR (KBr): 1684vs + 1665vs($\nu$ C=O), 1603vs + 1588vs($\nu$ C=C), 1457s, 1262s, 1245s, 1133vs.

$^1$H-NMR ($CDCl_3$, TMS): $\delta$ 4.59 (pst, $2 \times$ 2H), 4.77 (pst, $2 \times$ 2H), 6.32–6.35 (d, 1H, $J = 6.4$ Hz, –CH=), 9.89 (s, 1H, fec-CHO), 10.03–10.06 (d, 1H, $J = 6.4$ Hz, 1-vinylic-CHO).

$^{13}$C-NMR ($CDCl_3$, TMS): $\delta$ 69.63, 71.52, 73.05, 75.20, 80.53, 81,76, 121.62 (–CH=), 152.28 (=CCl–), 190.41 (fec –CHO), 192.54 (1-vinylic-CHO); m.p.: –, red oil.

#### *5.3.3. 1-Ethynyl-1′-formyl ferrocene (**9**)*

A 1-l three-necked flask, equipped with a reflux condenser, was charged with a solution of **7** and **8** (12.4 g, ca. 40 mmol) in 250 ml freshly distilled dioxane and brought to boiling for about 5 min. At the same time,

potassium hydroxide (14.5 g, 260 mmol = 6 equiv.) was dissolved in 500 ml water (resulting molarity 0.5 N); the caustic solution was also brought to boiling, and added as such (not though the condenser) to the preheated dioxane solution, whereupon an immediate color change to brown occurred. The reaction mixture was boiled further for 10 min, and subsequently chilled by addition of a mixture of ice and water. Afterwards, diluted hydrochloric acid was added for neutralisation. The product was extracted with diethyl ether. Workup as usual resulted in a product almost free from more polar impurities, usable for the following conversions without further purification. For analytical purposes, traces of contaminants are easily removed by chromatography ($SiO_2$; pentane/ether 2.1).

*5.3.3.1. Analytical data for **9**.* MS (EI, 70 eV): $m/z =$ 238 $M^+$.

IR (KBr): 3289m($\nu$ ≡C–H), 2110w(–C≡C–), 1684vs + 1667s($\nu$ C=O), 1456m, 1261m, 1246m, 1096s, 1038s, 804s.

$^1$H-NMR ($CDCl_3$, TMS): $\delta$ 2.78 (s, 1H, ≡C–H), 4.26 (pst, 2H), 4.50 (pst 2H), 4.59 (pst, 2H), 4.78 (pst, 2H), 9.93 (s, 1H, –CHO).

$^{13}$C-NMR ($CDCl_3$, TMS): $\delta$ 65.97, 68.44, 70.04, 71.04, 72.90, 74.98, 75.33, 80.38, 110.47, 136.90, 193.41(–CHO); m.p.: 58–60 °C.

*5.3.4. E/Z-1-(1-Chlorovinyl)-1′-ethynylferrocenes (**10a**, **10b**)*

'Instant-Ylide' (284 mg; 0.62 mmol) (Fluka No. 25302; = chloromethyl triphenyl phosphonium chloride/sodium amide; 2.2 mol/g) are weighed into a Schlenk tube and triturated with 4 ml THF. The resulting solution turned red and was cooled to −80 °C. Subsequently a cooled (−40 °C) solution of 1-ethynyl-1′-formylferrocene (**9**) (0.135 g, 0.57 mmol) in 4 ml anhydrous THF was added and allowed to come to ambient temperature. After 1 h, the mixture was worked up by quenching with water, followed by an extraction with diethyl ether (for even smaller scales, extraction with hexane is preferable in order to separate the by-product triphenylphosphine oxide, which is almost insoluble in hexanes). Otherwise, the apolar product (isomers **10a**, **10b**) is separated from the reaction matrix by silica-chromatography with petroleum ether as eluent. According to TLC, this eluate consists only of isomers **10a** and **10b** (Scheme 3).

Yield: 115 mg (ca. 67% theory) red–orange oil.

*5.3.4.1. Analytical data for E/Z-1-(1-Chlorovinyl)-1′-ethynylferrocenes **10a**, **10b**.* MS (EI, 70 eV): $m/z = 270$ $M^+$.

IR (KBr): 3395m($\nu$ –C–H), 2110m($\nu$ –C≡C–), 1633s + 1615s($\nu$ C=C), 1253m, 1094m, 1029s, 815s.

$^1$H-NMR ($C_6D_6$, TMS): $\delta$ 2.49 (s, 1H, C≡C–H), 3.73–4.52 (m, 8H, 1,1′-subst. fec), 5.78–6.01 (m, 2H, –CH=CHCl) isomer mixtures.

$^{13}$C-NMR ($CDCl_3$, TMS): isomer mixtures; signal domains at $\delta$ 70, and 110–135; m.p.: red–orange oil.

*5.3.5. 1,4-bis-[1′-(1-Chlorovinyl)-ferrocen-1-yl]-1,3-butadiyne (**11**; isomers **a**,**b**,**c**)*

(Glaser coupling) CuCl (34 mg, 0.35 mmol) was suspended in 10 ml dimethoxyethane (DME). Subsequently, tetramethylethylenediamine (0.090 ml, 61 mmol) was added, resulting in a deep bluish-green suspension. To this suspension was added drop-wise a solution 1′-(1-chlorovinyl)-1-ethynylferrocene (**10**), (470 mg, 0.84 mmol) in 20 ml DME, whereupon air was bubbled through by suction for 24 h. Afterwards the reaction mixture was quenched with saturated aqueous ammonium chloride solution. The somewhat sparingly soluble product was extracted with $CH_2Cl_2$ and worked up in the usual manner. The final purification was achieved by means of silica chromatography with petroleum ether as eluent. From about 500 mg crude product, 250 mg of 1,4-bis-[1′-(1-chlorovinyl)-ferrocen-1-yl]-1,3-butadiyne (**11**) were isolated as a red–orange powder (ca. 50% of theory).

*5.3.5.1. Analytical data for 1,4-bis-[1′-(1-chlorovinyl)-ferrocen-1-yl]-1,3-butadiyne (**11**; isomers **a**,**b**,**c**).* MS (EI, 70 eV): $m/z = 538/540$ $M^+$.

IR (KBr): 2962m, 2924m, 2854w, 2146w($\nu$ –C≡C–), 1631m (b)($\nu$ C=C), 1261vs, 1096vs, 1030vs, 802vs.

$^1$H-NMR ($C_6D_6$, TMS): $\delta$ 4.21 (pst, 4H), 4.45 (pst, 4H), 4.31 (m), 4.32(m), 4.35 (m), 4.72 (pst, 8H), 6.15–6.55 (m, 4H, 2 × –CH=CHCl).

$^{13}$C-NMR ($CDCl_3$, TMS): $\delta$ 68.23, 70.38, 70.59, 70.90, 71.14, 71.45, 73.14, 115.17/115.23(–CH=), 115.83(–C≡), 126.58/126.64(=CCl), 129.40(–C≡). m.p.: 140–165 °C (isomer mixture).

*5.3.6. Bis-([4]Ferrocenophane-1-one-2-ene-3,4-diyl) (**12**)*

1,4-Bis-[1′-(1-chlorovinyl)-ferrocen-1-yl]-1,3-butadiyne (**11**; isomers a,b,c), (270 mg, 0.50 mmol), was dissolved in 20 ml anhydrous THF. Afterwards potassium *tert*-butylate (560 mg, 5 mmol) was added and refluxed for 12 h. The THF was removed on the vacuum line, and the remainder quenched with water. Subsequently, the product was extracted with diethyl ether, and the combined organic phases washed with several portions of water. After drying with sodium sulfate, the ether was evaporated and the remainder was triturated with *n*-hexane in order to remove residual *tert*-butanol.

According to TLC($SiO_2$, $Al_2O_3$) the intermediate showed very low stability, therefore it was immediately used for the final conversion to the ferrocenophane (**12**).

*5.3.6.1. Analytical data for hypothetical intermediate 1,4-bis-[1′-(ethynyl)-ferrocen-1-yl]-1,3-butadiyne (as available).* MS (EI, 70 eV): no parent molecular ion was detectable.

IR (KBr): 3306w (*v* –C≡CH), 2150w (*v* –C≡C–), 2111w (*v* –C≡C–), 1621m (broad) (*v* –C=C–), 1260s, 1097vs, 1025vs, 805vs; m.p.: orange–red oil (not purified).

$^1$H-NMR; $^{13}$C-NMR ($CDCl_3$): no conclusive data due to instability.

(Authentic report of an attempted one-pot sequence towards a symmetric bimetallocenophane with serendipitous result: lithiation–iodination–cupration–cyclisation = intramolecular coupling according to Cadiot-Chodkiewicz.)

In a Schlenk tube, the product containing the hypothetical 1,4-bis-[1′-ethynylferrocen-1-yl]-1,3-butadadiyne (840 mg, ca. 1.80 mmol), prepared as described above, was dissolved in anhydrous THF, and cooled to −80 °C. Subsequently, *n*-butyllithium (1.24 ml, 1.6 M solution in hexane; 2.0 mmol) was added, and the reaction mixture was allowed to reach room temperature while stirring. During this period, the solution changed in color from orange to dark brown. The solution was again cooled to −80 °C, and then iodine (260 mg, 2.0 mmol) was added all at once (in our experience iodoethynes do not react freely with lithoacetylides before transmetallation); after the immediate discoloration of added iodine, no further color change was observable. The temperature of the slightly warmed up reaction mixture was again adjusted to −80 °C, and *n*-butyllithium (1.24 ml, 1.6 M solution in hexane; 2.0 mmol) was added. Afterwards, the solution was allowed to reach room temperature. Subsequently, the reaction mixture was recooled to −80 °C for a fourth time, and copper(I)bromide.dimethylsulfide (410 mg, 2.0 mmol) was added. Finally the reaction mixture was again allowed to warm to ambient temperature. The THF was removed by means of a vacuum line (oil pump), and the residue triturated with 30 ml anhydrous pyridine. Afterwards, the resulting mixture was refluxed for 15 h and then the pyridine was removed on the vacuum line. The remainder was quenched with saturated aqueous ammonium chloride solution and extracted with diethyl ether. The reddish-brown organic phase was separated, and the remaining brown insolubles filtered off from the aqueous phase and washed with ether for several times, yielding red-brown ethereal extract portions. By the usual workup of the combined organic layers, 60 mg of a purple powder were obtained. The insoluble residual part of the extraction procedure was subjected to a Soxhlet extraction with toluene for 24 h, whereupon another 150 mg of purple bis-([4]ferrocenophane-1-on-2-ene-3,4-diyl-) **12** could be isolated. Both portions proved to be identical and analytically pure according to TLC ($SiO_2$; diethyl ether). The overall yield amounted to about 30% of theory, with an absolutely insoluble remainder of an additional 620 mg. If intractable polymers, or a second elongated, very rigid biferrocenophane (likely to exhibit very low solubility) was also formed, it could possibly be clarified by attempts to oxidatively solubilize the rest of any insolubles.

*5.3.6.2. Analytical data for bis-([4]ferrocenophane-1-on-2-ene-3,4-diyl-) (**12**).* MS (EI, 70 eV): $m/z = 500$ $M^+$.

IR (KBr): 3084w, 2960w, 2925m, 2854w, 1620vs(*v* C=O + *v* C=C), 1453m, 1285m, 1120m, 1027m, 814m, 739m.

$^1$H-NMR ($C_6D_6$, TMS): $\delta$ 3.88 (s, 1H, CH), 4.02–4.05 (m, 1H), 4.30–4.32 (m, 3H), 4.44–4.47 (m, 1H), 4.54–4.61 (m, 3H), 6.46 (s, 1H, =CH–).

$^{13}$C-NMR ($CDCl_3$, TMS): $\delta$ 52.06 (CH), 67.00, 69.23, 69.41, 69.76, 72.02, 72.30, 73.40, 73.47, 74.08, 77.22, 79.08, 86.52, 122.27(=CH–), 152.81 (quaternary olefinic), 197.43(CO); m.p.: 250–270 °C, brownish-purple powder; (see also X-ray structure, Fig. 6).

*5.3.7. 1,4-Bis-(1′-formylferrocen-1-yl)-1,3-butadiyne (**13**)*

(Glaser coupling) CuCl (20 mg, 0.2 mmol) was suspended in 10 ml dimethoxyethane (DME). Subsequently, tetramethylethylenediamine (0.040 ml, 0.27 mmol) was added, resulting in a deep bluish-green suspension. To this suspension was added drop-wise a solution of 1-ethynyl-1′-formylferrocene (**9**), (200 mg, 0.84 mmol) in 20 ml DME, whereupon air was bubbled through by suction for 24 h. After this time, the reaction mixture still contained some **9**, which turned out to be not completely stable under these conditions. Therefore the coupling sequence was terminated. Afterwards the reaction mixture was quenched with saturated aqueous ammonium chloride solution. The sparingly soluble product was extracted with $CH_2Cl_2$ and worked up in the usual manner. By a final purification by chromatography ($SiO_2$-column with pentane/ether eluent) a few milligrams of starting material (**9**) were obtained; the target compound (**13**) was obtained in less than 25% of theory (50 mg) as orange–red powder. The silica column persistently remained red, even after flushing with pure diethyl ether.

*5.3.7.1. Analytical data for 1,4-bis-(1′-formylferrocen-1-yl)-1,3-butadiyne (**13**).* MS (EI, 70 eV): $m/z = 474$ $M^+$.

IR (KBr): 3105w, 2960w, 2925m, 2153w(*v* –C≡CH), 1685vs(*v* C=O), 1665s, 1457m, 1245m, 1040m, 1027m, 822m, 744m.

$^1$H-NMR ($C_6D_6$, TMS): $\delta$ 4.34 (pst, 4H), 4.57 (pst, 4H), 4.67 (pst, 4H), 4.85 (pst, 4H), 9.97 (s, 2 × 1H (2 × –CHO).

$^{13}$C-NMR ($CDCl_3$, TMS): $\delta$ 70.68, 71.21, 73.32, 75.24, 193.78(CHO); m.p.: > 180 °C dec.

*5.4. Preparative section of compounds depicted in Scheme 4*

*5.4.1. 1,4-Bis-(1′-acetylferrocen-1-yl)-1,3-butadiyne (**14**)*

(Glaser coupling) CuCl (16 mg, 0.16 mmol) was suspended in 10 ml dimethoxyethane (DME), whereupon the reaction mixture turned yellowish-green. Subsequently, tetramethylethylenediamine (0.040 ml, 27 mmol) was added, resulting in a deep bluish-green suspension. To this suspension was added drop-wise a solution of 1′-acetyl-1-ethynylferrocene (**10**) (200 mg, 0.80 mmol) in 20 ml DME, whereupon air was bubbled through by suction for 24 h. Afterwards the reaction mixture was quenched with saturated aqueous ammonium chloride solution. Most of the sparingly soluble product precipitated as orange solid (TLC: $SiO_2$/diethyl ether $R_f$ educt = 0.80, $R_f$ product = 0.60). Final purification was performed by trituration of the crude product in diethyl ether under ultrasonication by means of a cleaning bath. Afterwards, the suspension was loaded onto a column of about 20 cm silica gel, and the monomer starting compound was eluted with diethyl ether. Finally, the solid on top of the column was solubilized and eluted with dichloromethane.

*5.4.1.1. Analytical data for 1,4-bis-(1′-acetylferrocen-1-yl)-1,3-butadiyne (**14**).* MS (EI, 70 eV): $m/z = 502$ $M^+$.

IR (KBr) ($cm^{-1}$): 3078m; 2964w; 2925w; 2856w; 2153m(*v* –C≡C–); 1654vs(*v* C=O); 1457s; 1281s.

$^1$H-NMR ($C_6D_6$, TMS): $\delta$ 2.43 (s, 6H, 2 × –$CH_3$), 4.27 (pst, 2 × 2H), 4.49 (pst, 2 × 2H), 4.56 (pst, 2 × 2H), 4.81 (pst, 2 × 2H).

$^{13}$C-NMR ($CDCl_3$, TMS): $\delta$ 27.91(–$CH_3$), 70.95, 71.36, 73.53, 74.17; m.p.: 216–218 °C.

*5.4.2. 1,4-Bis(1′-acetylferrocen-1-ylethynyl)-benzene (**15**)*

(Sonogashira–Hagihara coupling) 1,4-Diiodobenzene (100 mg, 0.30 mmol), and 1′-acetyl-1-ethynylferrocene (185 mg, 0.73 mmol) are dissolved in 20 ml of diisopropylamine, which was previously saturated with argon. Afterwards, CuI (2 mg, 0.02 equiv.) and bis(triphenylphosphine) palladium dichloride (8 mg, 0.02 equiv.) were added as catalysts. The reaction mixture was stirred at room temperature under argon for 12 h. The primarily orange solution gradually turned into a dirty-brown suspension, separating a white precipitate (diisopropylammonium iodide). Workup was accomplished by evaporation of diisopropylamine, followed by column chromatography of the remainder with diethyl ether on silica gel (column size 30 × 3 cm), yielding three isolable compounds: 1-(1′-acetylferrocen-1-yl-ethynyl)-4-iodo-benzene (**16**), $R_f = 0.85$ (30 mg, 21% of theory with reference to 1,4-diiodobenzene); 125 mg 1,4-bis(1′-acetylferrocen-1-ylethynyl)-benzene (**15**), $R_f = 0.65$ (71% of theory with reference to 1,4-diiodobenzene); and 1,4-bis-(1′-acetylferrocen-1-yl)-1,3-butadiyne (**14**) (30 mg), see above.

*5.4.2.1. Analytical data for 1,4-bis(1′-acetylferrocen-1-ylethynyl)-benzene (**15**).* MS (EI, 70 eV): $m/z = 578$ $M^+$.

IR (KBr): 3108w; 2964w; 2223b, w(*v* –C≡C–); 1673vs(*v* C=O); 1509m; 1459m; 1277s; 857m; 820s.

$^1$H-NMR ($C_6D_6$, TMS): $\delta$ 2.40 (s, 6H, 2 × –$CH_3$), 4.27 (pst, 2 × 2H), 4.49 (pst, 2 × 2H), 4.53 (pst, 2 × 2H), 4.80 (pst, 2 × 2H), 7.44 (s, 4H, 1,4-disubst. phenyl).

$^{13}$C-NMR ($CDCl_3$, TMS): $\delta$ 27.64 (–$CH_3$), 67.04, 70.42, 71.17, 72.77, 73.69, 80.62, 86.87/88.12 (–C≡C–), 122.85(–C=phenyl–), 131.36(–CH–phenyl–), 201.38 (–CO–); m.p.: > 230 °C without perceptible decomp.

*5.4.2.2. Analytical data for 1-(1′-acetylferrocen-1-ylethynyl)-4-iodobenzene (**16**).* MS (EI, 70 eV): $m/z = 454$ $M^+$.

IR (KBr): 3089w; 2962w; 2925w; 2854w; 2209w(*v* –C≡C–); 1663vs(*v* C=O); 1493s; 1457s; 1370s; 1277s; 830vs.

$^1$H-NMR ($C_6D_6$, TMS): $\delta$ 2.39 (s, 3H, –$CH_3$), 4.67 (pst, 2H), 4.48 (pst, 2H), 4.53 (pst, 2H), 4.80 (pst, 2H), 7.24–7.44 (m, 4H, 1,4-disubst. phenyl–).

$^{13}$C-NMR ($CDCl_3$, TMS): $\delta$ 27.65 (–$CH_3$), 70.40, 71.17, 72.77, 73.67, 128.64, 132.70; m.p.: 91–94 °C.

*5.4.3. 1-(2-Ferrocenylethyn-1-yl)-4-bromobenzene.hexacarbonyldicobalt (**17**)*

*5.4.3.1. 4-Bromophenylethynylferrocene [**238099-24-6**] [3].* Since the synthesis of this starting compound was prepared by a route [58] deviating from the published [3] Stephens–Castro Reaction, details of the protocol followed are given below (Sonogashira–Hagihara coupling).

1-Bromo-4-iodobenzene (675 mg, 2.38 mmol) and ethynylferrocene (500 mg, 2.38 mmol) were dissolved in 100 ml of argon-saturated diisopropylamine. Afterwards, CuI (5 mg, 0.02 equiv.) and bis(triphenylphosphine) palladium dichloride (30 mg, 0.02 equiv.) were added as catalysts. The reaction mixture was stirred at room temperature under argon for 18 h. The primarily orange solution gradually turned into a dirty-brown suspension, separating a white precipitate (diisopropylammonium iodide) along with an orange colored precipitate of product. Workup was accomplished by evaporation of diisopropylamine, followed by column chromatography of the remainder with cyclohexane on silica gel. By this purification procedure also unconverted 1-bromo-4-iodobenzene ($R_f$ 0.75; 370 mg), the target product 1-(2-Ferrocenylethyn-1-yl)-4-bromobenzene ([**238099-24-6**], $R_f$ 0.40) and the dimerisation by-product 1,4-diferrocenyl-1,3-butadiyne ([**1273-18-3**], 130

mg) [36,52] were isolated. The yield of desired [**238099-24-6**] amounted to about 43% of theory.

The respective yield could be significantly improved for preparations on a larger scale, since the formation of dimer (1,4-diferrocenyl-1,3-butadiyne) was negligible.

Purification is also achievable by boiling the crude product in cyclohexane, with subsequent hot filtration and slow crystallisation, e.g. a preparative run with 3.00 g of 1-bromo-4-iodobenzene, 2.25 g of ethynylferrocene, 20 mg CuI, and 150 mg bis(triphenylphosphine) palladium dichloride in 100 ml diisopropylamine yielded, after stirring for 21 h at room temperature, and extractive distribution of the reaction mixture between water and diethyl ether, 3.85 g crude product. Recrystallisation from cyclohexane yielded a first crop of 1.0 g, and after further concentrating the mother liquor, another 1.5 g of 4-bromphenylethynylferrocene, which corresponds to a total yield of 68% of theory.

*Analytical data for 4-bromophenylethynylferrocene ([**238099-24-6**]).* MS (EI, 70 eV): $m/z = 364/366$ $M^+$.

IR (KBr): 3083w, 2956m, 2925m, 2205m($\nu$ –C≡C–), 1497s, 832vs, 824vs, 500vs.

$^1$H-NMR($CDCl_3$) (ppm): 4.25 (s/pst, 5H, unsubst. Cp/2H subst. Cp), 4.52 (pst, 2H), 7.29–7.45 (m, 4H, 1,4-subst. phenyl–).

$^{13}$C-NMR ($CDCl_3$, TMS): $\delta$ 65.07, 69.17, 70.18(unsubst Cp), 71.52, 84.65 + 89.66(–C≡C–), 121.62, 122.82, 131.42 + 132.72 (–CH–phenyl–); m.p.: 148–150 °C.

*5.4.3.2. 1-(2-Ferrocenylethyn-1-yl)-4-bromobenzene.hexacarbonyldicobalt (**17**).* In a Schlenk tube, carefully dried and purged with argon, was placed a solution of 4-bromophenylethynylferrocene ([**238099-24-6**]) (0.88 g, 2.40 mmol) 1-(2-Ferrocenyl in 50 ml of anhydrous THF. To this solution was added in small portions a total of 0.95 g $Co_2(CO)_8$ (2.64 mmol). Spontaneous effervescence of carbon monoxide was accompanied by a color change from orange to black-green. After stirring for about 6 h at room temperature under inert conditions, the complex had formed quantitatively. After filtration of the dark green solution through a glass sintered Schlenk frit and removal of the THF on a vacuum line, about 1.6 g of 4-bromophenylethynylferrocene hexacarbonyldicobalt was isolated as black powder, which was used in the following acetylation step without further purification. If required, the crude product can be recrystallized from anhydrous *n*-hexane.

*Analytical data for 1-(2-ferrocenylethin-1-yl)-4-bromobenzene.hexacarbonyldicobalt (**17**).* MS (EI, 70 eV): $m/z = 650/652$ $M^+$.

IR (KBr): 2086vs + 2047vs + 2022vs($\nu$ –$Co_2(CO)_6$–), 1484s, 828s, 563s, 515s, 496s.

$^1$H-NMR ($C_6D_6$, TMS): $\delta$ 4.15 (s, 5H, unsubst. Cp), 4.41 (pst, 2H), 4.45 (pst, 2H), 7.53–7.75 (m, 4H, 1,4-disubst. phenyl–).

$^{13}$C-NMR ($CDCl_3$, TMS): $\delta$ 69.39, 69.58(unsubst. Cp), 69.98, 85.03, 89.99, 92.63, 121.70, 130.98 + 131.97, 199.07(–$Co_2(CO)_6$–); m.p.: > 155 °C decomp.

*5.4.4. 1-(1′-Acetylferrocen-1-ylethynyl)-4-bromobenzene.hexacarbonyldicobalt (**18**)*

In a Schlenk flask (250 ml), carefully dried and purged with argon, was placed a solution of (4.54 g, 6.97 mmol) 1-(2-ferrocenylethyn-1-yl)-4-bromobenzene.hexacarbonyldicobalt (**17**) in about 100 ml of anhydrous $CH_2Cl_2$. To this solution was added drop-wise, by means of a dropping funnel (100 ml), a solution of acetyl chloride (0.60 g, 0.55 ml; 7.67 mmol = 1.1 equiv.) in 50 ml of anhydrous $CH_2Cl_2$, containing a suspension of $AlCl_3$ (2.08 g, 15.34 mmol = 2.2 equiv.), which was separately preprepared in a second Schlenk tube with stirring for 10–15 min at ambient temperature. Upon the addition of the acetyl chloride/aluminum chloride-complex (within 15–20 min) the color of the reaction mixture turned from green to brown under evolution of hydrogen chloride (use of excess acetyl chloride/aluminum chloride-complex has to be strictly avoided). The end-point of the reaction can be monitored efficiently by means of TLC ($SiO_2$; pentane/ether 1:2; $R_f$ educt = 0.8; $R_f$ product = 0.3). The workup of the reaction mixture was accomplished by evaporation of $CH_2Cl_2$, and subsequent ethereal extraction from an aqueous ammonium chloride solution. The resulting organic layer was thoroughly washed, dried with $Na_2SO_4$ and filtered, yielding about 4.6 g of a dark brown, very viscous oil (crude yield ca. 90% of theory). By means of column chromatography, the main components of the crude product mixture, 1-(1′-acetylferrocen-1-ylethynyl)-4-bromobenzene.hexacarbonyldicobalt (**18**) and 1-(3-acetylferrocen-1-ylethynyl)-4-bromobenzene.hexacarbonyldicobalt (**19**), could not be separated, and the ethyne-protecting group was removed with $(NH_4)_2Ce(NO_3)_6$ afterwards without further purification.

*5.4.4.1. Analytical data for the isomer mixture of 1-(1′-acetylferrocen-1-yl-ethynyl)-4-bromobenzenehexacarbonyldicobalt (**18**)/1-(3-acetylferrocen-1-yl-ethynyl)-4-bromobenzene.hexacarbonyldicobalt (**19**).* MS (EI, 70 eV): $m/z = 692/694$ $M^+$.

IR (KBr) ($cm^{-1}$): 3097w, 2964m, 2923m, 2852m, 2090vs + 2069vs + 2038vs + 1997vs($\nu$ –$Co_2(CO)_6$–), 1675vs($\nu$ C=O), 1482s, 1455s, 1277s, 826s, 515s, 496s.

$^1$H-NMR ($C_6D_6$, TMS): only broad signals due to formation of paramagnetic impurities.

$^{13}$C-NMR ($CDCl_3$, TMS): $\delta$ 27.45(–$CH_3$), 70.46, 70.71, 71.28, 71.65, 73.62, 74.37, 79.79, 87.13, 89.81, 121.88, 130.85, 132.17, 137.39, 198.79(–$Co_2(CO)_6$–), 201.59 (–C(O)$CH_3$); m.p.: oil.

*5.4.5. 1-(1′-Acetylferrocen-1-ylethynyl)-4-bromobenzene (**20**)*

The crude isomer mixture of 1-(1′-acetylferrocen-1-yl-ethynyl)-4-bromobenzene hexacarbonyldicobalt (**18**) and 1-(3-acetylferrocen-1-yl-ethynyl)-4-bromobenzene. hexacarbonyldicobalt (**19**), (4.60 g, ca. 6.6 mmol) was dissolved in 100 ml acetone (not anhydrous), and $(NH_4)_2Ce(NO_3)_6$ (11.3 g, 20.6 mmol) was subsequently added in powdered form, causing spontaneous effervescence of carbon monoxide and a color change from brownish black to orange. The completion of the reaction can be monitored efficiently by means of TLC ($SiO_2$; petroleum ether/diethyl ether 3:1).

After evaporation of acetone, the remainder was distributed between water/diethyl ether and extracted with diethyl ether. Afterwards, the ethereal phase was dried with $Na_2SO_4$. By the usual workup a total of about 1.5 g crude **18**/**19** product mixture was obtained. Afterwards, the product mixture was dissolved in ca 5 ml of THF (the solubility in diethyl ether is too low for proper column loading) and applied on top of the column. Impurities were eluted from the target isomers ($SiO_2$ G-60 Fluka, 220–440 mesh; $40 \times 4$ cm, eluent pentane/ether 3:1).

The 1′-acetylferrocene derivative (**20**) could not be separated from the 3-acetyl product (**21**) by means of this procedure. Total yield of isomer mixture: 1.32 g of orange powder (46% of theory based on 4-bromophenylethynylferrocene). This mixture was used without separation of the 3-acetyl isomer in the following step (dehydratative 1′-ethynylation).

*5.4.5.1. 1-(1′-Acetylferrocen-1-ylethynyl)-4-bromobenzene (**20**); via **3**.* (Sonogashira–Hagihara coupling) 1-Bromo-4-iodobenzene (100 mg, 0.40 mmol), and 1′-acetyl-1-ethynylferrocene (**3**) (100 mg, 0.40 mmol) were dissolved in 20 ml of diisopropylamine, which was previously saturated with argon. Afterwards, CuI (1 mg, 0.02 equiv.) and bis(triphenylphosphine) palladium dichloride (6 mg, 0.02 equiv.) were added as catalysts. The reaction mixture was stirred at room temperature under argon for 18 h.

The primarily orange solution gradually turned into a dirty-brown suspension, separating a white precipitate (diisopropylammonium iodide) along with an orange precipitate of product. Workup was accomplished by evaporation of diisopropylamine, followed by column chromatography of the remainder with diethyl ether on silica gel (eluent petroleum ether/diethyl ether 3:1). By this purification procedure, unconverted 1-bromo-4-iodobenzene ($R_f$ 0.89; 55 mg, 35% of theory), and the target product 1-(1′-acetylferrocen-1-yl)-2-(4-bromophenyl)-acetylene (**18**) ($R_f$ 0.31) were isolated. 1,4-Bis(1′-acetylferrocen-1-yl)-1,3-butadiyne (**14**) was retained at the starting zone of the column.

*5.4.5.2. Analytical data for 1-(1′-acetylferrocen-1-ylethynyl)-4-bromobenzene (**20**).* MS (EI, 70 eV): $m/z =$ 406/408 $M^+$.

IR (KBr): 3081w, 2223w/2209w($\nu$ –C≡C–), 1663vs($\nu$ C=O), 1495s, 1277s, 826s.

$^1$H-NMR ($C_6D_6$, TMS): $\delta$ 2.38 (s, 3H, $-CH_3$), 4.26 (pst, 2H), 4.48 (pst, 2H), 4.52 (pst, 2H), 4.79 (pst, 2H), 7.32–7.46 (m, 1,4-disubst.phenyl–).

$^{13}$C-NMR ($CDCl_3$, TMS): $\delta$ 27.64 ($-CH_3$), 67.00, 70.40, 71.16, 72.74, 73.66, 80.73, 86.12 + 87.42 (–C≡C–), 122.16 (–C=phenyl–), 131.55 + 132.89 (–CH–phenyl–), 201.29 (–CO–); m.p.: 123–125 °C.

*5.4.6. 1-[1′-(1-Chloro-2-formylvinyl)-ferrocen-1-ylethynyl]-4-bromobenzene (**22**)*

Crude 1-(1′-acetylferrocen-1-ylethynyl)-4-bromobenzene (**20**) (600 mg, 1.47 mmol) was dissolved in 5 ml DMF (not anhydrous) and cooled to 0 °C, resulting in an orange solution. At the same time (0.40 ml, 4.42 mmol) $POCl_3$ was added to 2 ml DMF and also cooled to 0 °C, resulting in a light orange solution. Subsequently, the $POCl_3$/DMF-solution was added drop-wise to the solution of 1-(1′-acetylferrocen-1-ylethynyl)-4-bromobenzene within 15 min. The resulting reaction mixture was stirred at room temperature for a further 2 h, whereupon the color changed from orange to brown and finally to an intense bluish-black. Workup was accomplished by neutralisation of $POCl_3$ with $NaOAc.3H_2O$ (2.41 g, 17.7 mmol), which was added in powdered form. While stirring was continued, the black–blue color turned into red. The reaction mixture was distributed between diethyl ether and water and the ethereal extracts of the crude product were subjected to column chromatography ($SiO_2$, eluent petroleum ether/diethyl ether 3:1). By this 1-[1′-(1-chloro-2-formylvinyl)-ferrocen-1-ylethynyl]-4-bromobenzene (**22**) was obtained as tiny black–red crystals (265 mg, 40% of theory) after evaporation of the mobile phase ($R_f$ 0.23). A further eluate ($R_f$ 0.75) afforded a yellow oil consisting of the isomers 1-[1′-(1-chlorovinyl)-ferrocen-1-ylethynyl]-4-bromobenzene) (**23**), and 1-[3-(1-chlorovinyl) - ferrocen - 1 - ylethynyl] - 4 - bromobenzene (**24**), respectively. No starting compounds (**20**, **21**) ($R_f$ 0.17) were recovered.

*5.4.6.1. Analytical data for 1-[1′-(1-chlorovinyl)-ferrocen-1-ylethynyl]-4-bromobenzene (**23**) which contained only traces of 1-[3-(1-chloro-2-formylvinyl]-ferrocen-1-ylethynyl)-4-bromobenzene (**22**).* MS (EI, 70 eV): $m/z =$ 452 $M^+$.

IR (KBr) ($cm^{-1}$): 3099w, 2964s, 2927m, 2854m, 2752w, 2225w/2213w($\nu$ –C≡C–), 1659vs($\nu$ C=O), 1600s, 1584s, 1262vs, 1098vs, 1027vs, 816vs, 803vs.

$^1$H-NMR ($C_6D_6$, TMS): $\delta$ 4.29 (pst, 2H), 4.50 (pst, 2H), 4.58 (pst, 2H), 4.75 (pst, 2H), 6.33 (d, 1H, $J = 6$ Hz, vinylic), 7.27–7.46 (m, 4H, 1,4-disubst. phenyl–), 9.96 (d, 1H, $J = 5$ Hz, formyl–H).

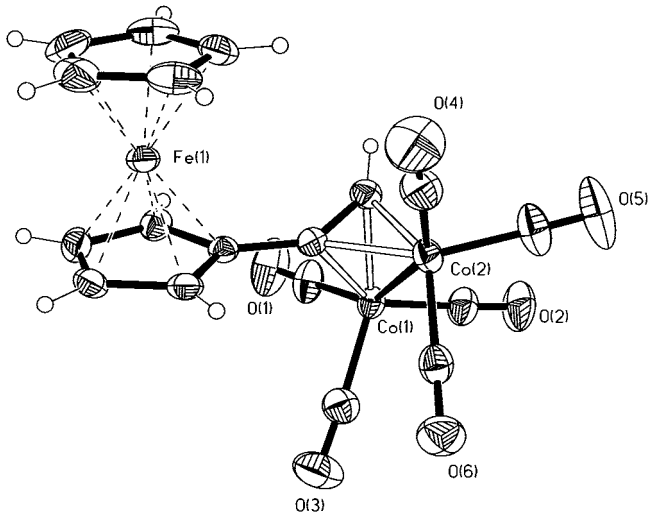



Fig. 7. X-Ray structure of [**56665-21-5**] (CCDC deposit no. 157913).

$^{13}$C-NMR ($CDCl_3$, TMS): $\delta$ 68.22, 70.11, 71.16, 73.42, 73.66, 81.58, 86.37, 86.85, 121.16, 122.21, 131.58 + 132.72 (–CH phenyl–), 153.36, 190.80 (–CO); m.p.: 110–112 °C.

Interestingly, depending on scale and reaction time, occasionally almost no target compound, the red 1-[1′-(1-chlor-2-formylvinyl]-ferrocen-1-ylethynyl)-4-bromobenzene (**22**) could be isolated, but only a red oil was obtained, which could by separated into its constituents chromatographically ($SiO_2$; petroleum ether). Based on a preparative run with 200 mg of 1-(1′-acetylferrocen-1-ylethynyl)-4-bromobenzene (**20**), (0.49 mmol), only 30 mg (13% of theory) of 1-[1′-(1-chloro-2-formylvinyl]-ferrocen-1-ylethynyl)-4-bromobenzene (**22**) was obtained, but instead 110 mg (53% of theory) of a mixture containing 1-[1′-(1-chlorovinyl]-ferrocen-1-ylethynyl)-4-bromobenzene (**23**), and 1-[3-(1-chlorovinyl]-ferrocen-1-ylethynyl)-4-bromobenzene (**24**). By means of the above-mentioned column chromatography (PE, $SiO_2$) 20 mg of both compounds could be isolated in pure form for analytical purposes (see also Section 2).

*5.4.6.2. Analytical data for 1-[1′-(1-chlorovinyl)-ferrocen-1-ylethynyl]-4-bromobenzene (**23**).* MS (EI, 70 eV): $m/z = 424$ $M^+$.

IR (KBr) ($cm^{-1}$): 2221w/2209w($\nu$ –C≡C–), 1611s($\nu$ CH=C), 1493s, 1262s, 820vs.

$^1$H-NMR ($C_6D_6$, TMS): $\delta$ 4.27 (pst, 2H), 4.33 (pst, 2H), 4.48 (pst, 2H), 4.55 (pst, 2H), 5.24 (d 1H, $J = 1.2$ Hz, vinyl-H), 5.44 (d, 1H, $J = 1.2$ Hz, vinyl-H), 7.30–7.45 (m, 4H, 1,4-disubst.phenyl–).

$^{13}$C-NMR ($CDCl_3$, TMS): $\delta$ 66.62, 68.90, 70.73, 71.36, 72.92, 84.65, 109.60(=$CH_2$), 121.84, 131.42 +132.72; m.p.: 91–93 °C.

*5.4.6.3. Analytical data for 1-[3-(1-chlorovinyl)-ferrocen-1-ylethynyl]-4-bromobenzene (**24**).* MS (EI, 70 eV): $m/z = 424$ $M^+$.

$^1$H-NMR ($C_6D_6$, TMS): $\delta$ 4.25 s 5H (unsubst. Cp), 4.57 m 2H, 4.84 m 1H, 5.24 d(1.2 Hz) 1H (vinyl-H), 5.46 (d, 1H, $J = 1.5$ Hz, vinyl-H), 7.28–7.46 (m, 4H, 1,4-disubst.phenyl–).

$^{13}$C-NMR ($CDCl_3$, TMS): $\delta$ 68.05, 70.22, 71.80(unsubst. Cp), 72.55, 84.19, 88.67, 109.55(=$CH_2$), 122.01, 131.47 + 132.72, 137.98; m.p.: 110–112 °C.

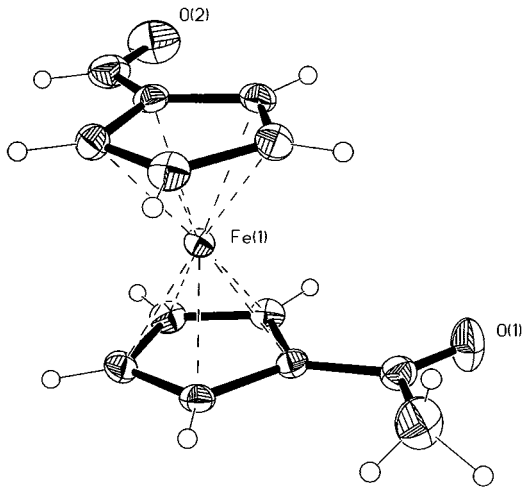



Fig. 8. X-Ray structure of 1-acetyl-1′-formylferrocene [**31798-68-2**] (CCDC deposit no. 157914).

## 6. Supplementary material

Tables of crystal data and structure refinement details, anisotropic thermal parameters, fractional atomic coordinates and isotropic thermal parameters for the non-hydrogen atoms, all bond lengths and angles, and fractional atomic coordinates for the hydrogen atoms for [**12085-68-6**], **4a**, [**152844-78-5**], **7**, **9**, **12**, [**56665-21-5**] and [**31798-68-2**] (Figs. 1–8 in the order given before) are available from the authors. The authors have deposited atomic coordinates for the structures with the Cambridge Crystallographic Data Centre (deposit numbers 157907–157914, also assigned in Figs. 1–8). The coordinates 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).

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