# Enol radical cations in solution. Part 12. Synthesis and electrochemical investigations of a stable enol linked to a ferrocene redox centre †

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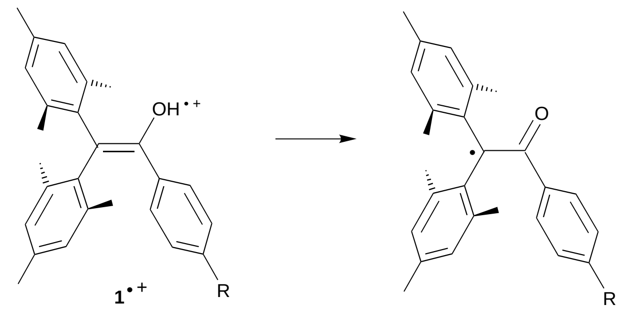
**The synthesis of the first stable enol linked to a ferrocene redox centre is reported. After one-electron oxidation of this compound we receive a persistent radical cation that can be activated by a second one-electron oxidation step. The resulting enol dication undergoes rapid deprotonation to a diradical cation which finally furnishes two benzofurans as products. The mechanism of this reaction and the role of the ferrocene as a redox relay is discussed.**

## Introduction

We have recently reported on the first characterisation of enol radical cations[1] in solution starting from simple stable enols **1** bearing aryl groups in the α-position (Scheme 1).[2] These short-lived intermediates exhibited lifetimes of $10^{-5}$ s in acetonitrile and of $10^{-2}$ s in dichloromethane. The kinetic isotope effect (OH *vs.* OD) as determined by fast-scan cyclic voltammetry identified deprotonation as the primary follow-up reaction of these short-lived species; this is not surprising in the light of the high acidity of these enol radical cations in acetonitrile ($pK_a = 4$–$5$) which renders them more acidic than sulfuric acid ($pK_a = 7.2$).[3]



$1^{\bullet +}$

R = H, Me, OMe

**Scheme 1**

As is well-known from thermochemical cycle calculations[4] the acidity of radical cations is generally much higher than that of their neutral precursors.[5] A look at the thermochemical cycle[5] shown in Fig. 1 indicates that the acidity is mainly a function of the oxidation potential of the neutral molecule and the homolytic bond dissociation energy of the bond of interest.

Since homolytic bond dissociation energy (BDE) data don't vary significantly within the stable enol series (the BDEs for the O–H bonds in β,β-dimesityl enols are about 80.7 ± 1.7 kcal $mol^{-1}$)[6] it is to be anticipated that the lower the oxidation potential the less acidic and the more persistent the enol radical cation. Accordingly, we hoped to prepare a persistent $3^{\bullet +}$ by oxidation of **3**. Herein, we will describe the synthesis of enol **3**, evidence for the persistency of $3^{\bullet +}$ and the activation of this system by one-electron oxidation. In addition, the role of the ferrocene unit as an internal redox relay centre will be addressed.

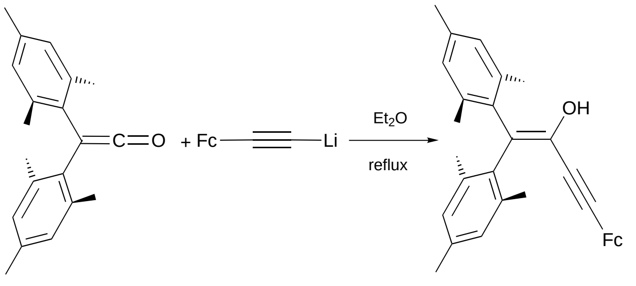
$$\begin{tikzcd}
R\text{—}H^{\bullet +} \arrow[r, "\Delta G\,(pK_a^{\bullet +})"] & R^{\bullet} + H^{+} \\
R\text{—}H \arrow[u, "E_{ox}(RH)"] \arrow[r, "\Delta G\,(BDE)"] & R^{\bullet} + H^{\bullet} \arrow[u, "E_{ox}(H^{\bullet})"']
\end{tikzcd}$$

**Fig. 1** Thermochemical cycle for the determination of the $pK_a$ of radical cations

## Results

### Synthesis

1,1-Dimesityl-4-(ferrocenyl)but-1-en-3-yn-2-ol (**3**) was prepared from the reaction of ferrocenylacetylide[7] with dimesityl ketene (**2**) (Scheme 2).[8] After aqueous work-up and column chromatography the pure enol **3** could be obtained in 34% yield as red–brown solid.



**2** **3**

**Scheme 2**

The structure of enol **3** was assigned on the basis of its characteristic IR, $^{1}H$ NMR and $^{13}C$ NMR spectroscopic data as well as by elemental analysis. The IR spectra of **3** (recorded in KBr) exhibits two O–H absorptions of almost the same intensity at 3464 and 3401 $cm^{-1}$, a pattern already reported for some other dimesityl enols.[9] Beside the strong C=C absorption at 1610 $cm^{-1}$, which is typical for conjugated systems, the yn–enol **3** additionally shows an absorption at 2201 $cm^{-1}$ indicative of a C≡C stretching vibration of a conjugated triple bond system. The $^{1}H$ NMR spectrum of **3** exhibits only a weak coalescence at room temperature, a phenomenon that is much more pronounced with R = alkyl or aryl substituted enols.[9] The six methyl groups belonging to the two β-mesityl groups appear only as two absorption signals. While the two *p*-methyl groups are observed as a sharp singlet, the four *o*-methyl groups give rise to a more or less broadened singlet. Rather sharp is the

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† For Part 11, see ref. 24.

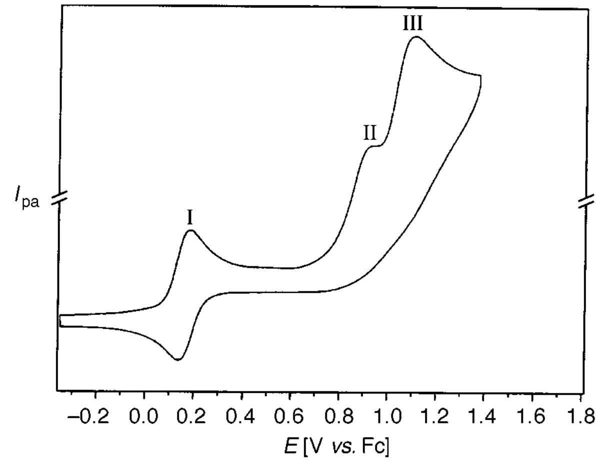


**Fig. 2** Cyclic voltammogram of enol **3** ($v = 100$ mV s$^{-1}$, $c = 1$ mM, working electrode = 1 mm platinum disk electrode, counter electrode = Pt wire, reference electrode = Ag wire)

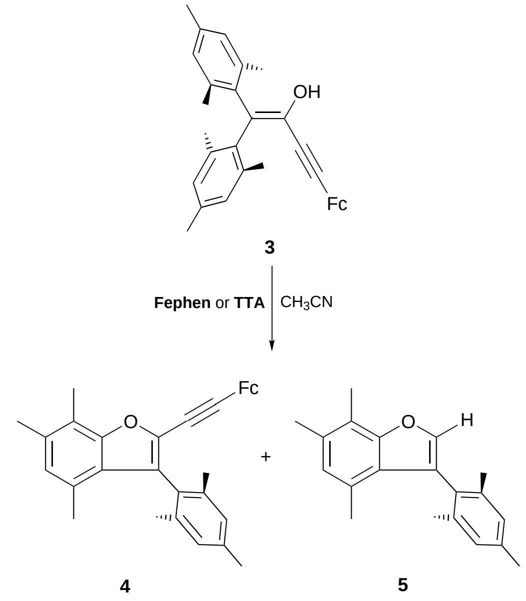
singlet for the OH group at $\delta$ 4.78. As already seen in the $^{13}$C NMR spectra of other alkynyl-substituted enols[10] the signal for C-2 in the yn–enol **3** is shifted downfield to $\delta$ 139.95 (usually the signal appears around 150 ppm). The sharp OH absorption in the IR and $^1$H NMR spectra, the lack of any C=O absorption in the IR and $^{13}$C NMR spectra and a comparison of spectroscopic data with those of other enols[9] are all in line with the structural assignment as an enol.

## Cyclic voltammetry and one-electron oxidation

Cyclic voltammetry (CV) investigations of **3** in acetonitrile revealed a completely reversible wave at $E_{1/2} = 0.13$ V$_{Fc}$‡,[11] at scan rates between 50–500 mV s$^{-1}$ indicative of a rather persistent $\mathbf{3}^{\bullet+}$ (Fig. 2). Unfortunately, UV–VIS investigations on the red–brown solutions of $\mathbf{3}^{\bullet+}$ and **3** revealed for both the radical cation and the neutral molecule rather broad tailing absorption bands up to 350 nm with little difference between them. Although it is quite common that solutions of ferrocenium salts are blue-to-green coloured, ferroceniums bound to a large delocalized system may exhibit a different colour.[12] While this hampered a detailed and precise kinetic analysis of the kinetic stability of $\mathbf{3}^{\bullet+}$, preparative oxidation of **3** disclosed that $\mathbf{3}^{\bullet+}$ must be very long-lived. When enol **3** was oxidised with one equivalent of tri-4-tolylaminium hexafluoroantimonate (TTA) ($E_{1/2} = 0.39$ V$_{Fc}$) and stirred for 2 h enol **3** could be reisolated in 97% yield after quenching with aqueous hydrazine solution.

Upon scanning to higher anodic potential in the CV experiment the reversible oxidation wave of **3** is followed by two irreversible ones at $E_{pa} = 0.91$ V$_{Fc}$ and $E_{pa} = 1.08$ V$_{Fc}$. The ratio of the anodic peak currents for the first two oxidation processes depends on the scan rate, with the ratio $I_{pa}$(II)/$I_{pa}$(I) decreasing with increasing scan rate.

When oxidising enol **3** using three equivalents of tris(1,10-phenanthroline)iron(III) hexafluorophosphate (Fephen) as a one-electron oxidant ($E_{1/2} = 0.69$ V$_{Fc}$) for 1 min the 2-ferrocenylethynyl-3-mesityl-4,6,7-trimethylbenzofuran (**4**) is formed in 54% yield along with a respectable amount (32%) of 3-mesityl-4,6,7-trimethylbenzofuran (**5**), which has lost the ferrocenylethynyl group (Scheme 3). However, when the analogous oxidation was quenched after a few seconds (3–5 s) benzofuran **4** was formed already to a significant amount (13–16%) while only a small trace of **5** (4%) could be found along with a significant amount of dimesityl ketone (23–36%). Noticeably, the dimesityl ketone is only formed when the oxidation reactions are stopped after a few seconds.

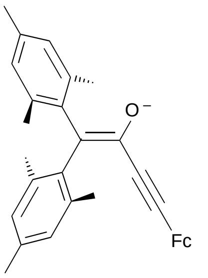


with 3 equiv. of **Fephen**: 54% 32%

**Scheme 3** Fephen = tris(1,10-phenanthroline) iron(III) hexafluorophosphate, TTA = tri-4-tolylaminium hexafluoroantimonate

In CV investigations benzofuran **4** revealed an almost reversible wave at $E_{1/2} = 0.19$ V$_{Fc}$ followed by an irreversible one at $E_{pa} = 1.07$ V$_{Fc}$. The ratio of the anodic peak currents of the oxidation processes (I) $\mathbf{4} \longrightarrow \mathbf{4}^{\bullet+}$ and (II) $\mathbf{4}^{\bullet+} \longrightarrow \mathbf{4}^{2+}$ depends on the scan rate, with the ratio $I_{pa}$(II)/$I_{pa}$(I) slightly increasing with increasing scan rates (50–500 mV s$^{-1}$). The wave at $E_{1/2} = 0.19$ V$_{Fc}$ in the benzofuran oxidation was fully reversible at a scan rate of 500 mV s$^{-1}$. Importantly, the second wave in the benzofuran oxidation coincides with the third wave in the enol oxidation.

The CV investigations on the corresponding enolate **6** which was prepared *in situ* from the enol by adding 1 equivalent of base (such as tetramethylammonium hydroxide) revealed a partially reversible redox wave for the enolate oxidation. The thermodynamic half-wave potential was determined as $E_{1/2} = -0.66$ V$_{Fc}$. Upon scanning to higher anodic potential a second wave showed up. At a scan rate of $v = 500$ mV s$^{-1}$ this oxidation wave was partially reversible with a thermodynamic half-wave potential of $E_{1/2} = 0.17$ V$_{Fc}$. At lower scan rates, however, *e.g.* $v = 100$ mV s$^{-1}$, only one sharp and irreversible oxidation wave was observed at $E_{pa} = 0.17$ V$_{Fc}$ which broadened at $v = 50$ mV s$^{-1}$ and finally separated into two irreversible waves at $v = 20$ mV s$^{-1}$. At this scan rate the corresponding anodic peak potentials were determined to $E_{pa} = 0.13$ V$_{Fc}$ and $E_{pa} = 0.18$ V$_{Fc}$.



**6**

In contrast to oxidations of similar enolates[13] the formed radical $\mathbf{7}^{\bullet}$ is only moderately persistent. The $I_{pc}/I_{pa}$ of enolate **6** clearly indicates that the radical undergoes a follow-up reaction which, however, is not bimolecular since the ratio $I_{pc}/I_{pa}$ proved to be concentration independent.

When the scan was extended to more anodic potentials a

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‡ All potentials in this paper are referenced against the ferrocene/ferrocenium couple (Fc/Fc$^{\bullet+}$). To obtain values against SCE, simply add +0.39 V. In line with Heinze,[11] the term $E_{1/2}$ is used to describe $E_{1/2} = E_{pa} - \Delta E_p/2 = (E_{pa} + E_{pc})/2$.

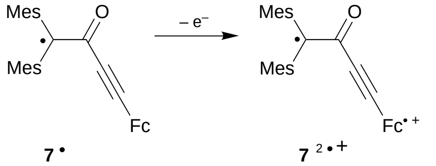
small partially reversible wave at $E_{1/2} = 0.46$ $V_{Fc}$ appeared at all scan rates and at higher anodic potential an irreversible oxidation wave at $E_{pa} = 1.08$ $V_{Fc}$ emerged, which is also present in the CV of the enol **3**.

Preparative oxidation of the enolate proceeded less cleanly than the enol oxidation. After reaction with one equivalent of TTA only 7% of the benzofuran **4** was obtained along with 29% of the enol **3**. With three equivalents of Fephen 22% of the anticipated benzofuran **4** and 13% of **5** were furnished. Notably no **5** is formed in the enolate oxidations when using only one or two equivalents of the one-electron oxidant.

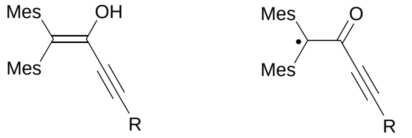
## Discussion

### Enol radical cation and enol dication

Compound **3** constitutes the first enol that after one-electron oxidation is persistent at room temperature, mostly because the system is better characterised as a ferrocenium salt than as an enol radical cation. The long lifetime is to be expected in the light of the acidity data. According to thermochemical cycle calculations[13] the acidity of the neutral enol **3** in acetonitrile (p$K_a$ = 25.1) is increased to p$K_a$ = 12.7 for the radical cation $\mathbf{3}^{\bullet+}$, which is comparable to that of dichloroacetic acid (p$K_a$ = 13.2) or that of 2,4-dimethylpyridinium salt (p$K_a$ = 14.0). The acidity of $\mathbf{3}^{\bullet+}$ is thus much lower than for other enol radical cations of similar structure (p$K_a$ = 3 for enols **8** and **9**). This certainly explains why the tendency to deprotonate is largely reduced in comparison with other enol radical cations.



**7•** **7 2•+**



R = Ph **8**
R = *p*An **9**

R = Ph **10**
R = *p*An **11**

Accordingly, we can assign the first wave in the CV investigation of **3** to the reversible oxidation of the ferrocenyl group. As $\mathbf{3}^{\bullet+}$ is long-lived it can be further oxidised, affording the dication $\mathbf{3}^{2+}$. We can derive from a second thermochemical cycle (see Fig. 3) that, again, with respect to $\mathbf{3}^{\bullet+}$ the acidity of $\mathbf{3}^{2+}$ should be increased.

An important question that must be answered to complete the thermochemical cycle is that of the oxidation potential of $7^{\bullet}$ and the identity of its oxidation product. Since the enolate **6** $\rightleftharpoons$ radical $\mathbf{7}^{\bullet}$ redox process proved to be reversible at higher scan rates, we could measure the oxidation potential of the persistent radical $\mathbf{7}^{\bullet}$ ($E_{1/2} = 0.17$ $V_{Fc}$) when scanning to higher anodic potentials. Comparison with the known oxidation potentials of other alkynyl-substituted α-carbonyl radicals[14] ($E_{pa} = 0.38$ and 0.31 $V_{Fc}$ for radicals **10** and **11**) and, more importantly, the fact that the oxidation wave at $E_{pa} = 0.17$ $V_{Fc}$ is partially reversible at higher scan rates (500 mV $s^{-1}$) indicate that in $\mathbf{7}^{\bullet}$ the ferrocenyl unit is oxidised yielding the 'diradical cation' $\mathbf{7}^{2\bullet+}$.

With the help of above redox data one can now calculate from the thermochemical cycle (Fig. 3) that the generated dication $\mathbf{3}^{2+}$ is very acidic (p$K_a$ = 0.2 in acetonitrile). This suggests that $\mathbf{3}^{2+}$ undergoes a fast deprotonation yielding the 'diradical cation' $\mathbf{7}^{2\bullet+}$ which after a sequence of reactions gives rise to benzofuran **4**.

$$\begin{tikzcd}
\mathrm{R{-}H}^{2+} \arrow[r, "\Delta G\,(\mathrm{p}K_a^{\;2+})"] & \mathrm{R}^{+} + \mathrm{H}^{+} \\
\mathrm{R{-}H} \arrow[u, "E_{ox}(\mathrm{RH})"] \arrow[r, "\Delta G\,(\mathrm{BDE})"] & \mathrm{R}^{\bullet} + \mathrm{H}^{\bullet} \arrow[u, "E_{ox}(\mathrm{H}^{\bullet})\,|\,E_{ox}(\mathrm{R}^{\bullet})"']
\end{tikzcd}$$

**Fig. 3** Thermochemical cycle to determine the p$K_a$ of dications

At higher potential in the enol oxidation the finally formed benzofuran radical cation $\mathbf{4}^{\bullet+}$ is further oxidised to the dication [$E_{pa}$ (wave III) = 1.08 $V_{Fc}$]. The oxidation current of this irreversible wave (III) increases in relation to that of wave I when the scan rate is decreased, indicating that benzofuran $\mathbf{4}^{\bullet+}$ formation is not completed on the timescale of the CV experiment. The assignment of wave III as oxidation of $\mathbf{4}^{\bullet+}$ is based on the observation that the second oxidation wave of **4** appears at $E_{pa} = 1.07$ $V_{Fc}$.

### Mechanism of benzofuran formation

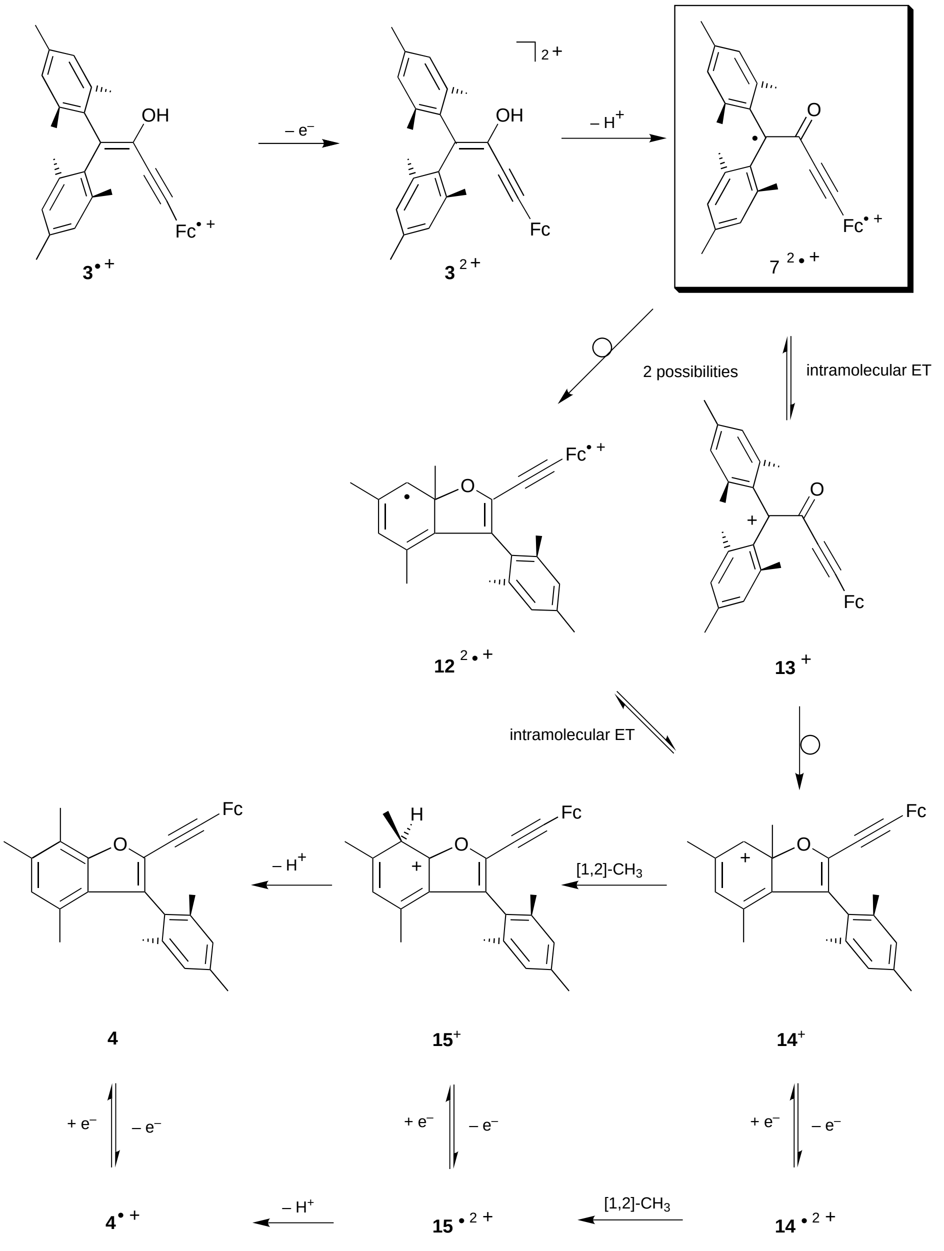
While formation of benzofuran **4** is fully consistent with earlier investigations,[10] it is important to stress the role of the ferrocene as a redox relay station. Since radical $\mathbf{7}^{\bullet}$ is rather long-lived as derived from the reversible enolate oxidation wave, we have to explain why, after oxidation at the remote ferrocene, it now undergoes rapid cyclisation. Two reaction pathways are plausible for $\mathbf{7}^{2\bullet+}$ (Scheme 4): Either a radical cyclisation to the cyclohexadienyl radical $\mathbf{12}^{2\bullet+}$ takes place, a process which could be driven by an intramolecular electron transfer from the radical site to the ferrocenium to afford $\mathbf{14}^{+}$. Or alternatively an intramolecular electron transfer between the ferrocenium group and the α-carbonyl radical furnishes the α-carbonyl cation $\mathbf{13}^{+}$ with a reduced ferrocenyl moiety. Such an electron transfer would be only moderately endergonic ($\Delta E \leqslant 0.2$ V) as judged by the oxidation potentials of similar α-carbonyl radicals **10**, **11** (*vide supra*). As the resulting α-carbonyl cations of type $\mathbf{13}^{+}$ are known to cyclise extremely rapidly to $\mathbf{14}^{+}$ ($k > 10^{4}$ $s^{-1}$)[14] this follow-up reaction would drive the endergonic electron transfer. Both mechanistic pathways are in line with the observation that in the CV oxidation of $\mathbf{7}^{\bullet}$ the ferrocene wave is irreversible at low scan rates ($v < 500$ mV $s^{-1}$). After a subsequent [1,2]-methyl shift to $\mathbf{15}^{+}$ and deprotonation the benzofuran **4** is afforded.

The above picture of the benzofuran formation, however, is further complicated by the fact that the ferrocene redox centre may interfere at other intermediates as well. Several observations indicate that between the rapid follow-up reaction of $\mathbf{7}^{2\bullet+}$ and formation of **4** there must be a slow step: (a) in the enolate CV investigation the wave of $\mathbf{4}^{\bullet+}$ shows up only at very slow scan rates (20 mV $s^{-1}$); (b) in the enolate CV investigation there is a unidentified reversible wave at $E_{1/2} = 0.46$ $V_{Fc}$; (c) when the preparative enol oxidation is stopped after a few seconds the maximum yield of **4** is not yet attained.

What could be a longer-lived intermediate ($\tau_{1/2}$ = several seconds)? We have detected a reversible wave at $E_{1/2} = 0.46$ $V_{Fc}$ in the enolate oxidation indicative of a ferrocene unit bound to an electron-withdrawing substituent. Of the two intermediates $\mathbf{14}^{+}$ and $\mathbf{15}^{+}$ the cyclohexadienyl cation $\mathbf{14}^{+}$ indeed is known to be long-lived when electron-releasing substituents are attached.[15] In contrast, intermediate $\mathbf{15}^{+}$ should be rather short-lived because (a) its deprotonation should proceed very rapidly even in neutral media; and (b) the oxidation wave at $E_{1/2} = 0.46$ $V_{Fc}$ appeared under basic conditions. Hence, we may tentatively assign the reversible oxidation wave at $E_{1/2} = 0.46$ $V_{Fc}$ to the oxidation of $\mathbf{14}^{+}$ to $\mathbf{14}^{\bullet 2+}$.

Usually stable simple enols are best reacted with 2 equivalents of one-electron oxidants, but, since the ferrocenyl electrophore in the enol **3** is oxidised (a) more easily than the enol moiety, and (b) the generated radical cation is very stable, the oxidation of the enol **3** requires three equivalents of the oxidant.

With the whole reaction scheme in mind we can now understand the unusual scan dependence of the waves at 0.1–0.2 $V_{Fc}$



**Scheme 4** Oxidation of the enol **3**

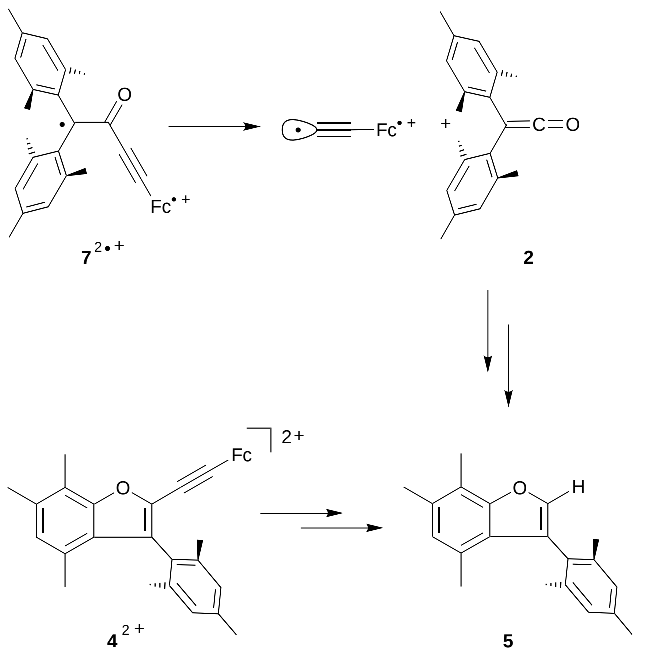
in the enolate oxidation. At a scan rate of 500 mV s$^{-1}$ the ferrocene in $\mathbf{7}^{\cdot}$ is reversibly oxidised at $E_{1/2} = 0.17\ \mathrm{V_{Fc}}$. At lower scan rates this wave becomes irreversible and moves to $E_{pa} = 0.13\ \mathrm{V_{Fc}}$ (kinetic shift). In addition, at $v = 50$ mV s$^{-1}$ a new oxidation wave starts to merge in, that at $v = 20$ mV s$^{-1}$ shows up at $E_{pa} = 0.18\ \mathrm{V_{Fc}}$. We assign this wave to the oxidation $\mathbf{4} \rightarrow \mathbf{4}^{\cdot +}$ that because of intermolecular electron transfer between $\mathbf{7}^{\cdot}$ and $\mathbf{4}^{\cdot +}$ is no longer reversible.

### Formation of benzofuran 5

Another issue which has not been addressed yet is the unexpected formation of benzofuran **5**. As derived from the preparative oxidation of the enol **3** it is only formed in a slow process which is too delayed for the timescale of our CV experiments. We have probed two mechanistic hypotheses (Scheme 5) and could eliminate both of them by control experiments. The benzofuran **5** is not a product which arises from oxidation of **4** to the $\mathbf{4}^{2+}$. This was demonstrated by independent CV investigations and preparative oxidations starting from pure **4**. Equally, benzofuran **5** is not formed from a β-cleavage of the radical $\mathbf{7}^{\cdot}$ or the diradical cation $\mathbf{7}^{2\cdot +}$ to yield the ketene **2** or ketene radical cation $\mathbf{2}^{\cdot +}$. Independent CV investigations and preparative oxidations starting from pure **2** did not reveal formation of the smallest traces of the benzofuran **5**. Also mechanistic scenarios with nucleophilic assistance of the solvent acetonitrile could be excluded, since the benzofuran **5** is also formed when using dichloromethane as solvent, although in much smaller yield.

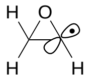
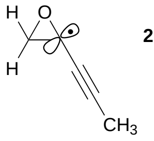
A more promising mechanistic proposal is borne from the observation that in enol oxidations the ratio **4**/**5** is much higher after a few seconds than after longer reaction times. This proposed that a rather long-lived intermediate gives rise to formation of **5**. When quenching the enol oxidation after several seconds we have observed the formation of dimesityl ketone in 23–36% yield by $^1$H NMR spectroscopy. Since dimesityl ketone is not a product when the reaction mixture is quenched after one minute or later, it is obviously derived from the postulated longer-lived intermediate which in the original solution slowly reacts to benzofuran **5**.

With this limited amount of information it remains highly speculative to draw a mechanism for the formation of benzofuran **5**. However, we should bear in mind that this unexpected reaction mode has to be a consequence of the redox properties of the ferrocene moiety at the enol **3**, since other alkyne enols such as **8** or **9** did not yield any **5** upon oxidation.[10] In addition, our mechanistic proposal should explain why **5** is only formed

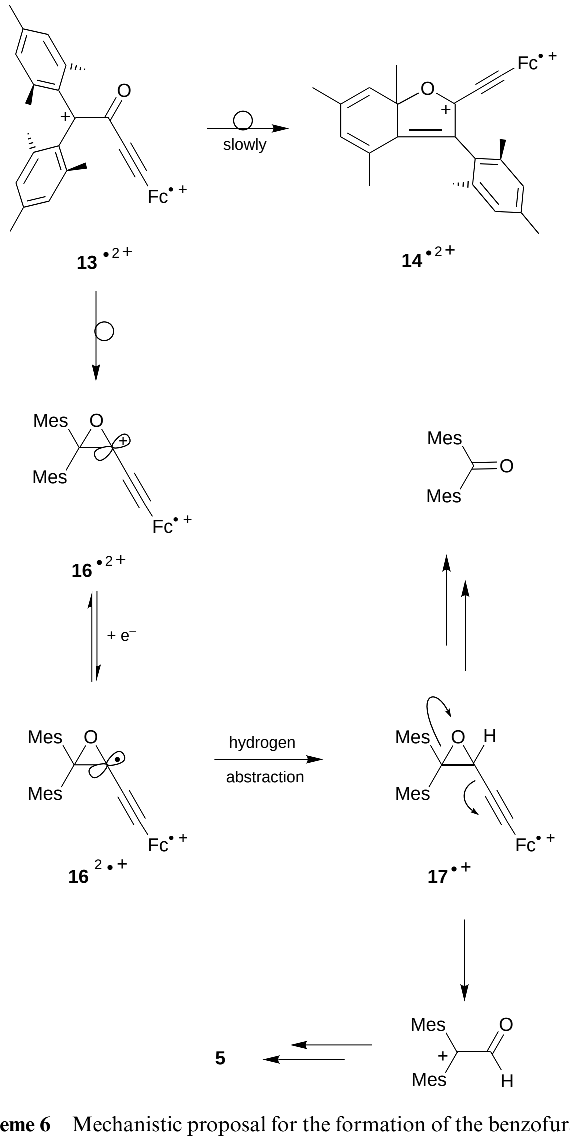


**Scheme 5** Two mechanistic proposals for the formation of **5** both of which could be disproved

**Table 1** Calculated (AM1) vertical ionisation potentials $IP_v = -E_{HOMO}$ and redox potentials in acetonitrile derived from the known potential of $MeOCH_2^{\bullet}$ §

| Compound | | $IP_v$/eV | Redox potential $E_{1/2}^{ox}/V_{Fc}$ |
|---|---|---|---|
| $MeOCH_2^{\bullet}$ | **18** | 3.37 | −0.63[a] |
|  | **19** | 4.18 | 0.18 |
|  | **20** | 4.48 | 0.48 |

[a] See ref. 17.



**Scheme 6** Mechanistic proposal for the formation of the benzofuran **5** and dimesityl ketone

with larger amounts of oxidant present (higher than two equivalents when starting from the enol or enolate).

An interesting intermediate for diverting the reaction is cation **13**$^+$. We would expect that **13**$^+$ should react to the benzofuran in analogy to other arylalkynyl-substituted enols upon oxidation (analogous to Scheme 4),[10] but in the presence of large amounts of oxidant **13**$^{\bullet 2+}$ should form that may give rise to the unexpected formation of **5**.

The following scenario (Scheme 6) seems likely: cation **13**$^{\bullet 2+}$ undergoes formation of oxiranyl cation **16**$^{\bullet 2+}$ followed by a one-electron reduction to the corresponding radical. AM1[16] calculations revealed that such an electron transfer step should be possible (Table 1):[17] reduction of **16**$^{\bullet 2+}$ ($E_{1/2} > 0.48$ $V_{Fc}$)§ by a ferrocene in the mixture should be exergonic. After hydrogen abstraction the resulting oxirane **17**$^{\bullet +}$ slowly opens with elimination of the ferrocenylethinyl unit yielding the known α-carbonyl cation $Mes_2C^+$–C(O)H[18] which leads to the formation of **5**. Alternatively, if the reaction is quenched and hydrolysed at an early stage dimesityl ketone is obtained.

While this mechanistic proposal remains speculative, it is fully consistent with the fact that respectable amounts of **5** are only formed when using more than two equivalents of one-electron oxidant since this reaction pathway requires three electrons to be transferred. It also explains why this reaction pathway is not relevant when oxidising other alkynyl substituted enols since a good electrophor (such as ferrocene) must be present at the alkynyl unit.

## Conclusions

We have synthesised and characterised for the first time a stable simple enol with a ferrocene attached. Although benzofuran formation could be established when oxidising the enol with an appropriate amount of oxidant, the oxidation of this enol proved to be much more complex than that of other yn–enols as a result of an attached electron transfer relay.[10]

## Experimental

### Materials

Commercial reagents were purchased from standard chemical suppliers and were used without further purification. Dimesityl

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§ Since $E_{1/2}$ is known for radical **18** the AM1 calculated vertical ionisation energies $IP_v$ of **19** and **20** can be used to predict the redox potential in acetonitrile according to $E_{1/2}^{ox}$ (**18**) − $E_{1/2}^{ox}$ (**19**,**20**) = $IP_v$ (**18**) − $IP_v$ (**19**,**20**). In comparison with the oxidation of **20** ($E_{1/2} = 0.48$ $V_{Fc}$) the redox process $\mathbf{16}^{2\bullet +} \longrightarrow \mathbf{16}^{\bullet 2+}$ should take place at even higher anodic potential because of the presence of a oxidised ferrocenium substituent.

**Table 2** Preparative enol and enolate oxidations

| Compound | Reaction time | Equivalents of oxidant | Product | Yield (%) |
|---|---|---|---|---|
| enol **3** | 1 min | 1 equiv. of TTA | **3** | 97 |
| enol **3** | 1 min | 3 equiv. of Fephen | **4** | 54 |
| | | | **5** | 32 |
| enolate **6** | 2 h | 1 equiv. of TTA | **4** | 7 |
| | | | **3** | 29 |
| enolate **6** | 1 min | 2 equiv. of Fephen | **4** | 15 |
| enolate **6** | 2 h | 3 equiv. of Fephen | **4** | 22 |
| | | | **5** | 13 |

ketene was prepared as described in ref. 19. Acetonitrile used for the cyclic voltammetry investigations and the one-electron oxidation reactions was of HPLC quality (Riedel-de Haen) and distilled from CaH$_2$.

Melting points were recorded with a Büchi Smp-20 apparatus. Infrared Spectra: Perkin-Elmer 1605 FTIR infrared spectrophotometer. $^1$H NMR spectra: Bruker AC 200 (200 MHz), Bruker AC 250 (250 MHz), tetramethylsilane as internal standard; $J$ values are given in Hz; $^{13}$C NMR: Bruker AC 200 (50 MHz), [$^2$H]chloroform and tetramethylsilane as internal standard. Mass spectra: MAT 90, Finnigan; MAT 8200, Finnigan. Combustion analyses for elemental composition were performed by the Analytical Division of the Institute of Inorganic Chemistry, University of Würzburg (Carlo Erba 1106).

### Preparation of model compounds

**1,1-Dimesityl-4-(ferrocenyl)but-1-en-3-yne-2-ol (3).** To an ice-cooled solution of diisopropylamine (720 μm$^3$, 518 mg, 5.12 mmol) in dry THF (50 cm$^3$) *n*-butyllithium (1.5 M in *n*-hexane, 2.56 cm$^3$, 3.84 mmol) was added dropwise. After 30 min stirring at 0 °C a solution of ferrocenylacetylene (537 mg, 2.56 mmol) in dry THF (20 cm$^3$) was added. The reaction mixture was then stirred for 2 h at room temperature. Then a solution of dimesityl ketene (713 mg, 2.56 mmol) in dry THF (15 cm$^3$) was added and the whole solution was stirred for 24 h at room temperature. After quenching with half-saturated aqueous NH$_4$Cl solution (25 cm$^3$) and extraction with Et$_2$O (3 × 20 cm$^3$) the combined organic layers were dried (Na$_2$SO$_4$). The solvent was removed *in vacuo* and the remaining brown oil was chromatographed on silica gel (*n*-hexane–ethyl acetate 10:1) yielding the desired enol **3** (428 mg, 876 μmol, 34%) as red–brown solid. Mp 50–52 °C (Found: C, 78.66; H, 6.84. C$_{32}$H$_{32}$OFe requires C, 78.69; H, 6.60%); $\nu_{max}$(KBr)/cm$^{-1}$ 3464 (m, O–H), 3401 (m, O–H), 2918 (s, C–H), 2201 (w, C≡C), 1654 (C=C), 1610 (C=C); $\delta_H$(250 MHz; CDCl$_3$) 2.14–2.27 (coalescence, 18 H, Mes–CH$_3$), 4.02 (s, 5 H, Cp-H), 4.16 (t, 2 H, $J$ 1.8, 2′-H, 5′-H), 4.32 (t, 2 H, $J$ 1.8, 3′-H, 4′-H), 4.78 (s, 1 H, OH), 6.89 (s, 4 H, Mes–H); $\delta_C$(50 MHz; CDCl$_3$)¶ 20.7, 20.9, 21.1, 21.2, 21.3, 64.1, 68.8, 69.9, 71.3, 81.6, 91.2, 120.6, 129.0, 129.6, 129.8, 131.6, 131.7, 134.3, 134.9, 136.1, 137.2, 138.5, 139.95.

**2-(Ferrocenylethynyl)-3-mesityl-4,6,7-trimethylbenzofuran (4).** Enol **3** (16.8 mg, 34.4 μmol) and Fephen (106 mg, 103 μmol) were separately weighed into different test tubes. 3 cm$^3$ of acetonitrile was added by means of gas-tight syringes to each test tube. When both compounds had dissolved, the one-electron oxidant solution was given to the solution of the enol and after 1 min 0.1 cm$^3$ of an aqueous hydrazine solution (70% in water) was added. After 30 min stirring dichloromethane (10 cm$^3$) was added and the organic layer was washed with sat. aqueous NaHCO$_3$ solution (10 cm$^3$) and sat. aqueous NaCl solution (10 cm$^3$). The combined aqueous layer was again extracted with dichloromethane (2 × 15 cm$^3$). The solvent was evaporated and the remaining solid was extracted with diethyl ether. Drying (Na$_2$SO$_4$), removal of the solvent *in vacuo* and column chromatography (cyclohexane–dichloromethane, 3:1) of the remaining crude product yielded the desired pure benzofuran **4** as an orange solid (9.0 mg, 19 μmol, 54%). $\delta_H$(200 MHz; CDCl$_3$) 1.94 (s, 3 H, *p*-Mes–CH$_3$), 2.13 (s, 6 H, *o*-Mes–CH$_3$), 2.32 and 2.36 (2s, 6 H, 4, 6-Bf-CH$_3$), 2.44 (s, 3 H, 7-Bf-CH$_3$), 4.01 (s, 5 H, Cp–H), 4.19 (t, 2 H, $J$ 1.5, 2′-H, 5′-H), 4.39 (t, 2 H, $J$ 1.5, 3′-H, 4′-H), 6.79 (s, 1 H, Bf-H), 6.96 (s, 2 H, Mes–H); $\delta_C$(50 MHz; CDCl$_3$) 11.4, 17.25, 19.2, 20.5, 21.3, 64.2, 69.5, 70.5, 72.0, 75.8, 95.9, 117.4, 117.9, 125.0, 125.4, 126.5, 128.0, 128.5, 133.8, 135.4, 137.35, 137.5, 148.8; *m*/*z* (EI) 486.1652. C$_{32}$H$_{30}$OFe requires 486.1646.

**3-Mesityl-4,6,7-trimethylbenzofuran (5).** This compound was characterised on the basis of its $^1$H NMR spectra and comparison with the literature data.[20] $\delta_H$(200 MHz; CDCl$_3$) 1.91 (s, 3 H, *p*-Mes–CH$_3$), 2.06 (s, 6 H, *o*-Mes–CH$_3$), 2.33 and 2.36 (2s, 6 H, 4, 6-Bf-CH$_3$), 2.44 (s, 3 H, 7-Bf-CH$_3$), 6.77 (s, 1 H, 5-Bf-H), 6.94 (s, 2 H, Mes–H), 7.35 (s, 1 H, 2-Bf-H).

The dimesityl ketone was characterised on the basis of its spectral data such as $^1$H NMR,[21] $^{13}$C NMR,[22] MS and IR.[23]

### General procedure for the one-electron oxidation of the enol 3 or the enolate 6 with various amounts of Fephen

Under nitrogen, enol **3** and the appropriate amount of Fephen were weighed in two different flasks and CH$_3$CN (each 3.0 cm$^3$) was added. In the case of the enolate oxidations the equimolar amount of Me$_4$NOH was given to the enol solution to generate the enolate. Then the solution of the oxidant was added quickly to the enol or enolate solution. The reaction was quenched (see Table 2) with aqueous hydrazine solution (0.1 cm$^3$) and the mixture was stirred for 30 min. Thereafter CH$_2$Cl$_2$ (5 cm$^3$) was added and the resulting solution was washed once with sat. aqueous NaHCO$_3$ and once with sat. aqueous NaCl. The solvent was evaporated and the remaining residue was extracted with diethyl ether. The ether layer was dried (Na$_2$SO$_4$) and evaporated *in vacuo*. The yields were determined by the use of *m*-nitroacetophenone as $^1$H NMR standard.[24]

### Cyclic voltammetry

The cyclic voltammetry experiments were undertaken with a potentiostat Model 362 (Princeton Applied Research) and recorded with the help of a x,y,t recorder Model PM 8271 (Philips). The electrochemical cell was equipped with a platinum disc (1.0 mm diameter) working electrode, a platinum auxiliary electrode and a silver wire as reference electrode. A 1 mM solution of the enol or benzofuran in dry acetonitrile (6 cm$^3$) containing tetra-*n*-butylammonium hexafluorophosphate (0.1 M) was prepared under nitrogen. At room temp. oxidation waves‡ were recorded by using scan rates between 500 and 20 mV s$^{-1}$ (Tables 3 and 4).

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¶ Due to the nature of the β,β-dimesityl unit some resonances are superimposed.

**Table 3** Ratios of peak currents of waves II/I and III/I in the cyclic voltammogram of enol **3** as a function of the scan rate

| Scan rate $v$/mV s$^{-1}$ | 20 | 50 | 100 | 200 | 500 |
|---|---|---|---|---|---|
| $I_{pa}$ (II)/$I_{pa}$ (I) | 1.61 | 1.48 | 1.47 | 1.42 | 1.38 |
| $I_{pa}$ (III)/$I_{pa}$ (I) | 1.52 | 1.34 | 1.14 | 1.11 | 0.84 |

**Table 4** CV data of the enolate **6** in acetonitrile

| Scan rate/mV s$^{-1}$ | $I_{pc}/I_{pa}$ of **6** |
|---|---|
| 50 | 0.59 |
| 100 | 0.78 |
| 200 | 0.83 |
| 500 | 0.89 |

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