

# Internal ferrocenylalkynes—a comparative electrochemical and mass spectrometric study

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## Abstract

A series of ferrocenylalkynes  $\text{FcC}\equiv\text{CY}$ , where Fc is ferrocenyl and  $\text{Y} = \text{H}$  (**1**), Me (**2**), Ph (**3**),  $\text{EMe}_3$  [ $\text{E} = \text{C}$  (**4**), Si (**5**), and Ge (**6**)], I (**8**),  $\text{CPh}_2(\text{OR})$  [ $\text{R} = \text{H}$  (**9**), Me (**10**)], CHO (**11**),  $\text{C(O)Me}$  (**12**), and  $\text{CO}_2\text{R}$  [ $\text{R} = \text{H}$  (**13**), Et (**14**)] was synthesized (some representatives for the first time) and subjected to spectroscopic (IR, NMR, UV–vis, MS) and electrochemical study. In electron-impact mass spectra, all alkynes fragment via processes typical for the ferrocene skeleton and the substituent Y. Besides, the molecular ions of alkynes **1–3** decompose by a loss of  $\{\text{FeH}_2\}$  affording likely a Y-substituted fulvene as the result of a cyclopentadienyl-ring transfer. The carbonyl group containing alkynes **11–14** tend to fragment so that ions isobaric with  $\text{I}^{\bullet+}$  are produced. Similarly, the fragmentation of alcohol **10** appears as a superposition of fragmentation pathways due to  $\text{Ph}_2\text{CO}^{\bullet+}$  and  $\text{I}^{\bullet+}$ . In cyclic voltammograms, all alkynes exhibit one-electron reversible wave of the ferrocene/ferrocenium couple, whose redox potential correlates linearly with Hammett  $\sigma_p$  constants. A similar correlation with inductive  $\sigma_I$  constants is less pronounced due to neglecting resonance effects. An influence of the triple bond spacer between the substituent Y and the ferrocene unit is discussed. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Ferrocene; Alkynes; Electrochemistry; Mass spectrometry; Synthesis

## 1. Introduction

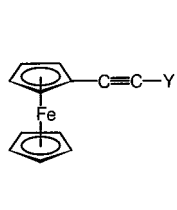
Alkynes are reactive building blocks for organic and organometallic synthesis. In this regard, alkynes bearing an organometallic substituent, particularly those derived from ferrocene, play a specific role since an introduction of such alkyne into a newly formed molecule leads simultaneously to an incorporation of a metallic centre, thus widening the spectrum of accessible organoelement compounds (such as complexes with ferrocenyl  $\eta^1$ - or  $\mu$ - $\eta^1$ : $\eta^2$ -alkynides(1–) [1],  $\eta^2$ -alkynes [2], alkyne-derived  $\eta^1$ -carbene ligand [3] or clusters [4]). Vice versa, catalytic transformations of alkynes involving organometallic catalysts or intermediates as well as stoichiometric reactions of (organometallic) alkynes have been successfully applied towards the synthesis of

numerous organometallic compounds (e.g. cross-coupling reactions [5] and transition-metal-catalyzed head-to-tail dimerization [6]). Ferrocenylalkynes were also used as the starting materials for synthesis of conjugated redox-active ligands [7], new materials with defined magnetic and electronic properties (e.g. molecular wires, mixed valence materials, etc. [8]), compounds with large optical non-linearities [9], redox-active self-assembled multilayers [10], metal-rich arene derivatives [11] and polymers [12].

Many ferrocenylalkynes and compounds prepared thereof have been reported in the literature since the discovery of ferrocene. However, data so far collected are scattered over the literature of the past decades with no comparative study yet available up to the best of our knowledge. This prompted us to examine a series of internal ferrocenyl alkynes  $\text{FcC}\equiv\text{CY}$  with various substituents Y. Their preparation and a study of their properties by electrochemical, spectroscopic and spectrometric methods are the subject of the present work.

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	Y	Y
1	H	8
2	Me	9
3	Ph	10
4	CMe <sub>3</sub>	11
5	SiMe <sub>3</sub>	12
6	GeMe <sub>3</sub>	13
7	SnMe <sub>3</sub>	14

Chart 1.

## 2. Results and discussion

### 2.1. Syntheses and spectra

The series of alkynes (see Chart 1) were prepared by literature procedures (**1–3**, **5**, **8**, **11**, **13**), alternative procedures (**14**) or newly synthesized by methods established in alkyne chemistry (**4**, **6**, **9–12**). An overview of the syntheses is given in Scheme 1. The *tert*-butyl derivative (**4**) was obtained by Sonogashira coupling of iodoferrocene with excess 3,3-dimethylbutyne in anhydrous diisopropylamine. The reaction is sluggish but provides the desired alkyne in 77% isolated yield (after 72 h at room temperature). Compound **4** has been synthesized previously by a multi-step procedure from  $\text{FcC(O)CHCMe}_3$  in a very poor yield [13]. Trimethylgermyl compound **6** was obtained by simple metathesis of (lithioethynyl)ferrocene with  $\text{GeMe}_3\text{Cl}$  in 77% yield after chromatography. Its stannylated analogue (**7**) was prepared similarly from  $\text{FcC}\equiv\text{CLi}$  and  $\text{SnMe}_3\text{Cl}$ . However, it was excluded from this study because of its notorious contamination by the parent alkyne **1**, which might influence mass spectrometric and electrochemical measurements.

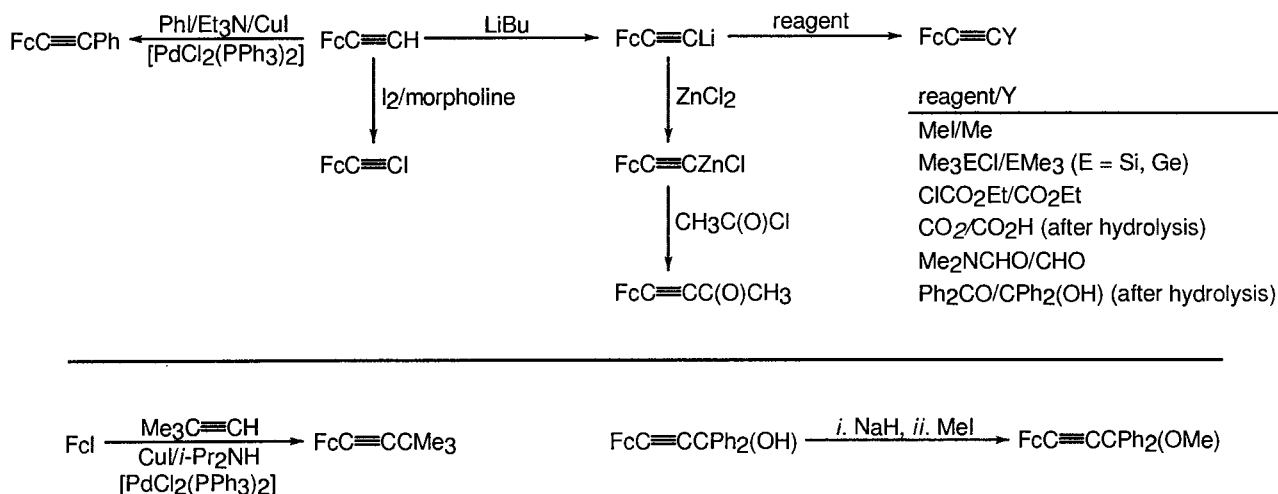
In situ transmetalation of  $\text{FcC}\equiv\text{CLi}$  with  $\text{ZnCl}_2$  followed by a coupling reaction with acetyl chloride gave ketone **12**. A reaction of the lithioalkyne with ethyl

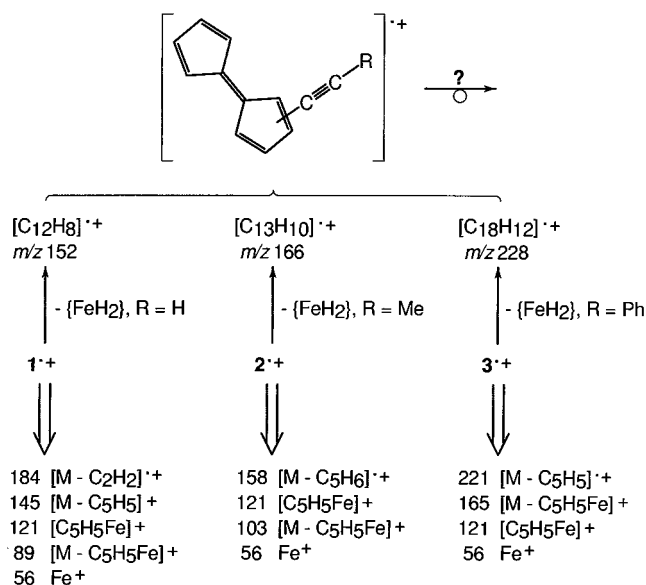
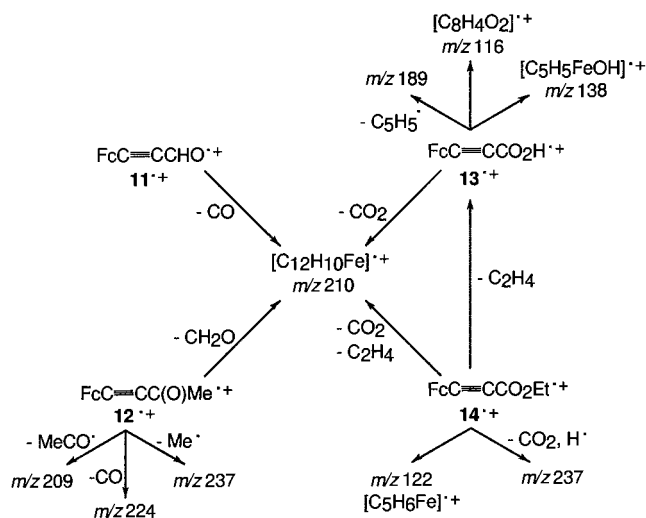
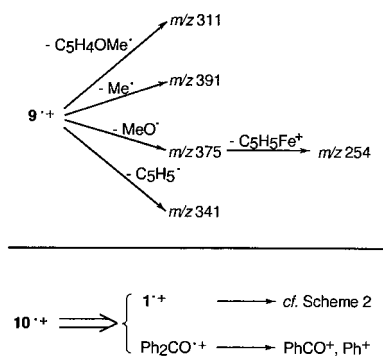
chloroformate afforded ethyl propiolate **14** (80% isolated yield). This route is simple and more efficient than the reported reaction of  $\text{FcC(O)Cl}$  with Wittig reagent  $\text{Ph}_3\text{P}=\text{CHCO}_2\text{Et}$  followed by pyrolysis of a phosphorane intermediate [14]. The alcohol **9** was synthesized by the reaction of  $\text{FcC}\equiv\text{CLi}$  with benzophenone [15] and then converted to the corresponding methyl ether **10** by the standard deprotonation-alkylation procedure.

All alkynes were characterized by  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR, IR, UV–vis and mass spectra. The most significant features in IR spectra of the alkynes are, besides diagnostic bands of the functional groups Y, bands due to  $\nu_{\text{C}\equiv\text{C}}$  vibrations. The latter dominate in the spectra of alkynes bearing polar substituents (**9–14**) while only very weak or almost no bands are observed for non-polar substituents Y (**2**, **3**, **4**). This is a consequence of different changes in dipole moment accompanying the respective  $\nu_{\text{C}\equiv\text{C}}$  stretching. The variation of  $\text{C}\equiv\text{C}$  bond length in electronically asymmetric alkynes (**9–14**) causes a large change of the molecular dipole whereas only small variation and, hence, weak IR bands can be expected for alkynes bearing two donor groups on the triple bond. An introduction of a polar group capable of conjugation onto the (ferrocenyl)ethynyl moiety leads to a remarkable bathochromic and hyperchromic shift of the long-wave ferrocene bands in UV–vis spectra. The extremes in the series studied are alkynes **1** ( $\lambda_{\text{max}}/\text{nm}$ ,  $\epsilon/\text{m}^2 \text{mol}^{-1}$ ; 445, 14) and **11** (470, 149).

### 2.2. EI Mass spectra

With the exception of the iodo derivative **8** whose decomposition upon heating in the probe to a mixture of **1**, **8** and  $\text{FcC}\equiv\text{CC}\equiv\text{CFc}$  prevented its mass spectra to be evaluated, the alkynes were studied by mass spectroscopy. Their electron impact (EI) mass spectral data are given in Section 3 and the fragmentation patterns are presented in Schemes 2–4.

Scheme 1. Synthesis of ferrocenyl alkynes  $\text{FcC}\equiv\text{CY}$ .

Scheme 2. EI Induced fragmentation of alkynes **1**, **2** and **3**.Scheme 3. EI Induced fragmentation of alkynes bearing the  $FcC=CC(O)$  moiety.Scheme 4. EI Induced fragmentation of alkynes **9** and **10**.

The simplest representative **1** fragment upon EI by elimination of either ethyne molecule ( $\rightarrow m/z$  184), cyclopentadienyl radical ( $\rightarrow m/z$  145),  $[C_5H_5Fe]^+$  cation ( $\rightarrow m/z$  89) and a  $[C_7H_6]^\bullet$  (or  $[C_5H_5C_2H]^\bullet$ ) radical ( $\rightarrow m/z$  121,  $[C_5H_5Fe]^+$ ). Besides the molecular ion  $1^+$ , the most abundant is the signal of  $Fe^+$  at  $m/z$  56. Such a behavior corresponds well to EI-induced fragmentation of simple ferrocene derivatives which usually fragment by a cyclopentadienyl ring–Fe bond rupture or by decomposition processes analogous to arene derivatives [16]. The most interesting feature in the mass spectrum of **1** is the occurrence of ions at  $m/z$  152 that apparently arise from elimination of Fe and  $H_2$  (or  $FeH_2$ ) from the molecular ion  $1^+$ . A similar fragmentation was observed in the spectra of **2** and **3**: ions due to the loss of  $C_5H_6$  molecule or  $C_5H_5^\bullet$  radical, respectively, and ionic species formed by a loss of  $[C_7H_5R]^\bullet$  and  $[C_5H_5Fe]^+$  from their molecular ions. More importantly, spectra of **2** and **3** exhibit fragments resulting from a simultaneous loss of Fe a  $H_2$  at  $m/z$  166 and 228, respectively (Scheme 2). The fact, that the triple bond substituent (R) remains incorporated in the homologous ions  $m/z$  152 (**1**, R = H), 166 (**2**, Me) and 228 (**3**, Ph) implies the ions to formally originate by a simple transfer of one cyclopentadienyl ring to the another with or without subsequent skeletal rearrangements. Nevertheless, a participation of the iron centre in this cyclopentadienyl group transfer cannot a priori be ruled out although this is rather the case of ferrocene derivatives bearing polar functional groups [17].

The *tert*-butyl derivative **4** fragments differently to **2** and **3**; ionic species corresponding to the loss of  $FeH_2$  from the molecular ion are not observed. The spectrum is dominated by the molecular ion. Also observed are ions due to a loss of one or two methyl groups from  $4^+$ , weakly abundant ions corresponding to an elimination of butene and further fragment ions typical for ferrocene derivatives ( $m/z$  186  $[M - C_6H_8]^+$ , 121 and 56). Similarly to  $4^+$ , the molecular ions of trimethylsilyl- and trimethylgermyl-substituted ethynylferrocenes,  $5^+$  and  $6^+$  decompose preferably by the loss of up to three methyl groups. Further fragments include ions typical for the ferrocene moiety, i.e. ions  $[C_5H_5Fe]^+$ ,  $Fe^+$  and ions  $[Me_3E]^+$ , E = Si ( $m/z$  73) and Ge ( $m/z$  117).

Fragmentations of all carbonyl-substituted alkynes—aldehyde **11**, ketone **12**, propionic acid **13** and its ethyl ester **14** follow the same trend: apart from some less populated fragmentation processes that are shown in Scheme 3, the alkynes **11**–**14** tend to eliminate parts of their substituents on the triple bond in such a way that ions  $m/z$  210 are formed. Thus, decarbonylation of **11**, decarboxylation of **13**, the loss of ethene and  $CO_2$  molecules from **14** and, more interestingly, a loss of formaldehyde molecule from acetyl derivative **12** generate ions similar (or even the same) to those originating from EI-ionization of **1**. Furthermore, the elimination

of ethene molecule from  $14^{+}$  affords ionic species at  $m/z$  254 isobaric with the molecular ions of acid **13**. The ions  $13^{+}$  decompose by a cleavage of one cyclopentadienyl ring–iron bond with a simultaneous transfer of the carboxyl hydroxyl group onto the iron centre, thus generating ions at  $m/z$  138 ( $[C_5H_5FeOH]^{+}$ ) and 116 ( $[C_8H_5O]^{+}$ ) that are both observed in the spectra. A similar hydroxyl-group transfer to the iron atom upon elimination of  $[C_5H_5]^{\bullet}$  radical has already been observed for ferrocenecarboxylic acid. In the latter case, however, the cyclopentadienyl ring is eliminated as a neutral  $[C_6H_4O]$  species [17b].

Analogously to the mentioned carbonyl derivatives, an elimination of benzophenone molecule from the

Table 1  
Electrochemical data for alkynes  $FcC\equiv CY^a$

Compound	Y	$E^{Fc}$ (V) <sup>b</sup>	$\sigma_p$	$\sigma_I$
1	H	0.11	0.00	0.00
2	Me	0.04	−0.17	−0.01
3	Ph	0.06	−0.01	0.12
4	<i>t</i> -Bu	0.05	−0.20	−0.01
5	SiMe <sub>3</sub>	0.00	−0.07	−0.11
6	GeMe <sub>3</sub>	0.00	0.00	− <sup>c</sup>
8	I	0.09	0.18	0.40
9	CPh <sub>2</sub> (OH)	0.10	− <sup>c</sup>	− <sup>c</sup>
10	CPh <sub>2</sub> (OMe)	0.10	− <sup>c</sup>	− <sup>c</sup>
11	CHO	0.22	0.42	(0.25) <sup>d</sup>
12	C(O)Me	0.20	0.50	0.30
14	CO <sub>2</sub> Et	0.21	0.45	0.30

<sup>a</sup> Conditions: platinum disc electrode, 100 mV s<sup>−1</sup> scan rate; measured for  $(0.2\text{--}1.0) \times 10^{-4}$  M solutions in 0.05 M Bu<sub>4</sub>NPF<sub>6</sub> in CH<sub>2</sub>Cl<sub>2</sub> at room temperature. Potentials are given relative to ferrocene standard.

<sup>b</sup>  $E^{Fc} = 1/2(E_{pa}^{Fc} + E_{pc}^{Fc})$ , where  $E_{pa}^{Fc}$  and  $E_{pc}^{Fc}$  denote anodic and cathodic peak potentials, respectively. The  $(E_{pa}^{Fc} - E_{pc}^{Fc})$  difference varied in the range 80–90 mV.

<sup>c</sup> Not found.

<sup>d</sup> Value uncertain.

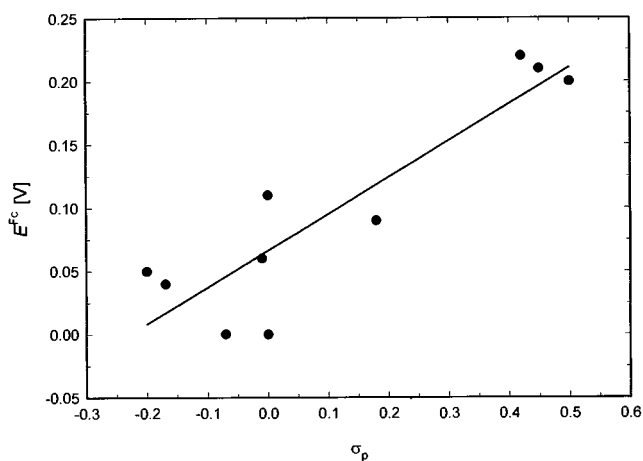


Fig. 1. Relationship between redox potential of the ferrocene/ferrocenium couple and Hammett  $\sigma_p$  constants.

molecular ion of alcohol **9** affords ions at  $m/z$  210 (isobaric with  $1^{+}$ ). Therefore, the spectrum appears as a superposition of mass spectra of  $1^{+}$  and  $[Ph_2CO]^{+}$ . On the other hand, there is no simple way of generation  $1^{+}$  from ionized molecules of ether **10**. Hence, the fragmentation of ether **10** differs markedly from that of its parent alcohol **9** (Scheme 4). The molecular ion  $10^{+}$  splits off either  $[C_5H_5]^{\bullet}$ ,  $Me^{\bullet}$ ,  $[C_6H_7O]^{\bullet}$  (i.e.  $[C_5H_4OMe]^{\bullet}$ ) or  $MeO^{\bullet}$  radical, the latter case being prominent ( $\rightarrow m/z$  375). The ions at  $m/z$  375 further eliminate  $[C_5H_5Fe]^{+}$  ion giving rise to ions at  $m/z$  254.

### 2.3. Electrochemistry

Ferrocene/ferrocenium itself represents a strictly reversible one-electron redox couple. However, the reversibility may be significantly lowered in the case of some ferrocenium species by a subsequent decomposition of the electrogenerated ferrocenium species (EC processes) [18]. Unique redox properties of ferrocene framework have been applied towards design of molecular sensors, ion-selective electrodes, potential scale standards, etc. [19]. The ferrocene substituent may also be regarded as a redox active probe on the molecular level since following the ferrocene/ferrocenium redox potentials offers a unique opportunity to detect alterations in electronic structure of ferrocene-derived molecules as well as in the nature of metal- $\pi$ -ligand bonding by providing information about changes of electron density distribution ( $|\psi(r=0)|^2$ ) and HOMO energies in series of related compounds. Many correlations of the ferrocene/ferrocenium redox potential with substituent constants (Hammett and inductive) have already been presented in the literature; the series of ferrocenyl derivatives  $FcX$  (and  $[Fe(\eta^5-C_5H_5X)(\eta^5-C_5H_4Z)]$ ) [20],  $FcC_6H_4X$  [21],  $FcCHXZ$ ,  $FcC(X)=Z$  [22] may serve as few representative examples.

All alkynes studied exhibit reversible one-electron redox reactions attributable to a ferrocene/ferrocenium couple in their cyclic voltammograms under the applied experimental conditions. Redox potential of the ferrocene/ferrocenium oxidation (Table 1, Fig. 1) linearly correlates with Hammett  $\sigma_p$  constants [23] of the substituent Y:  $E^{Fc}$  [V] = 0.29(9)  $\sigma_p$ (Y) + 0.07(1),  $r = 0.89$  (Fig. 1). A similar correlation with inductive constants  $\sigma_I$  [24] is rather loose:  $E^{Fc}$  [V] = 0.33(10)  $\sigma_I$ (Y) + 0.06(3),  $r = 0.72$  (Fig. 2). The correlations indicate that the triple bond in alkynes  $FcC\equiv CY$  transfers efficiently the influence of the substituent Y onto the ferrocene core. However, the spacer lowers its sensitivity towards minor changes in the structure of the substituent Y; for instance, alcohol **9** and ester **10** cannot be distinguished.

As the  $\sigma_p$  parameters include both inductive and resonance effects, a tighter correlation with  $\sigma_p$  is natural since it can be expected that the inductive effects are

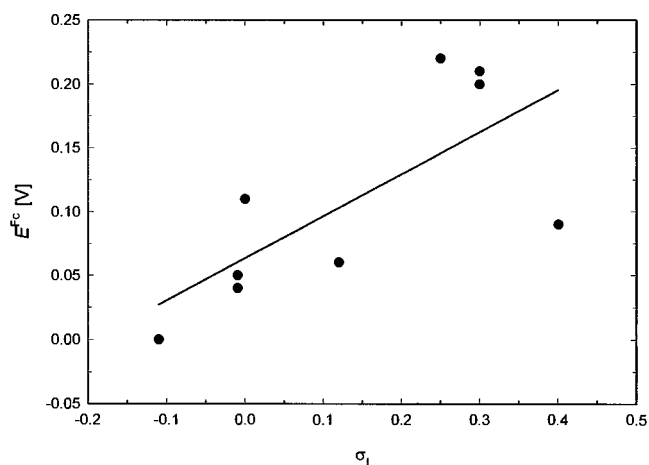


Fig. 2. Relationship between redox potential of the ferrocene/ferrocenium couple and inductive  $\sigma_I$  constants.

(at least in part) converted into mesomeric by changing the ability of the triple bond to conjugate with the ferrocene unit. In accordance with this assumption, ferrocene/ferrocenium redox potential of directly substituted ferrocenes  $FcX$  correlates very well with  $\sigma_p(X)$  (direct conjugation) while that of spaced derivatives  $FcCH_2X$  correlates with  $\sigma_I(X)$  [22a]. A further support comes from previous reports that  $\pi$ -donating ability of the triple bond in alkynes  $R_3EC\equiv CZ$  ( $E = C, Si, Ge$  and  $Sn$ ;  $R =$  alkyl;  $Z$  are various substituents) increase with electron donating strength of the substituents, the substituents  $R_3E$  and  $Z$  directly influencing each other [25].

It was shown that the potential metal-centered redox processes in first-row transition metals sandwich complexes can be parametrized as

$$E_{\text{calc}}(M^{(n+1)}/M^n) = S_M \% E_L(L) + I_M$$

where  $S_M$  and  $I_M$  are parameters of the  $M^{(n+1)}/M^n$  redox couple and  $E_L(L)$  represents properties of the metal-bonded ligand(s). The parameter  $E_L(L)$  correlate linearly with  $\sigma_p$  constants of the ligand substituents (e.g.  $E_L(L) = 0.45\Sigma\sigma_p(R) + 0.36$  for substituted cyclopentadienyls  $C_5H_{5-m}R_m$  in normal hydrogen electrode scale) [26]. The above results indicate that this approach is not restricted to substituents directly bonded to the aromatic  $\pi$ -ligand(s) such as  $R$  in  $C_5H_{5-m}R_m$  but may also be extended to systems in which the substituents are separated by the same (conjugated) spacer, thus allowing one to quantify the influence of the substituents in a part of a molecule which is more remote from the redox centre—nonetheless with a sensitivity lower compared to directly bonded modifying groups.

### 3. Experimental

#### 3.1. General comments

NMR spectra were measured on a Varian UNITY Inova 400 spectrometer ( $^1H$  399.95,  $^{13}C$  100.58 MHz) at 298 K. Chemical shifts ( $\delta$ /ppm) are given relative to an internal tetramethylsilane standard. Infrared spectra were recorded in the range of 400–4000  $cm^{-1}$  on an FT IR Mattson Genesis instrument. UV–vis spectra were measured on a diode array HP 8453 spectrometer in acetone ( $c$   $10^{-2}$ – $10^{-3}$  M, quartz cells 1.0 cm). Mass spectra were measured on a VG 7070E instrument (EI, 70 eV, direct inlet at the temperature given below). All electrochemical measurements were performed in argon atmosphere at 25 °C on a multipurpose polarograph PA4 connected to XY Recorder 4103 (Laboratorní přístroje, Prague) using standard three-electrode cell equipped with a static platinum disc working electrode (0.5 mm diameter), a platinum foil auxiliary electrode and a platinum wire quasi-reference electrode. Cyclic voltammograms were recorded at the scan rate of 100  $mV s^{-1}$  in dichloromethane solutions (Merck, p.a.; sample concentrations  $(0.2$ – $1.0) \times 10^{-4}$  M; 0.05 M  $[Bu_4N][PF_6]$  supporting electrolyte). Potentials are given in Volts relative to the redox potential of the ferrocene/ferrocenium couple.

Iodoferrocene [27] and the alkynes  $FcC\equiv CY$ , where  $Y = H$  (**1**) [28], Me (**2**) [29], Ph (**3**) [30],  $SiMe_3$  (**5**) [30], I (**8**) [31], CHO (**11**) [29],  $CO_2H$  (**13**) [32] were synthesized by literature procedures. All preparations were carried out in an argon atmosphere using solvents freshly distilled from potassium.

#### 3.2. Syntheses

##### 3.2.1. (3,3-Dimethylbut-1-yn-1-yl)ferrocene (**4**)

Iodoferrocene (157 mg, 0.50 mmol),  $[PdCl_2(PPh_3)_2]$  (16 mg, 25  $\mu$ mol) and  $Me_3CC\equiv CH$  (0.20  $cm^3$ , 1.6 mmol) were mixed with diisopropylamine (10  $cm^3$ ). After stirring for 2 min, CuI (10 mg, 50  $\mu$ mol) was added and the mixture was stirred in dark for 36 h. As the TLC ( $SiO_2$ , hexane) showed the presence of unreacted iodoferrocene, the Pd(II) complex, CuI and alkyne were added (the same amount as before) and stirring was continued for further 36 h. Finally, all volatiles were evaporated under reduced pressure, the residue was taken up in hexane, and the extract was filtered through cellulose pad and evaporated. The crude product was purified by chromatography ( $SiO_2$ , hexane then hexane:diethyl ether, 10:1 v/v) to give **4** as a rusty orange solid. Yield: 102 mg (77%). M.p. 90–92 °C (Ref. [13]: 91–92 °C). NMR ( $CDCl_3$ , 298 K):  $\delta_H$  1.28 (s, 9 H,  $CMe_3$ ), 4.11 (apparent t, 2 H,  $C_5H_4$ ), 4.16 (s, 5 H,  $C_5H_5$ ), 4.33 (apparent t, 2 H,  $C_5H_4$ );  $\delta_C$  28.0 ( $CMe_3$ ), 31.3 ( $CMe_3$ ), 66.6 ( $C_5H_4$ ,  $C_{ipso}$ ), 68.1 ( $C_5H_4$ , CH), 69.8

(C<sub>5</sub>H<sub>5</sub>), 71.2 (C<sub>5</sub>H<sub>4</sub>, CH), 76.3, 94.7 (C≡C). IR (Nujol):  $\tilde{\nu}/\text{cm}^{-1}$  3100w, 3090w, 1285m, 1280m, 1215m, 1206m, 1104s, 1063m, 1042m, 1025m, 1005m, 999m, 872w, 825s, 812s, 808s, 511s, 493m, 477s. EI MS (40 °C):  $m/z$  (relative abundance) 266 (100, [M<sup>+</sup>]), 251 (73, [M – Me]<sup>+</sup>), 236 (18, [M – 2Me]<sup>+</sup>), 210 (2, [M – C<sub>4</sub>H<sub>8</sub>]<sup>+</sup>), 186 (7), 185 (4), 152 (3), 129 (8), 128 (8), 122 (3), 121 (33, [C<sub>5</sub>H<sub>5</sub>Fe]<sup>+</sup>), 95 (4), 89 (15), 81 (8), 73 (5), 71 (5), 69 (8), 65 (3), 63 (6), 60 (5), 57 (13), 56 (51, Fe<sup>+</sup>). UV–vis (acetone):  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon/\text{m}^2 \text{mol}^{-1}$ ) 445 (17).

### 3.2.2. ((Trimethylgermyl)ethynyl)ferrocene, FcC≡CGeMe<sub>3</sub> (**6**)

A solution of *n*-BuLi in hexane (3.1 cm<sup>3</sup> 2.5 M, 7.7 mmol) was added dropwise to a solution of **1** (1.50 g, 7.0 mmol) in diethyl ether (30 cm<sup>3</sup>) at –20 °C and the mixture was stirred for 30 min at the same temperature. Neat Me<sub>3</sub>GeBr (1.4 g, 7.2 mmol) was added to the resulting solution of FcC≡CLi, cooling bath was removed and stirring was continued for 3 h at room temperature (r.t.). After quenching with saturated aqueous NaHCO<sub>3</sub> (10 cm<sup>3</sup>) and stirring for 30 min, the organic layer was separated, washed with water (2 × 10 cm<sup>3</sup>) and dried over MgSO<sub>4</sub>. Evaporation and chromatography on alumina with hexane as the eluent gave an orange viscous oil which solidified upon standing at 4 °C to an orange solid. Yield: 1.81 g (77%). Anal. Found: C, 55.46; H, 5.53. Calc. for C<sub>15</sub>H<sub>18</sub>FeGe: C, 55.14; H, 5.55%. M.p. 56–7 °C. NMR (CDCl<sub>3</sub>, 298 K):  $\delta_{\text{H}}$  0.40 (s, 9 H, GeMe<sub>3</sub>), 4.15 (apparent t, 2 H, C<sub>5</sub>H<sub>4</sub>), 4.18 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 4.41 (apparent t, 2 H, C<sub>5</sub>H<sub>4</sub>);  $\delta_{\text{C}}$  0.1 (GeMe<sub>3</sub>), 65.4 (C<sub>5</sub>H<sub>4</sub>, C<sub>ipso</sub>), 68.5 (C<sub>5</sub>H<sub>4</sub>, CH), 70.1 (C<sub>5</sub>H<sub>5</sub>), 71.6 (C<sub>5</sub>H<sub>4</sub>, CH), 90.7, 102.8 (C≡C). IR (Nujol):  $\tilde{\nu}/\text{cm}^{-1}$  3313w, 3098w, 2155m, composite ( $\nu_{\text{C}\equiv\text{C}}$ ); 1239m, 1107s, 1023m, 1001s, 924m, 829s, composite; 766m, 687s, 609s, 575w, 535m, 503m, 473m, 450m. EI MS (120 °C):  $m/z$  (relative abundance) 328 (100, [M<sup>+</sup>]), 313 (31, [M – Me]<sup>+</sup>), 298 (29, [M – 2Me]<sup>+</sup>), 283 (28, [M – 3Me]<sup>+</sup>), 223 (7), 177 (4), 176 (3), 175 (4), 162 (4), 156 (22, [313]<sup>2+</sup>), 152 (5), 139 (10), 121 (24, [C<sub>5</sub>H<sub>5</sub>Fe]<sup>+</sup>), 117 (12, Me<sub>3</sub>Ge<sup>+</sup>), 115 (8), 104 (3), 95 (4), 89 (5), 81 (4), 56 (23, Fe<sup>+</sup>). UV–vis (acetone):  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon/\text{m}^2 \text{mol}^{-1}$ ) 445 (19).

### 3.2.3. 1,1-Diphenyl-3-ferrocenylpropargyl alcohol, FcC≡CCPh<sub>2</sub>(OH) (**9**)

Benzophenone (3.1 g, 16.3 mmol) in diethyl ether (20 cm<sup>3</sup>) was added at –50 °C to a solution of FcC≡CLi prepared from **1** (2.6 g, 12.5 mmol) and *n*-BuLi (6 cm<sup>3</sup> 2.5 M, 15.0 mmol) in diethyl ether (40 cm<sup>3</sup>) as described above. Cooling bath was removed and the mixture was stirred for 3 h at r.t. Aqueous H<sub>3</sub>PO<sub>4</sub> was added (10 cm<sup>3</sup>, 1:20 v/v), the organic layer was separated, washed with water, saturated aqueous NaHCO<sub>3</sub> solution and water (25 cm<sup>3</sup> each), dried over MgSO<sub>4</sub> and evaporated. Chromatography on silica gel with toluene as the eluent

and drying in vacuum (60 °C, 2 h, 2 Torr) afforded pure **9** as an orange oil which solidified to an orange waxy material upon standing at 4 °C. Yield: 4.6 g (95%). Anal. Found: C, 76.51; H, 5.13. Calc. for C<sub>26</sub>H<sub>22</sub>FeO: C, 76.55; H, 5.14%. NMR (CDCl<sub>3</sub>, 298 K):  $\delta_{\text{H}}$  2.78 (s, 1 H, OH), 4.21 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 4.21, 4.48 (2 × apparent t, 2 H, C<sub>5</sub>H<sub>4</sub>); 7.23–7.69 (m, 10 H, Ph);  $\delta_{\text{C}}$  64.2 (C<sub>5</sub>H<sub>4</sub>, C<sub>ipso</sub>), 68.8 (C<sub>5</sub>H<sub>4</sub>, CH), 69.8 (C<sub>5</sub>H<sub>5</sub>), 71.6 (C<sub>5</sub>H<sub>4</sub>, CH), 74.9 (CPh<sub>2</sub>), 86.3, 88.1 (C≡C); 126.7, 127.5, 128.1, 143.7 (Ph). IR (Nujol):  $\tilde{\nu}/\text{cm}^{-1}$  2227m ( $\nu_{\text{C}\equiv\text{C}}$ ), 1666m, 1276m, 1176m, 1105m, 1069s, 1018m, 939m, 807m, 774s, 748m, 701s, 640m, 539m, 498m, 455m. EI MS (160 °C):  $m/z$  (relative abundance) 392 (8, [M<sup>+</sup>]), 327 (3, [M – C<sub>5</sub>H<sub>5</sub>]<sup>+</sup>), 254 (4), 211 (11), 210 (70, [M – Ph<sub>2</sub>CO]<sup>+</sup>), 182 (38, Ph<sub>2</sub>CO<sup>+</sup>), 152 (12, [C<sub>12</sub>H<sub>8</sub>]<sup>+</sup>), 145 (4), 121 (21, [C<sub>5</sub>H<sub>5</sub>Fe]<sup>+</sup>), 105 (100, C<sub>6</sub>H<sub>5</sub>CO<sup>+</sup>), 95 (4), 94 (3), 89 (7, [C<sub>7</sub>H<sub>5</sub>]<sup>+</sup>), 81 (4), 77 (56, C<sub>6</sub>H<sub>5</sub><sup>+</sup>), 76 (4), 63 (3), 56 (26, Fe<sup>+</sup>). UV–vis (acetone):  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon/\text{m}^2 \text{mol}^{-1}$ ) 446 (24).

### 3.2.4. 1,1-Diphenyl-3-ferrocenylpropargyl methyl ether, FcC≡CCPh<sub>2</sub>(OMe) (**10**)

A solution of alcohol **9** (2.70 g, 7.0 mmol) in THF (30 cm<sup>3</sup>) was slowly added to an ice-cooled suspension of sodium hydride (0.25 g, 10.4 mmol) in THF (15 cm<sup>3</sup>). The resulting mixture was stirred for 15 min at 0 °C and methyl iodide (0.50 cm<sup>3</sup>, 7.7 mmol) was slowly introduced. After stirring for 15 h at r.t., an excess of NaH was destroyed by careful addition of methanol (4 cm<sup>3</sup>) and water (10 cm<sup>3</sup>) and the volatiles were removed under reduced pressure. The residue was extracted with diethyl ether (40 cm<sup>3</sup>), the extract was washed with water and dried over MgSO<sub>4</sub>. Evaporation and chromatography on silica gel with toluene as the eluent followed by drying in vacuum (60 °C, 2 h, 2 Torr) afforded **10** as an oil which solidified at 4 °C to an orange waxy solid. Yield 2.60 g (94%). Anal. Found: C, 76.51; H, 5.09. Calc. for C<sub>26</sub>H<sub>22</sub>FeO: C, 76.86; H, 5.46%. NMR (CDCl<sub>3</sub>, 298 K):  $\delta_{\text{H}}$  3.42 (s, 3 H, OMe), 4.21 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 4.22, 4.51 (2 × apparent t, 2 H, C<sub>5</sub>H<sub>4</sub>); 7.22–7.64 (m, 10H, Ph);  $\delta_{\text{C}}$  52.4 (OMe), 64.4 (C<sub>5</sub>H<sub>4</sub>, C<sub>ipso</sub>), 68.8 (C<sub>5</sub>H<sub>4</sub>, CH), 69.8 (C<sub>5</sub>H<sub>5</sub>), 71.6 (C<sub>5</sub>H<sub>4</sub>, CH), 81.4 (CPh<sub>2</sub>), 84.8, 88.5 (C≡C); 126.7, 127.5, 128.1, 143.7 (Ph). IR (Nujol):  $\tilde{\nu}/\text{cm}^{-1}$  2227m ( $\nu_{\text{C}\equiv\text{C}}$ ), 1666m, 1276m, 1176m, 1105m, 1069s, 1018m, 939m, 807m, 774s, 748m, 701s, 640m, 539m, 498m, 455m. EI MS (150 °C):  $m/z$  (relative abundance) 406 (95, [M<sup>+</sup>]), 391 (2, [M – Me]<sup>+</sup>), 375 (100, [M – OMe]<sup>+</sup>), 341 (3, [M – C<sub>5</sub>H<sub>5</sub>]<sup>+</sup>), 329 (3), 325 (4), 314 (4), 311 (12, [M – C<sub>6</sub>H<sub>7</sub>O]<sup>+</sup>, likely an elimination of C<sub>5</sub>H<sub>4</sub>OMe<sup>•</sup>), 255 (12), 254 (49, [M – C<sub>5</sub>H<sub>5</sub>FeOMe]<sup>+</sup>), 253 (22), 252 (35), 239 (6), 226 (3), 188 (9, [375]<sup>2+</sup>), 176 (3), 165 (8, [329]<sup>2+</sup>), 152 (4, [C<sub>12</sub>H<sub>8</sub>]<sup>+</sup>), 121 (23, [C<sub>5</sub>H<sub>5</sub>Fe]<sup>+</sup>), 105 (11), 77 (15, C<sub>6</sub>H<sub>5</sub><sup>+</sup>), 56 (18, Fe<sup>+</sup>). UV–vis (acetone):  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon/\text{m}^2 \text{mol}^{-1}$ ) 446 (56).

### 3.2.5. 2-(Ferrocenyl)ethynyl methyl ketone (**12**)

To a solution of  $\text{FcC}\equiv\text{CLi}$  prepared from **1** (2.35 g, 11.7 mmol) and *n*-BuLi (5.1 cm<sup>3</sup> 2.5 M, 12.8 mmol) in THF/hexane (30 cm<sup>3</sup>, 1:1 v/v) as given above was added a solution of anhydrous  $\text{ZnCl}_2$  (1.75 g, 12.8 mmol) in THF (25 cm<sup>3</sup>) at  $-50^\circ\text{C}$  and the mixture was stirred for 30 min at  $0^\circ\text{C}$ . Acetyl chloride (1.0 cm<sup>3</sup>, 12.8 mmol) was added to the resulting suspension of  $\text{FcC}\equiv\text{CZnCl}$  at  $0^\circ\text{C}$ , cooling bath was removed and the mixture was stirred for 1 h at r.t. (colour of the mixture turned from light orange to red). After addition of saturated aqueous  $\text{NH}_4\text{Cl}$  solution (20 cm<sup>3</sup>) and stirring for another 30 min, aqueous layer was separated, washed with saturated aqueous  $\text{NH}_4\text{Cl}$  solution ( $3 \times 20$  cm<sup>3</sup>), water (20 cm<sup>3</sup>) and dried over  $\text{MgSO}_4$ . Evaporation and chromatography on silica gel using toluene as the eluent (unreacted **1** is eluted first as a yellow-orange band followed by the band of the product) gave **12** as a deep red solid. Yield: 2.2 g (78%). Anal. Found: C, 66.37; H, 4.99. Calc. for  $\text{C}_{14}\text{H}_{12}\text{FeO}$ : C, 66.70; H, 4.80%. M.p.  $106\text{--}108^\circ\text{C}$ . NMR ( $\text{CDCl}_3$ , 298 K):  $\delta_{\text{H}}$  2.39 (s, 3 H, *Me*), 4.26 (s, 5 H,  $\text{C}_5\text{H}_5$ ), 4.38, 4.58 (2  $\times$  apparent t, 2 H,  $\text{C}_5\text{H}_4$ );  $\delta_{\text{C}}$  32.5 (*Me*), 60.1 ( $\text{C}_5\text{H}_4$ ,  $C_{\text{ipso}}$ ), 70.4 ( $\text{C}_5\text{H}_5$ ), 70.7, 73.1 ( $\text{C}_5\text{H}_4$ , 2  $\times$  CH); 86.9, 93.7 ( $\text{C}\equiv\text{C}$ ); 184.3 (*CO*). IR (Nujol):  $\tilde{\nu}/\text{cm}^{-1}$  2207m, 2181s ( $\nu_{\text{C}\equiv\text{C}}$ ); 1659s ( $\nu_{\text{C}=\text{O}}$ ), 1279s, 1173s, 1104m, 1001m, 974s, 822s composite, 609m, 535m, 504s, 481s, 461m. EI MS ( $60^\circ\text{C}$ ):  $m/z$  (relative abundance) 252 (100,  $[\text{M}^{\bullet+}]$ ), 237 (12,  $[\text{M} - \text{Me}]^+$ ), 224 (3,  $[\text{M} - \text{CO}]^+$ ), 210 (28,  $[\text{M} - \text{CH}_2\text{CO}]^+$ ), 209 (12,  $[\text{M} - \text{CH}_3\text{CO}]^+$ ), 166 (3), 157 (4), 152 (18,  $[\text{C}_{12}\text{H}_8]^+$ ), 145 (3), 144 (3), 121 (24,  $[\text{C}_5\text{H}_5\text{Fe}]^+$ ), 118 (11), 95 (4), 94 (6), 89 (5,  $[\text{C}_7\text{H}_5]^+$ ), 81 (10), 56 (36,  $\text{Fe}^+$ ). UV-vis (acetone):  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon/\text{m}^2 \text{mol}^{-1}$ ) 459 (81).

### 3.2.6. Ethyl ferrocenepropiolate, $\text{FcC}\equiv\text{CCO}_2\text{Et}$ (**14**)

Ethyl chloroformate (0.90 cm<sup>3</sup>, 9.2 mmol) was added to a solution of  $\text{FcC}\equiv\text{CLi}$  [prepared from **1** (1.50 g, 7.1 mmol) and *n*-BuLi (3.4 cm<sup>3</sup> 2.5 M, 8.5 mmol) in diethyl ether (30 cm<sup>3</sup>)] at  $-50^\circ\text{C}$ . After the mixture had been stirred at r.t. for 5 h, saturated aqueous  $\text{NaHCO}_3$  solution (20 cm<sup>3</sup>) was added, organic phase was separated and the aqueous layer was extracted with diethyl ether. Combined organic layers were dried over  $\text{MgSO}_4$  and evaporated. The residue was purified by chromatography (silica gel, toluene) to afford **14** as an orange-red solid. Yield 1.60 g (80%). M.p.  $94\text{--}96^\circ\text{C}$  (Ref. [14]:  $96\text{--}97^\circ\text{C}$ ). NMR ( $\text{CDCl}_3$ , 298 K):  $\delta_{\text{H}}$  1.35 (t, 3 H,  $^3J_{\text{HH}} = 7.2$  Hz,  $\text{CH}_3$ ), 4.26 (s, 5 H,  $\text{C}_5\text{H}_5$ ), 4.27 (q, 2 H,  $^3J_{\text{HH}} = 7.2$  Hz,  $\text{CH}_2$ ), 4.34, 4.59 (2  $\times$  apparent t, 2 H,  $\text{C}_5\text{H}_4$ );  $\delta_{\text{C}}$  14.2 ( $\text{CH}_3$ ), 61.8 ( $\text{CH}_2$ ), 70.0 ( $\text{C}_5\text{H}_4$ ,  $C_{\text{ipso}}$ ), 70.35 ( $\text{C}_5\text{H}_4$ , CH), 70.37 ( $\text{C}_5\text{H}_5$ ), 72.9 ( $\text{C}_5\text{H}_4$ , CH), 78.2, 88.5 ( $\text{C}\equiv\text{C}$ ); 154.2 ( $\text{CO}_2\text{Et}$ ). IR (Nujol):  $\tilde{\nu}/\text{cm}^{-1}$  2247m, 2206s ( $\nu_{\text{C}\equiv\text{C}}$ ); 1691s ( $\nu_{\text{C}=\text{O}}$ ); 1289s, 1197s, 1105m, 1045s, 1020s, 837s,

820s, 740s, 524m, 485m, 468w. EI MS ( $90^\circ\text{C}$ ):  $m/z$  (relative abundance) 282 (100,  $[\text{M}^{\bullet+}]$ ), 254 (42,  $[\text{M} - \text{C}_2\text{H}_4]^+$ ), 237 (12,  $[\text{M} - \text{CO}_2 - \text{H}]^+$ ), 210 (38,  $[\text{M} - \text{C}_2\text{H}_4 - \text{CO}_2]^+$ ), 189 (6,  $\{[254]^+ - \text{C}_5\text{H}_5\}^+$ ), 161 (6), 157 (5), 153 (11), 152 (19,  $[\text{C}_{12}\text{H}_8]^+$ ), 145 (8), 138 (13,  $[\text{C}_5\text{H}_5\text{FeOH}]^+$ ), 122 (21), 121 (21,  $[\text{C}_5\text{H}_5\text{Fe}]^+$ ), 119 (3), 118 (9), 116 (13,  $[\text{C}_8\text{H}_4\text{O}]^+$ ), 105 (4), 95 (4), 94 (7), 89 (7,  $[\text{C}_7\text{H}_5]^+$ ), 88 (8), 81 (10), 56 (42,  $\text{Fe}^+$ ). UV-vis (acetone):  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon/\text{m}^2 \text{mol}^{-1}$ ) 452 (55).

### 3.3. EI mass, IR and UV-vis spectral data for other alkynyl ferrocenes

**1** EI MS ( $40^\circ\text{C}$ ),  $m/z$  (relative abundance): 210 (100,  $[\text{M}^{\bullet+}]$ ), 184 (3,  $[\text{M} - \text{C}_2\text{H}_2]^+$ ), 152 (13,  $[\text{C}_{12}\text{H}_8]^+$ ), 145 (5,  $[\text{M} - \text{C}_5\text{H}_5]^+$ ), 128 (3), 121 (27,  $[\text{C}_5\text{H}_5\text{Fe}]^+$ ), 105 (5), 95(5), 89 (10,  $[\text{C}_7\text{H}_5]^+$ , i.e.:  $[\text{M} - \text{C}_5\text{H}_5\text{Fe}]^+$ ), 81 (6), 63 (3), 56 (35,  $\text{Fe}^+$ ). IR (Nujol):  $\tilde{\nu}/\text{cm}^{-1}$  2104s ( $\nu_{\text{C}\equiv\text{C}}$ ). UV-vis (acetone):  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon/\text{m}^2 \text{mol}^{-1}$ ) 445 (14).

**2** EI MS ( $60^\circ\text{C}$ ),  $m/z$  (relative abundance): 224 (100,  $[\text{M}^{\bullet+}]$ ), 166 (7), 158 (13,  $[\text{M} - \text{C}_5\text{H}_6]^+$ ), 133 (4), 121 (18,  $[\text{C}_5\text{H}_5\text{Fe}]^+$ ), 112 (5), 103 (4), 102 (4), 95 (3), 81 (8), 77 (4), 56 (30,  $\text{Fe}^+$ ). IR (Nujol):  $\tilde{\nu}/\text{cm}^{-1}$  ca. 2200vw ( $\nu_{\text{C}\equiv\text{C}}$ ). UV-vis (acetone):  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon/\text{m}^2 \text{mol}^{-1}$ ) 447 (15).

**3** EI MS ( $90^\circ\text{C}$ ),  $m/z$  (relative abundance): 286 (100,  $[\text{M}^{\bullet+}]$ ), 228 (5), 221 (1,  $[\text{M} - \text{C}_5\text{H}_5]^+$ ), 165 (15,  $[\text{M} - \text{C}_5\text{H}_5\text{Fe}]^+$ ), 143 (5), 139 (4), 121 (16,  $[\text{C}_5\text{H}_5\text{Fe}]^+$ ), 56 (15,  $\text{Fe}^+$ ). IR (Nujol):  $\tilde{\nu}/\text{cm}^{-1}$  2224w, 2208w ( $\nu_{\text{C}\equiv\text{C}}$ ). UV-vis (acetone):  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon/\text{m}^2 \text{mol}^{-1}$ ) 448 (16).

**5** EI MS ( $50^\circ\text{C}$ ),  $m/z$  (relative abundance): 282 (100,  $[\text{M}^{\bullet+}]$ ), 267 (24,  $[\text{M} - \text{Me}]^+$ ), 253 (1,  $[\text{M} - \text{C}_2\text{H}_5]^+$ ), 237 (1,  $[\text{M} - 3\text{Me}]^+$ ), 145 (3), 134 (19), 121 (8,  $[\text{C}_5\text{H}_5\text{Fe}]^+$ ), 93 (4), 73 (6,  $\text{Me}_3\text{Si}^+$ ), 56 (8,  $\text{Fe}^+$ ). IR (Nujol):  $\tilde{\nu}/\text{cm}^{-1}$  2147s ( $\nu_{\text{C}\equiv\text{C}}$ ). UV-vis (acetone):  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon/\text{m}^2 \text{mol}^{-1}$ ) 445 (24).

**11** EI MS ( $60^\circ\text{C}$ ),  $m/z$  (relative abundance): 238 (100,  $[\text{M}^{\bullet+}]$ ), 210 (18,  $[\text{M} - \text{CO}]^+$ ), 152 (18,  $[\text{C}_{12}\text{H}_8]^+$ ), 145 (6), 128 (3), 121 (39,  $[\text{C}_5\text{H}_5\text{Fe}]^+$ ), 119 (5), 118 (5), 95 (6), 94 (6), 89 (12,  $[\text{C}_7\text{H}_5]^+$ ), 81 (8), 63 (4), 56 (49,  $\text{Fe}^+$ ). IR (Nujol):  $\tilde{\nu}/\text{cm}^{-1}$  2207s ( $\nu_{\text{C}\equiv\text{C}}$ ), 1659s ( $\nu_{\text{C}=\text{O}}$ ). UV-vis (acetone):  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon/\text{m}^2 \text{mol}^{-1}$ ) 470 (149).

**13** EI MS ( $70^\circ\text{C}$ ),  $m/z$  (relative abundance) 254 (5,  $[\text{M}^{\bullet+}]$ ), 210 (100,  $[\text{M} - \text{CO}_2]^+$ ), 208 (7), 184 (4), 154 (4), 153 (10), 152 (17), 145 (5), 138 (2), 129 (3), 128 (4), 121 (27,  $[\text{C}_5\text{H}_5\text{Fe}]^+$ ), 119 (4), 105 (4), 97 (3), 95 (7), 93 (3), 89 (15), 83 (8), 81 (10), 70 (3), 69 (8), 67 (3), 66 (3), 57 (12), 56 (51,  $\text{Fe}^+$ ). It is likely that the carboxylic acid decarboxylates partially upon heating in the probe of the spectrometer. IR (Nujol):  $\tilde{\nu}/\text{cm}^{-1}$  2204vs ( $\nu_{\text{C}\equiv\text{C}}$ ), 1667vs ( $\nu_{\text{C}=\text{O}}$ ). UV-vis (acetone):  $\lambda_{\text{max}}/\text{nm}$  454 ( $\epsilon$  not determined).

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