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First synthesis and spectroscopic characterization of isolated butatrienylidene complexes of transition metals

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Abstract

The complex $Cp^*Fe(dippe)Fe(C{\equiv}CC{\equiv}C)Fe(CO)_2Cp^*$ (**3b**, dippe = 1,2-bis(diisopropylphosphino)ethane, Cp* = pentamethylcyclopentadienyl) was prepared by activation of the terminal butadiyne $Cp^*(CO)_2FeC{\equiv}CC{\equiv}CH$ (**2**) with the chloro iron complex Cp*(dippe)FeCl (**1b**) in the presence of KPF_6 and $KOBu^t$. Treatment of $Cp^*(P_2)Fe((C{\equiv}CC{\equiv}C)Fe(CO)_2Cp^*$ (**3a**, P_2 = dppe, dppe = 1,2-bis(diphenylphosphinoethane); **3b**, P_2 = dippe) with $HBF_4 \cdot Et_2O$ produced the secondary iron butatrienylidene complexes $[Cp^*(P_2)Fe\{{=}C{=}C{=}C{=}C(H)Fe(CO)_2Cp^*\}][BF_4]$ (**4a**, P_2 = dppe, 75%; **4b**, P_2 = dippe, 93%). The slightly more stable tertiary butatrienylidene iron derivatives $[Cp^*(P_2)Fe\{{=}C{=}C{=}C{=}C(CH_3)Fe(CO)_2Cp^*\}][OSO_2CF_3]$ (**5a**, P_2 = dppe, 22%; **5b**, P_2 = dippe, 75%) were made by reacting the precursor complexes **3a**–**b** with methyl triflate under similar conditions. All the compounds **4a**–**b** and **5a**–**b** are almost stable in solution at 20°C. They are light and air sensitive, even in solid state. The solid samples can be stored under argon for few days in the dark at 5°C. The complexes **4a**–**b** and **5a**–**b** were characterized by multinuclear NMR, IR, UV–vis, and Mössbauer spectroscopies, mass spectrometry and cyclic voltammetry. Their electronic structures are discussed in connection with the spectroscopic data. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Organoiron(II); Iron; Butatrienylidene complex

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1. Introduction

A large variety of mononuclear transition metal complexes containing highly unsaturated carbon chains are known:

$[M]{=}(C)_xR_2$

The importance of metal stabilized carbene ($x = 1$), vinylidene ($x = 2$), and allenylidene ($x = 3$) complexes in organometallic chemistry, organic synthesis and catalysis is now well established and has been the subject of several reviews [1–6]. Complexes with pentatetraenylidene ($x = 5$) ligands coordinated to Ru [7], Ir [8], Cr, and W [9] centers were also synthesized. However, metal complexes containing a butatrienylidene ($x = 4$) ligand were never isolated or spectroscopically characterized. These compounds are usually reported to be reactive intermediates in different reactions. Thus, a ruthenium butatrienylidene was trapped as a trifluoroacetate adduct [10] whereas a wide variety of compounds were prepared by addition of protic and aprotic nucleophiles to such intermediates [11,12]. For instance, reactions of transient butatrienylidene derivatives with aromatic imines has allowed the access to complexes containing 1-azabuta-1,3-diene or ethynylquinoline ligands [13].

We have previously reported the synthesis and the physical properties of a 'D–C≡C–C≡C–A' carbon chain. The termini were an organometallic donor (D = Cp*(dppe)Fe) and an organometallic acceptor (A = $Cp^*(CO)_2Fe$) with quite different electronic densities. We have found that the electrochemical and spectroscopic properties of this molecular assembly are distinct from those of the individual organoiron building

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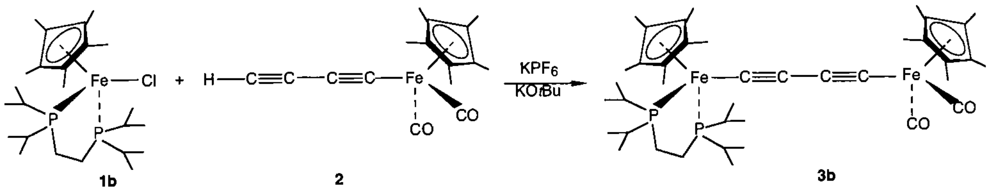


Scheme 1.

blocks. This establishes the key role played by the all-carbon spacer which acts as a polarized molecular wire [14,15]. We now report the reactivity of the $\mathrm{D{-}C{\equiv}C{-}C{\equiv}C{-}A}$ core ($\mathrm{D = Cp^*(dppe)Fe}$, $\mathrm{Cp^*(dippe)Fe}$ and $\mathrm{A = Cp^*(CO)_2Fe}$) towards different electrophiles ($\mathrm{HBF_4}$, $\mathrm{CH_3OSO_2CF_3}$) together with the synthesis, the isolation, and the characterization of the first thermally stable butatrienylidene complexes.

2. Results and discussion

*2.1. Synthesis and characterization of binuclear μ-butadiyndiyl complex $Cp^*(dippe)Fe(C{\equiv}CC{\equiv}C)Fe(CO)_2Cp^*$ (**3b**)*

Complex **3b** was prepared by activation of the terminal butadiyne $\mathrm{Cp^*(CO)_2FeC{\equiv}CC{\equiv}CH}$ (**2**) with the chloro iron complex $\mathrm{Cp^*(dippe)FeCl}$ (**1b**) in the presence of $\mathrm{KPF_6}$ and $\mathrm{KOBu^t}$ following the procedure previously described for $\mathrm{Cp^*(dppe)Fe(C{\equiv}CC{\equiv}C)Fe(CO)_2Cp^*}$ (**3a**, Scheme 1) [14]. The binuclear complex **3b** was isolated as a red powder after recrystallization from pentane at −20°C in a 77% yield. Interestingly, similar reactions of the trimethylsilylbutadiyne or the bis(trimethylsilyl)butadiyne with $\mathrm{Cp^*(dppe)FeCl}$ (**1a**) did not afford the mononuclear complex $\mathrm{Cp^*(dppe)FeC{\equiv}C{-}C{\equiv}CR}$ ($\mathrm{R = H}$, or $\mathrm{SiMe_3}$) but the binuclear symmetric compound $\mathrm{Cp^*(dppe)FeC{\equiv}C{-}C{\equiv}CFe(dppe)Cp^*}$. This latter complex was also at the origin of very interesting properties [16]. The second activation of a σ-metallated butadiynyl ligand is a very favored reaction. On the other hand, our attempts to isolate a monometallated precursor in the absence of base were not successful either. The reaction of the chloro complex **1a** with $\mathrm{Me_3SiC{\equiv}CC{\equiv}CH}$ under neutral conditions produces the allenylidene complex $\mathrm{[Cp^*(dppe)Fe({=}C{=}C{=}C(OCH_3)CH_3][BPh_4]}$ (**6**) which results from an addition of methanol to the putative butatrienylidene intermediate $\mathrm{[Cp^*(dppe)Fe({=}C{=}C{=}C{=}CH_2)][BPh_4]}$ [17].

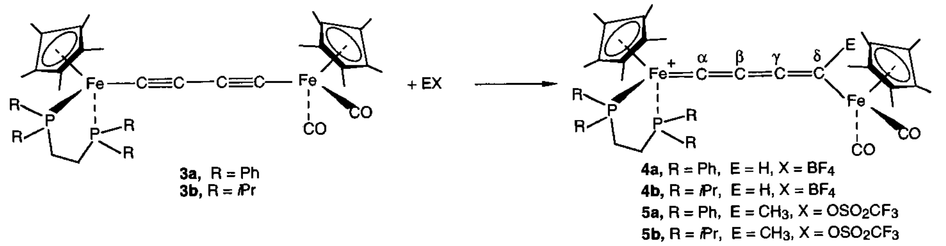
*2.2. Synthesis of the butatrienylidene complexes $[Cp^*(P_2)Fe\{{=}C{=}C{=}C{=}C(E)Fe(CO)_2Cp^*\}][BF_4]$ ($P_2 = dppe$, $E = H$, **4a**; $P_2 = dippe$, $E = H$, **4b**; $P_2 = dppe$, $E = CH_3$, **5a**; $P_2 = dippe$, $E = CH_3$, **5b**)*

Treatment of a dichloromethane solution of **3a** [14] with a diethylether solution of $\mathrm{HBF_4 \cdot Et_2O}$ immediately darkens the initially ruby-red solution from which a precipitate can be recovered by addition of *n*-pentane. After removal of the supernatant liquor, the solid was washed with diethylether. Compound **4a** was isolated in a 75% yield as purple powder and identified as iron butatrienylidene complex $\mathrm{[Cp^*(P_2)Fe\{{=}C{=}C{=}C{=}C(H)Fe(CO)_2Cp^*\}][BF_4]}$ (Scheme 2). Complex **4b** was prepared in a similar way using diethylether as solvent. Both compounds **4a** and **4b** are unstable and light sensitive in solution at 20°C. They are also very air and moisture sensitive even in solid state. Nevertheless, the solid samples can be stored for few weeks in the dark at 5°C. Complexes **4a**–**b** were characterized by NMR, IR, UV–vis, and Mössbauer spectroscopies, mass spectrometry and cyclic voltammetry. Attempts to grow crystals and to prepare analytically pure samples were unsuccessful due to the slow but unavoidable decomposition of these compounds in solution even at low temperature.

In order to gain more information from an analog likely to be more stable, synthesis of the tertiary butatrienylidene iron derivatives, $\mathrm{[Cp^*(P_2)Fe\{{=}C{=}C{=}C{=}C(CH_3)Fe(CO)_2Cp^*\}][OSO_2CF_3]}$ (**5a**–**b**) was undertaken. These complexes were made by methylation of the precursors **3a**–**b**, using methyl triflate as the electrophilic reagent. Whereas **5b** was obtained easily in $\mathrm{Et_2O}$, the complex in the dppe series **5a** was quite difficult to recover from the reaction medium. The microcrystalline solid went partly through the glass and paper filters used. The complexes **5a** and **5b** appear slightly more stable in solution and less moisture sensitive than the secondary butatrienylidene **4a** and **4b**. However, attempts to grow crystals from dichloromethane/pentane or THF/pentane mixtures (at 5°C in dark) also failed, with only decomposition materials being recovered.

*2.3. IR and NMR characterization of the butatrienylidene complexes $[Cp^*(P_2)Fe\{{=}C{=}C{=}C{=}C(E)Fe(CO)_2Cp^*\}][BF_4]$ ($P_2 = dppe$, $E = H$, **4a**; $P_2 = dippe$, $E = H$, **4b**; $P_2 = dppe$, $E = CH_3$, **5a**; $P_2 = dippe$, $E = CH_3$, **5b**)*

Comparison of the IR spectra of **3a**–**b** with those of the corresponding cationic complexes **4a**–**b** and **5a**–**b**



3a, R = Ph
3b, R = *i*Pr

4a, R = Ph, E = H, X = BF_4
4b, R = *i*Pr, E = H, X = BF_4
5a, R = Ph, E = CH_3, X = OSO_2CF_3
5b, R = *i*Pr, E = CH_3, X = OSO_2CF_3

Scheme 2.

reveals a weak decrease of the two ν_{CO} frequencies (ca. 3–15 cm^{-1}). Thus, the electron density on the Cp*Fe(CO)$_2$ moiety decreases slightly, but the frequency is still suggestive of a neutral iron(II) center. The IR bands corresponding to the butatrienylidene stretch are difficult to assign with certainty. A vibration mode is observed in the IR spectrum of these compounds at (ν, cm^{-1}, Nujol) 1952, 1945, 1942, 1946 for **4a**, **4b**, **5a**, and **5b**, respectively. The position of this band is quite close to that of the $\nu_{C=C=C}$ observed for the metal–allenylidene complexes [3]. This band is not present in the spectra of **3a**–**b** and could be attributed to C=C band stretching of the butatrienylidene. However, in the dppe series, the spectra display other absorption bands at {ν, cm^{-1}, Nujol (CH_2Cl_2)} 1776 (1892, 1905) and 1830, 1882 (1863, 1882) for **4a** and **4b**, respectively. Similar bands were not observed in the spectra of the corresponding complexes of the dippe series, but it cannot be excluded that these bands also originate from another vibration mode of the butatrienylidene ligand. At this point, it is also important to emphasize the absence of a band in the 1500–1650 cm^{-1} range. This allows us to exclude the presence of an ethynylvinylidene bridge between the iron centers (vide infra).

The ^{13}C-NMR resonances of the –C_4– chain were easily observed, and are quite similar for the four butatrienylidene iron complexes (Table 1). The carbon resonances are downfield shifted when the dppe ligand is replaced by the dippe. Moreover, all the resonances of the –C_4– spacer are less shifted for the tertiary butatrienylidene group than for the secondary one. In the complexes **4a** and **4b**, the four resonances of the carbon chain were assigned making the assumption that C_α would have the lowest field shift and the chemical shifts of the carbon atoms would gradually move upfield as one moves along the chain and on the basis of the J_{CP} and J_{CH} coupling constants. Note that only the $^2J_{CP}$ coupling was observed whereas the $^1J_{CH}$, $^2J_{CH}$, and $^3J_{CH}$ were clearly visible in the ^{13}C-NMR spectra of **4a** and **4b**. The difference between the $^2J_{CH}$ and $^3J_{CH}$ coupling constants is small, therefore the C_β and C_γ resonances cannot be definitely assigned.

Table 1
^{13}C-NMR chemical shifts (ppm), coupling constants (Hz) for the butatrienylidene ligands

Compound (solvent, T °C)	C_α	C_β	C_γ	C_δ
4a	258.7	167.4	128.3	58.4
($CDCl_3$, 20)	$^2J_{CP} = 36$	$^3J_{CH} = 8.1$	$^2J_{CH} = 8.4$	$^1J_{CH} = 180.2$
4b	260.8	170.9	133.3	59.0
(CD_2Cl_2, −40)	$^2J_{CP} = 34.8$	$^3J_{CH} = 5.7$	$^2J_{CH} = 6.0$	$^1J_{CH} = 176.6$
5a	250.5	149.8	121.6	69.3
($CDCl_3$, 20)	$^2J_{CP} = 35$			$^2J_{CH} = 18$
5b	264.9	166.2	131.9	73.6
(Acetone, −40)	$^2J_{CP} = 36$	$^4J_{CH} = 6.5$	$^3J_{CP} = 2.4$	$^2J_{CH} = 7.8$

Assignment of the carbon resonances for the methylbutatrienylidene ligands are achieved on the basis of the $^2J_{CH}$ which indicates that the methyl group is bound to the C_δ atom. The C_β and C_γ resonances of **5a** and **5b** were assigned by analogy to the compounds **4a** and **4b**. The C_α, C_β, and C_γ resonances of the butatrienylidene are upfield shifted relative to the corresponding resonances of butadiynediyl bridge in the binuclear precursors **3a** and **3b** [14]. In contrast, and in agreement with its sp^2 hybridization, the C_δ is downfield shifted with respect to **4a** and **4b**.

2.4. Mössbauer characterization of the butatrienylidene complexes

The Mössbauer spectra of microcrystalline samples of the iron complexes **3a**, **4a**, **5a** and **5b** are characteristic of pure bis(iron) complexes with two different environments around the metal centers. As depicted (Fig. 1) for complex **4a**, the experimental Mössbauer spectra of these compounds display two quadrupole doublets. Assuming that the two doublets have the same surface, a single set of fitting parameters was obtained (Table 2). The doublet with the larger isomeric shift, δ, was assigned to the Cp*Fe(P$_2$) iron center. Indeed, larger δ values were invariably observed in this series, either for neutral or cationic mononuclear complexes, than in the Cp*Fe(CO)$_2$ series [17]. Moreover, the isomeric shift of the Cp*Fe(P$_2$) unit in the butatrienylidene complexes is smaller than the value determined for the same iron unit in the neutral complex **3a**. As δ is generally related to the electronic density on the metal center, this obser-

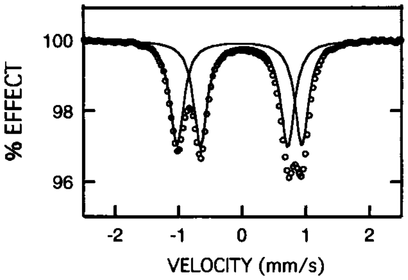


Fig. 1. Mössbauer spectrum of **4a** at 80 K.

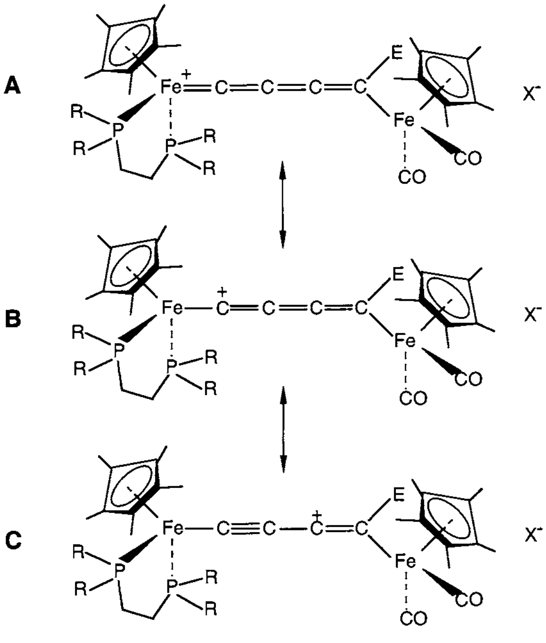
vation is strongly indicative of the localization of the positive charge on the Cp*Fe(P_2) fragment in **4** and **5**.

On the other hand, the Mössbauer parameters of the Cp*Fe$(CO)_2$ group in the butatrienylidene complexes are characteristic of the Fp* fragment and compare very well with those of the complex Cp*Fe$(CO)_2$Me taken as a reference compound [18]. The parameters determined for the Cp*Fe(P_2) moiety are quite close to those previously obtained for the allenylidene [Cp*(dppe)Fe{=C=C=C(OCH_3)CH_3}][BPh_4] (**6**) in the same iron series. In the Cp*Fe(dppe)L series, we have found that a quadrupole splitting in the range 1.0–1.5 is diagnostic of an iron–carbon double bond between the metal and the terminal sp hybridized carbon atom of the ligand L. Moreover, we observed that the larger the quadrupole separation is, the weaker the strength of the iron–carbon π-bond will be [17]. Accordingly, the decrease of ΔE_Q from **5a** to **5b** constitutes an indication of the increase of the bond order between the iron and the carbon ligand concomitantly with the electron releasing properties of the coordinated organometallic. Note that significantly smaller ΔE_Q were found for the stable vinylidene complexes in the same series [17]. Finally, since most of the organometallic fragments are less electron rich than the Cp*Fe(P_2) group, they possibly coordinate butatrienylidene ligands less strongly, and consequently the C_4 ligand may be more reactive (see below).

Table 2
^{57}Fe Mössbauer fitting parameters determined at 80 K for compounds **3–5**

Compound	Cp*Fe(P_2)		Cp*Fe$(CO)_2$	
	δ (mm s^{-1})	ΔE_Q (mm s^{-1})	δ (mm s^{-1})	ΔE_Q (mm s^{-1})
3a[a]	0.257	1.973	0.029	1.974
4a	0.161	1.316	0.087	1.888
5a	0.163	1.424	0.103	1.786
5b	0.170	1.264	0.094	1.778
6[b]	0.160	1.451		
Fp*CH_3[c]			0.120	1.88

[a] From Ref. [14].
[b] From Ref. [17].
[c] From Ref. [18].



Scheme 3.

Comparison of the spectroscopic data of the butatrienylidene with those of allenylidene transition metal complexes for which both X-ray and spectroscopic data are available, is instructive. Several studies suggested that there is a significant contribution to electron distribution from two mesomeric forms: $[M{=}C{=}C{=}CR_2]^+$ and $[M{-}C{\equiv}C{-}CR_2]^+$ [11,19,20]. Thus, the electron delocalization for the butatrienylidene derivatives **4** and **5** can be depicted by the three resonance structures **A**, **B** and **C** of Scheme 3. These were previously proposed to account for the reactivity of related compounds as intermediates [13]. In agreement with a relatively weak Fe=C π-bond suggested by the Mössbauer quadrupole splitting parameters, a significant contribution of the forms **B** and **C** in the description of the electron delocalization for the butatrienylidene complexes appears plausible. It is noteworthy that the ^{13}C chemical shifts of the butatrienylidene fragment compare well with those of the hetero allenylidene **6** and other allenylidenes reported from other groups [11,17,21]. Such a comparison between allenylidene and butatrienylidene complexes has however to be regarded with caution since these two kinds of compounds have different stabilities. It has been pointed out, from X-ray data for purely organic molecules, that there is a clear difference between cumulenes with even and odd numbers of double bonds. In both cases some triple bond character was observed for internal bonds [22].

2.5. UV–vis absorption of the complexes **4a–b** and **5a–b**

All the new compounds show a deep purple color that has no counterpart in the corresponding monometallic species. For example alkynyl and butadiynyl complexes show only an intense UV absorption that tails into the visible and accounts for the orange color of these complexes [23]. The visible spectra of the butatrienylidene compounds show a characteristic absorption at (λ, nm; $\varepsilon/10^3$, M^{-1} cm^{-1}) 527 (15.5), 546 (15.6), and 538 (13.6) for **4a**, **5a**, **5b**, respectively. Due to the high sensitivity of these compounds to light, air and moisture, the real values of the molecular extinction coefficient ε are certainly higher than the determined values. Indeed, the intensity of the absorption band decreases during the measurement and concomitantly a new absorption band appears in the red (Fig. 2). The evolution is particularly fast for the secondary iron butatrienylidene complexes **4a–b**. In the Schlenk cell, the disappearance of the spectrum of **3a** is complete in ca. 30 min and the final spectrum corresponds to a mixture of unidentified species. In the initial spectrum of **4a**, the mixed valence complex $[Cp^*(dppe)Fe{-}C{\equiv}C{-}C{\equiv}C{-}Fe(CO)_2Cp^*][PF_6]$ (**3a**+) is clearly detected (see Fig. 2 and Section 2.6). The solvent effects were probed with **4a** as a representative complex in this series (λ, nm; toluene/CH_2Cl_2/acetonitrile; 528/527/524). The position of the maxima varied only very slightly with polarity indicating similar ground and excited state polarities. Some allenylidene and related complexes are also intensely colored with a strong absoptions in the 500–600 nm region assigned to charge-transfer bands [24]. In our series of iron butatrienylidene complexes, the optical transition centered in the 520–550 nm range would be consistent with charge transfer from an iron (of the Cp*(dppe)Fe unit) based orbital.

2.6. Acidic and redox properties of the butrienylidene iron complexes **4a–b** and **5a–b**

In order to gain information on the acidity of the hydrogen atom on C_δ of the butatrienylidene ligand, **4a** was reacted with one equivalent of DBU at −80°C in THF. After 15 min of reaction, the dimetallabutadiynediyl complex **3a** was almost quantitatively recovered and identified by ^{1}H-NMR, IR and cyclic voltammetry (CV). The facile deprotonation of **4a** indicates that the butatrienylidene complexes should be more acidic than the corresponding allenylidene described as resistant to deprotonation in the Ru series [21]. More surprisingly, we found by CV that **4a** is partly deprotonated by water.

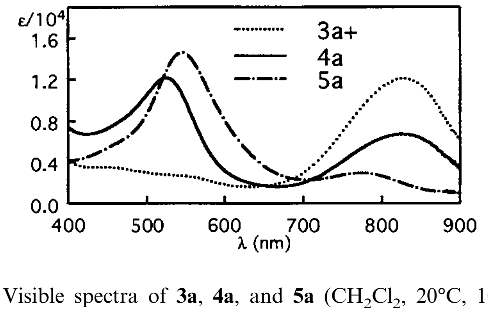


Fig. 2. Visible spectra of **3a**, **4a**, and **5a** (CH_2Cl_2, 20°C, 10^{-4} M).

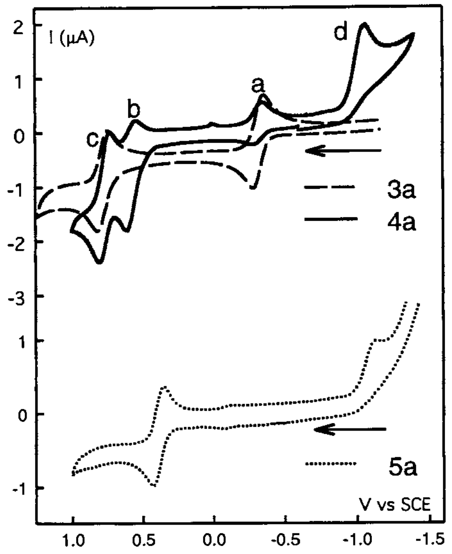
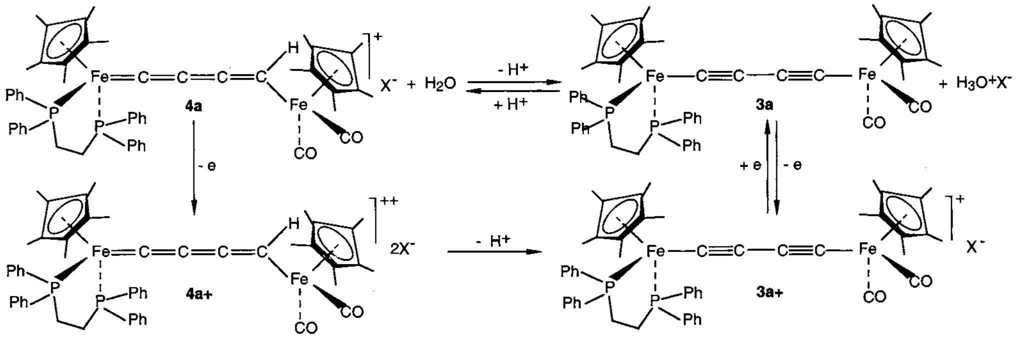


Fig. 3. Cyclic voltammograms for **3a**, **4a**, and **5a** in 0.1 M $[nBu_4N][PF_6]/CH_2Cl_2$ (Pt electrode, V vs. SCE, scan rate 0.100 V s^{-1}).

The initial scans in the CV of the complex **4a** between 1.0 and −1.5 V at a platinum electrode (dichloromethane, 0.1 M tetrabutylammonium hexafluorophosphate, 0.100 V s^{-1}, 20°C, Fig. 3) display a complex behavior corresponding to the presence of both the complexes **3a** and **4a** in the electrochemical cell (Scheme 4). Starting from −0.600 V the oxidation waves **a** and **c** belong to the redox couple **3a**/**3a**+ and **3a**+/**3a**++, respectively, as previously described [14]. The waves **b** and **d** are characteristic of the butatrienylidene complex **4a**. The surprising formation of **3a** in the electrochemical cell is attributed to the reaction of **4a** with adventitious traces of water. This assumption was confirmed by addition of small amounts of water which produced the decrease in the current corresponding to the waves **b** and **d** and, conversely, the increase of the waves **a** and **c**. Addition of a base like DBU or NEt_3 in the cell also produced the total disparition of the waves **b** and **d**. An irreversible reduction of **4a** is also observed on the CV (Fig. 3, Table 3) in addition to the reversible oxidation of **4a**.

In the case of **4b**, the CV displays a similar behavior with a shift of the potential towards the negative values (Table 3). The deprotonation of the butatrienylidene complex **4b** by water is more difficult and the wave **a** is



Scheme 4.

Table 3
Electrochemical data for compounds **3–5**, in CH_2Cl_2 (0.1 M $[nBu_4N][PF_6]$; 20°C; Pt electrode; sweep rate 0.100 V s^{-1})[a]

Compound	$E_0{}^{\#}$	ΔE_p	i^c/i^a
3a[b]	−0.36	0.07	1
	+0.74	0.07	0.9
3b	−0.53	0.06	1
	+0.69	0.06	1
4a	−1.13		NR
	+0.40	0.07	1
4b	−0.88		NR
	0.35	0.09	0.9
5a	−1.13		
	+0.40	0.07	1
5b	[c]		
	+0.28	0.08	1

[a] V versus SCE, ferrocene–ferrocenium couple (0.460 V/SCE) was used as an internal reference for the potential measurements.

[b] From Ref. [14].

[c] Reduction wave not observed.

[#] For the non reversible systems the peak potential is reported instead of the E_0 value.

not clearly observed in the initial scan. The water seems not to be a strong enough base to deprotonate this complex. However, in the reverse reduction and in the following scans, the wave **a** is present in the voltammogram. For both complexes **4a** and **4b**, we found that the current ratio i^c/i^a for the waves **a** is always above unity and increases with the scan rate. This result indicates that the radical dication **4a** $++^{\bullet}$ and **4b** $++^{\bullet}$ decompose in **3a** + and **3b** +, respectively, by spontaneous loss of a proton (Scheme 4). The CVs of the tertiary butatrienylidene complexes **5a** and **5b** display a reversible one-electron oxidation process and an irreversible reduction process (Fig. 1).

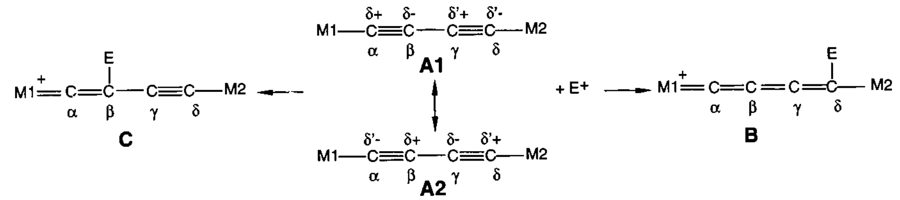
3. Conclusions

Theoretical calculations on unsaturated carbon chains σ-bound to transition metals indicates that the carbon atoms are alternatively electron-poor and electron-rich as one moves along the chain from the metal atom [24,25]. Considering a polyyne with two different organometallic building blocks σ-bound at both ends there are formally two different electronic structures for the carbon chain (**A1**, **A2**, Scheme 5). The terminal electron-poor and electron-rich carbon could be connected either to the more or the less electron releasing metal centers. From this work, it is strongly suggested that the most electron rich terminal carbon atom is bound to the electron poor metal center and conversely, the most electron poor one is connected to the most electron-rich iron atom (structure A1). A steric control of the reaction cannot definitely be excluded, however we think this alternative unlikely, especially for the protonation reaction in the dippe series.

The reaction is highly specific since only the butatrienylidene compounds were observed even after analysis of the isolated crude materials. We have no experimental evidence to know whether the isolated material is the kinetic or the thermodynamic product of the reaction. In fact, both molecules **C** and **B** should have almost the same stability, as was shown by ab initio calculations for the related ligands :C=CHC≡CH and :C=C=C=CH_2 [26].

From a molecular electronics point of view the reactions depicted in Scheme 4 are relevant from the concept of molecular switches [27–29]. Indeed, the study of physical properties of the mixed-valence complex **3a** + allowed evidence that this molecule acts as a wire [14]. The reduction of **3a** + followed by its protonation switches off the electronic exchange between the remote ends and also locks it chemically. Thus this communication can be restored either by the reverse operations, i.e. chemical deprotonation and one-electron oxidation at the same potential, or by another one-electron oxidation at a more positive potential, producing a spontaneous deprotonation to give back **3a** +.

In a related and simultaneous work, we have found that the formally cumulene complex [Cp*(dppe)-Fe=C=C=C=C=Fe(dppe)Cp*]$[PF_6]_2$ is in thermal equilibrium with the paramagnetic diradical form [Cp*-(dppe)$Fe^{\bullet}-C\equiv C-C\equiv C-{}^{\bullet}Fe$(dppe)Cp*]$[PF_6]_2$ [16,30].



Scheme 5.

The energy gap between the diamagnetic ground state and the ferromagnetic excited state is small enough to render the complex paramagnetic at liquid nitrogen temperature. At that time, we were curious about the spectroscopic properties of the iron complexes with non ambiguous metal–butatrienylidene structure. In this respect, this work contributes greatly to our knowledge of such carbon rich bridges. In particular, it is now more and more clear that the {Fe$^{\bullet}$–C≡C–C≡C–$^{\bullet}$Fe}$^{++}$ and {Fe=C=C=C=C=C=C=C=Fe}$^{++}$ might be distinguished from their Mössbauer quadrupole splittings. This point is of importance, since a cumulenic structure was found for the related rhenium complex [31]. Current work is now underway in order to control the magnetic properties of these molecules and their evolution either upon bridge extension or upon tuning of electronic properties of the terminal ends.

4. Experimental

4.1. *General data*

Reagent grade THF, diethylether and *n*-pentane were dried and distilled from sodium benzophenone ketyl prior to use. Pentamethylcyclopentadiene was prepared according to the published procedure [32] and other chemicals were used as received. All the manipulations were carried out under an argon atmosphere using Schlenk techniques or in a Jacomex 532 dry box under nitrogen. The FTIR spectra were recorded using Nicolet instrument (Model 205) and KBr windows. High field NMR spectra experiments were performed on a multinuclear Bruker 300 MHz instrument (AM300WB). Chemical shifts are given in ppm relative to TMS for ^{1}H- and ^{13}C-NMR spectra, H_3PO_4 for ^{31}P-NMR spectra. Elemental analyses were performed at the Center for Microanalyses of the CNRS at Lyon-Solaise, France. Mössbauer spectra were recorded with a 2.5×10^{-2} C (9.25×10^{8} Bq) ^{57}Co source using a symmetric triangular sweep mode.

4.2. Cp*(dippe)Fe(C≡C–C≡C)Fe(CO)$_2$Cp* (**3b**)

To a solution of 0.260 g Cp*Fe(CO)$_2$(C≡C–C≡CH) (0.88 mmol) in MeOH (50 ml) at −80°C was added successively 0.440 g of Cp*Fe(dippe)Cl (0.88 mmol), 0.194 g of KPF_6 (1.056 mmol) and 0.120 g of *t*BuOK (1.056 mmol). The mixture was stirred overnight and allowed to warm up to room temperature. After removal of the solvent under vacuum, the crude residue was extracted with pentane (2 × 25 ml). Crystallization from cold pentane (−20°C) yielded a red powder which was identified as Cp*(dippe)Fe(C≡C–C≡C)Fe(CO)$_2$Cp* (0.507 g, 0.67 mmol, 77%). Anal. Calc. for $C_{40}H_{62}P_2O_2Fe_2$: C, 64.18, H, 8.35, P, 8.3. Found: C, 64.36, H, 8.31, P, 8.0. FTIR (Nujol, cm^{-1}): 2112(w, $\upsilon_{C\equiv C}$), 2019,1969 (vs, υ_{CO}). ^{1}H-NMR: (300 MHz, C_6D_6, 25°C): $\delta_H = 3.08$, 2.08 (m, 2 × 2H, CH isopropyl); 1.75 (m, 4H, CH_2); 1.75 (s, 15H, [Fe(C_5*Me*$_5$)(dippe)]); 1.49 (s, 15H, [Fe(C_5*Me*$_5$)(CO)$_2$]); 1.44, 1.25 and 0.92, 1.05 (m, 2 × 12H, CH_3 isopropyl). ^{13}C-NMR {^{1}H} (75 MHz, C_6D_6, 25°C): $\delta_C = 216.0$ (s, CO); 111.7 (t, C_α, $^2J_{CP} = 39$ Hz); 106.5 (t, C_β, $^3J_{CP} = 2$ Hz); 102.5 (t, C_γ, $^4J_{CP} = 2$ Hz); 65.0 (s, C_δ); 96.5 (s, [Fe(*C*$_5$Me$_5$)(CO)$_2$]); 85.9 (s, [Fe(*C*$_5$Me$_5$)(dippe)]); 27.4, 25.5 (m, CH isopropyl); 22.0, 19.9 and 21.1, 19.2 (m, CH_3 isopropyl); 19.6 (m, CH_2–P); 11.6 (q, [Fe(*C*$_5$Me$_5$)(CO)$_2$]); 9.74 (m, [Fe(*C*$_5$Me$_5$)(dippe)]). ^{31}P-NMR (121.5 MHz, C_6D_6, 25°C): $\delta_P = 98.9$ (s).

4.3. [Cp*(dppe)Fe{=C=C=C=C=(H)Fe(CO)$_2$Cp*}][OTf] (**4a**)

Complex **3a** (0.270 g, 0.30 mmol) was dissolved in dichloromethane (20 ml, −70°C). To this cold solution 48 µl of a commercial solution of $HBF_4\cdot Et_2O$ 85% in diethylether (0.27 mmol) was added under argon and the reaction medium was allowed to come back to −20°C with stirring over 1 h. The purple solution was subsequently concentrated (5 ml) and an excess of *n*-pentane was added to precipitate the complex **4a** as a purple powder, which was washed with several fractions of 10 ml diethylether and dried in vacuo to give 0.210 g of [{Fe(η^5-C_5Me_5)(η^2-dppe)}(μ^2=C=C=C=CH)-{Fe(η^5-C_5Me_5)(CO)$_2$}][BF$_4$] (75%). FTIR (KBr/Nujol, cm^{-1}) *v* 2015, 1966 (s, CO); 1952, 1882, 1830 (w, C=C=C); 1052 (vs, BF_4^-). (KBr/CH_2Cl_2, cm^{-1}) *v* 2015, 1964 (s, CO); 1882, 1863 (w, C=C=C), 1060 (vs, s, BF_4^-). ^{31}P-NMR (121 MHz, $CDCl_3$, 20°C) $\delta_P = 94.4$ (s, dppe). ^{19}F-NMR (188 MHz, $CDCl_3$) $\delta_F = -154.8$ (s, BF_4^-). ^{1}H-NMR (300 MHz, $CDCl_3$, 20°C) δ_H 7.60–7.10 (m, 20H, *Ph*); 3.86 (s, 1H, C_d*H*–); 2.90; 2.55 (2m, 4H, C*H*$_{2(dppe)}$); 1.72 (s, 15H, {(C_5*Me*$_5$)Fe(dppe)}); 1.42

(s, 15H, $\{(C_5Me_5)Fe(CO)_2\}$). ^{13}C-NMR (75 MHz, $CDCl_3$, −40°C) δ_C 258.7 (t, $^2J_{CP}=36$ Hz, C_α); 215.5 (s, CO); 167.5 (s, $^3J_{CH}=8.1$, C_β); 135.0–133.1 (m, C_{ipso}, *Ph*); 133.6 (m, C_{ortho}, *Ph*); 131.3 (d, $^3J_{CP}=26$ Hz, C_{meta}, *Ph*); 128.8 (s, C_{para}, *Ph*); 128.5 (s, $^2J_{CH}=168.4$, C_γ); 97.2 (s, $\{(C_5Me_5)Fe(CO)_2\}$); 97.0 (s, $\{(C_5Me_5)Fe(dppe)\}$); 58.6 (s, $^1J_{CH}=183$ Hz, C_δ); 30.9 (m, CH_2); 10.0 (q, $^1J_{CH}=128$ Hz, $\{(C_5Me_5)Fe(dppe)\}$ and $\{(C_5Me_5)Fe(CO)_2\}$). UV–vis (CH_2Cl_2) λ_{max} (ε dm^3 M^{-1} cm^{-1}) 526 nm (≥ 15200). MS (FAB$^+$, *m*-NBA) *m*/*z* 885 ($M-BF_4^-$, 70%); 828 ($M-\{BF_4+H+2CO\}$, 35%); 638 ($M-\{BF_4+Fp\}$, 30%); 589 ($M-\{BF_4+H+C{\equiv}CC{\equiv}C-Fp\}$, 100%).

4.4. [Cp(dippe)Fe{=C=C=C=C(Me)Fe(CO)$_2$Cp*}][BF$_4$] (**4b**)*

To a −60°C solution of **3b** (0.446 g, 0.59 mmol) in diethylether (20 ml), were added 111 µl of $HBF_4\cdot Et_2O$ (0.65 mmol) and the solution was allowed to warm up to 20°C upon stirring (1 h). After additon of pentane (75 ml), the solution was removed and the precipitate washed with pentane (2 × 20 ml). Complex **4b** was isolated as a pink powder (0.460 g, 93%). FTIR (Nujol, cm^{-1}): 2003, 1962 (vs, υ_{CO}), 1945 (w, $\upsilon_{C=C=C}$). ^{1}H-NMR (300 MHz, CD_2Cl_2, −40°C) δ_H 3.54 (s, C=C*H*); 1.71 (s, 15H, $(C_5Me_5)Fe(dippe)$); 1.65 (s, 15H, $(C_5Me_5)Fe(CO)_2$); 1.40–1.02 (m, isopropyl). ^{13}C-NMR (75 MHz, CD_2Cl_2, −40°C) $\delta_C=260.8$ (t, C_α, $^2J_{CP}=34.8$ Hz); 216.5 (s, CO); 170.9 (d, C_β, $^3J_{CH}=5.7$ Hz); 133.3 (d, C_γ, $^2J_{CH}=6$ Hz); 97.2 (s, $[(C_5Me_5)Fe(CO)_2]$); 96.9 (s, $[(C_5Me_5)Fe(dippe)]$); 59.0 (d, C_δ, $^1J_{CH}=176.6$ Hz); 29.5, 25.1 (m, CH isopropyl); 22.0, 19.5, 19.0, 18.8 (m, CH_3 isopropyl); 10.3 (q, $[(C_5Me_5)Fe(CO)_2]$, $^1J_{CH}=127$ Hz); 9.9 (s, $[(C_5Me_5)Fe(dippe)]$, $^1J_{CH}=128$ Hz). ^{31}P-NMR (121.5 MHz, CD_2Cl_2, −40°C, H_3PO_4 ext): $\delta_P=94.3$ (s, dippe).

4.5. [Cp(dppe)Fe{=C=C=C=C(Me)Fe(CO)$_2$Cp*}]-[OSO$_2$CF$_3$] (**5a**)*

Complex **3a** (0.270 g, 0.97 mmol) was dissolved in dichloromethane (20 ml) and the solution was cooled to −70°C. To this solution 30 µl of methyl triflate (0.28 mmol) were added and the reaction medium was allowed to come back to −20°C upon stirring over 1 h. The ruby-red color of the reaction medium darkens upon addition. The purple solution was subsequently concentrated (5 ml) and an excess of *n*-pentane was added to precipitate the complex **5a** as a purple powder, which was washed with two fractions of 5 ml diethylether and dried in vacuo to give 0.070 g of **5a** (22%). FTIR (KBr/Nujol, cm^{-1}) ν 2015, 1949 (s, CO); 1942, 1905, 1892 (w, C=C=C). IR (KBr/CH_2Cl_2, cm^{-1}) ν 2016, 1964 (s, CO); 1949 (w, C=C=C). ^{31}P-NMR (121 MHz, $CDCl_3$, 20°C) $\delta_P=95.2$ (s, dppe). ^{19}F-NMR (188 MHz, $CDCl_3$, 20°C) $\delta_F=-78.2$ (s, $CF_3(O)_2SO^-$). ^{1}H-NMR (300 MHz, $CDCl_3$, 20°C) δ_H 7.60–7.10 (m, 20H, *Ph*); 2.95; 2.55 (2m, 4H, $CH_{2(dppe)}$); 2.07 (s, 3H, $=C{=}C(CH_3)-Fe$); 1.62 (s, 15H, $(C_5Me_5)Fe(dppe)$); 1.42 (s, 15H, $(C_5Me_5)Fe(CO)_2$). ^{13}C-NMR (75 MHz, $CDCl_3$) δ_C 250.5 (t, $^2J_{CP}=35$ Hz, C_α); 215.1 (s, CO); 149.8 (s, C_β); 136.1–128.6 (m, Ph_{dppe}); 121.5 (q, $^1J_{CF}=321$ Hz, $CF_3S(O)_2O^-$ and Ph_{dppe}); 121.6 (q, $^3J_{CH}=7$ Hz, C_γ); 97.9 (s, $(C_5Me_5)Fe(CO)_2$); 96.4 (s, $(C_5Me_5)Fe(dppe)$); 69.3 (s, $^2J_{CH}=183$ Hz, $C_\delta(Me)$); 31.0 (m, CH_2); 16.5 (q, $^1J_{CH}=127$ Hz, $=C{=}C{=}C{=}C(Me)-$); 10.2 (q, $^1J_{CH}=127$ Hz, $(C_5Me_5)Fe(dppe)$); 9.8 (q, $^1J_{CH}=128$ Hz, $(C_5Me_5)Fe(CO)_2\}$). UV–vis (CH_2Cl_2) λ_{max} (ε dm^3 M^{-1} cm^{-1}) 546 nm (≥ 15540). MS (FAB$^+$, *m*-NBA) *m*/*z*, 889.3 ($M-\{CF_3S(O_2)O^-\}$), 652.2 ($M-\{CF_3S(O_2)O^-\}-\{Cp^*Fe(CO)_2\}$), 589.0 ($Cp^*Fe(dppe)^+$).

4.6. [Cp(dippe)Fe{=C=C=C=C(Me)Fe(CO)$_2$Cp*}]-[OSO$_2$F$_3$] (**5b**)*

To a −80°C diethyl ether solution (20 ml) of **3b** (0.360 g, 0.48 mmol) 59.8 µl (0.53 mmol) of $MeOSO_2CF_3$ were added and the solution was allowed to warm up upon stirring. A pink suspension was formed at −60°C, but the compound essentially remained in solution. An excess of pentane (100 ml) was added at 20°C to precipitate the salt. After filtration a purple powder was obtained and washed twice with pentane (20 ml) to give 0.330 g of **5b** (75%). FTIR (Nujol, cm^{-1}): 2004, 1957 (υ_{CO}), 1946 ($\upsilon_{C=C=C}$). ^{1}H-NMR (300 MHz, C_3D_6O, −40°C) δ_H 2.09 (s, 3H, *Me*–C=C); 1.85 (s, 15H, $(C_5Me_5)Fe(dippe)$); 1.77 (s, 15H, $(C_5Me_5)Fe(CO)_2$); 1.06–1.50 (m, dippe). ^{13}C-NMR (75 MHz, C_3D_6O, −40°C): $\delta_C=264.9$ (t, C_α, $^2J_{CP}=35.8$ Hz); 217.0 (s, CO); 166.2 (tq, C_β, $^3J_{CP}=2.4$ Hz, $^4J_{CH}=6.5$ Hz); 131.9 (s, C_γ); 98.4 (s, $[(C_5Me_5)Fe(CO)_2]$); 96.9 ($[(C_5Me_5)Fe(dippe)]$); 73.6 (q, C_δ, $^2J_{CH}=7.8$ Hz); 29.5, 25.6 (m, CH isopropyl, $^1J_{CP}=5.7$ Hz); 22.6 (q, CH_3, $^1J_{CH}=128$ Hz); 20.0, 19.5, 18.9, 18,7 (m, CH_3 isopropyl); 19.7, 19.2 (m, CH_2–P); 10.9 (q, $[(C_5Me_5)Fe(CO)_2]$, $^1J_{CH}=127$ Hz); 9.9 (q, $[(C_5Me_5)Fe(dippe)]$, $^1J_{CH}=128$ Hz). ^{31}P-NMR (121.5 MHz, C_3D_6O, −40°C): $\delta_P=95.2$ (s, dippe).

*4.7. Deprotonation of **4a***

To a −80°C THF solution (10 ml) of **4a** (0.070 g, 0.07 mmol.) 1.0 equivalent of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 0.011 g) were added. After stirring 15 min the solution was warmed up to 20°C and the solvent removed under reduced pressure. After extraction of the crude residue with diethyl ether a red powder characterized by ^{1}H-NMR, IR and CV as **3a** was quantitatively recovered.

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