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Preparation, properties and coordination of new conjugated ferrocenyl-based ligands with an end-capped nitrile

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Abstract

New ferrocenyl-nitrile conjugated ligands have been obtained by several routes in which we combined Wittig and Horner–Emmons–Wadsworth (HEW) reactions, being the latter the one that shows better results both in yield and selectivity for the *E* isomers. The coordination capabilities of these new ligands have been proved using different metal carbonyls and the electronic spectra of the compounds have been studied, showing a clear dependence on the length of the conjugated chain and in the nature of the coordinated metal carbonyl fragment. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Ferrocenes; Metal containing oligomers; Heterobimetallic complexes; Metal carbonyl; Electrochemistry

1. Introduction

The synthesis and characterization of new ferrocenyl-based compounds has become an intriguing area of research [1], specially because of their potential applications in fields such as organic synthesis, catalysis and material science. The preparation of ferrocenyl-conjugated systems offers the possibility of electronic communication between terminal subunits, this being of particular interest in either nonlinear optics, magnetism, molecular sensors or liquid crystals. Molecular wires, that is, mixed-valence bimetallic compounds with a conjugating bridging ligand that allow electronic communication between the two termini, have also been the subject of extensive research during the last decade [2]. These systems can be formed by oligoene bridging ligands between ruthenium pentamine complexes or between simple ferrocenes, where the electronic coupling has been experimentally verified for up to 40 Å [3,4].

The introduction of a metallocene unit into one-dimensional oligomers promotes a large range of properties that differ from those shown by conventional organic polymers. Although a large number of works have been reported in which metallocene-based oligomers are obtained [5], there is still a lack of systematic descriptions of synthesis leading to useful starting materials. All the reported metal-containing polymers have in common that they are only conducting if charge carriers can be delocalized over both the metal and the organic fragments.

We and others have used ferrocenyl-based conjugated ligands in order to obtain bimetallic and heterometallic push–pull complexes [6–8]. In fact, some heterobimetallic complexes, not all of them ferrocenyl-based, have shown high non linear optical responses, although the list of such compounds used in NLO is still scarce [9]. We have recently reported the syntheses, characterization and NLO behavior of new ferrocenyl heterobimetallic neutral compounds with a series of electron-accepting moieties derived from $M(CO)_6$ ($M =$ Cr, Mo or W) [6]. These compounds exhibited static hyperpolarizabilities up to 164×10^{-30} esu, which are among the largest measured up to date for ferrocenyl-based derivatives.

We now report, based on our previous findings, several efficient routes to the preparation of ferrocenyl conjugated compounds with an end-capped nitrile group. These compounds are obtained by combined

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Wittig and/or Horner–Emmons–Wadsworth (HEW) reactions, for which the corresponding ferrocenyl-aldehydes have also been obtained. The electrochemistry of the compounds and the electronic spectra has also been investigated.

2. Results and discussion

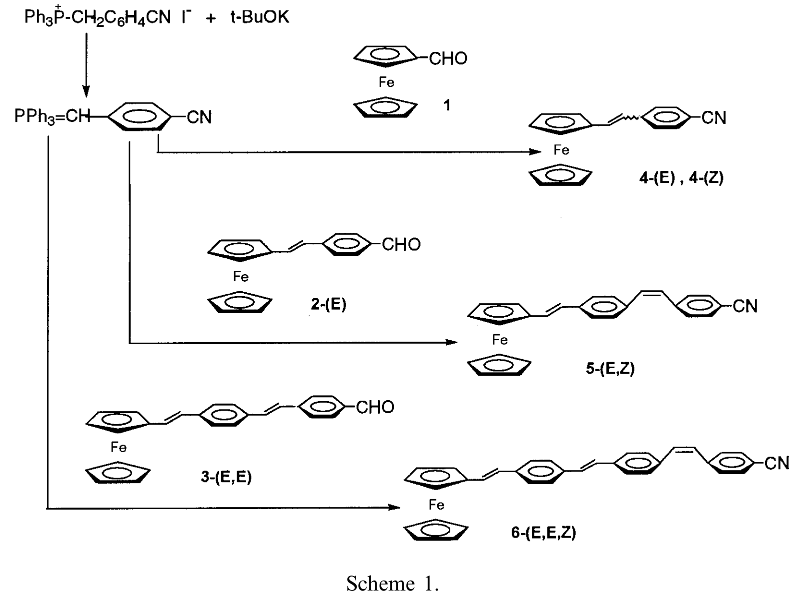
2.1. Synthesis and characterization of the compounds

Most of the ferrocenyl-based oligomers reported to date, have been obtained by conventional Wittig reactions but these reactions usually lead to the formation of *E* and *Z* isomer mixtures [4b,9a,10]. Several authors have reported the advantages of the *E*-type isomers over the *Z*-type for effective electronic coupling [10c,11]. The lack of coplanarity between donor and acceptor groups in the *Z* isomers leads to a decrease in their coupling. In addition, the reduction of the through space distance (in the *Z*-type) between donor and acceptor results in the change in dipole per unit charge separation being less. Since most of the times the aim of the synthetic procedures is to obtain linear oligomers with effective electronic coupling, the *E* isomers are the ones that are mainly pursued, but the separation of the mixtures of the *E* and *Z* isomers is not always easy. However, in some cases, effective *Z* to *E* isomerizations have been reported for some conjugated ferrocenyl compounds [10].

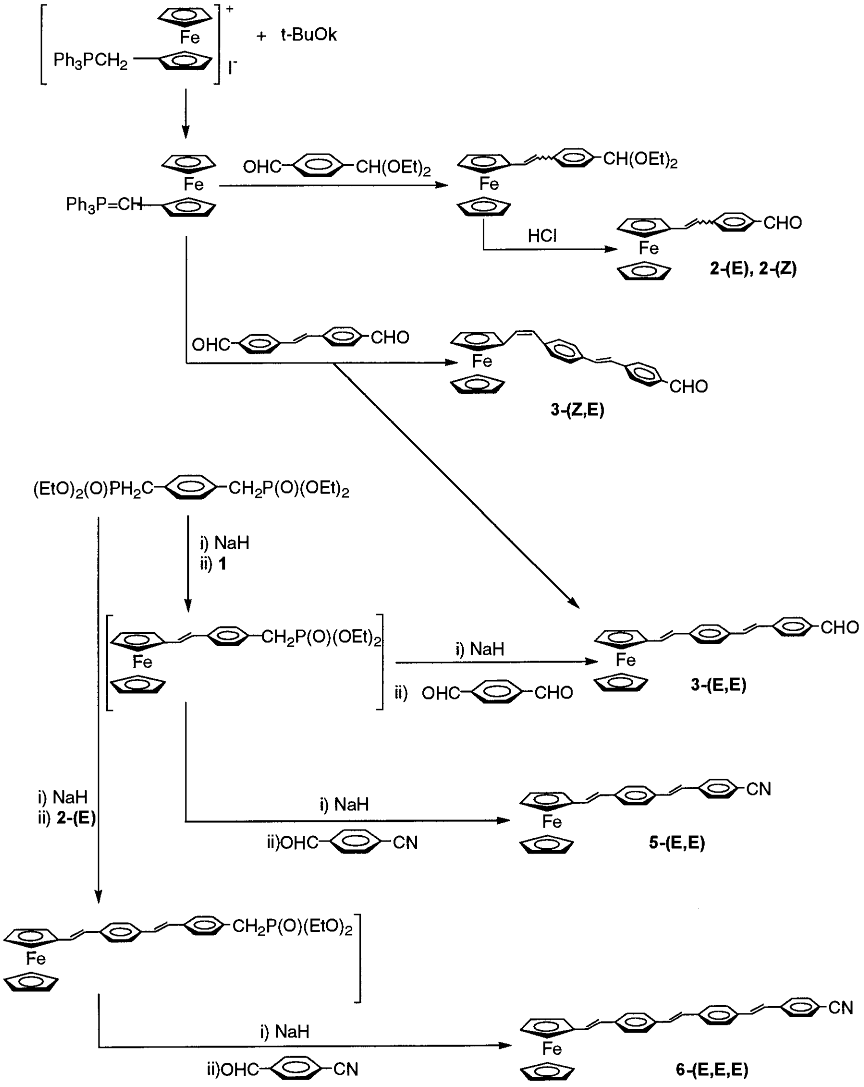
We have obtained several ferrocenyl-nitrile derivatives, following different synthetic procedures, as shown in Schemes 1 and 2. We have used Wittig–Horner (WH) reaction in previous works, this being the most appropriate method for the short-length chained complexes **2** and **4** [6,10d]. Usually this procedure led to reasonable yields of both *Z*- and *E*-isomers which could be separated by column chromatography, as described in Section 4.

When we used the same reaction (WH) in order to obtain the longer chained compounds **5** and **6**, we unexpectedly observed that the only characterizable spectroscopically and isolable compound were the (*E*,*Z*) and (*E*,*E*,*Z*) isomers. (The first lyric always corresponds to the double bond nearest to the ferrocenyl group). For reasons that we still unknow, the stereolinear isomers (*E*,*E*) and (*E*,*E*,*E*) were not obtained by this procedure. In order to obtain these isomers we performed the corresponding HEW reaction that stereoselectively lead to the formation of double bonds in the *E*-configuration [13]. As it is shown in Scheme 2 compounds **5-(*E*,*E*)** and **6-(*E*,*E*,*E*)** were obtained by double olefination of *p*-xylenebis(diethylphosphonate) with the ferrocenyl–aldehyde compound **1** or **2-(*E*)** and 4-cyanobenzaldehyde. This procedure leads to reasonably good yields for compound **5-(*E*,*E*)**, but compound **6-(*E*,*E*,*E*)** was only obtained in very low yield and it could only be characterized spectroscopically. We tried to obtain the *E*-isomers by isomerization of the *Z* isomers using *N*-Bromosuccinimide and I_2 or with basic alumina, but no conversion was observed.

Another problem that we found in the preparation of the ferrocenyl-nitrile complexes, came from the synthetic routes to the carboxaldehyde intermediates **2-(*E*)** and **3-(*E*,*E*)**. The synthetic routes for such complexes in most cases lead to moderate to poor yields [4b], and the separation workups make the overall process complicated. In order to simplify the preparation of these intermediates, we modified their synthesis as it is shown in Scheme 2. The use of terephtalaldehydemono-(diethylacetal) [p-OHC–C_6H_4–CH(OEt)$_2$] instead of the more widely used terephtaldehyde (p-OHC–C_6H_4–



Scheme 1.



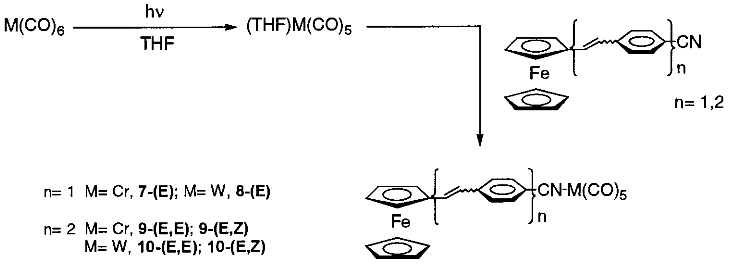
Scheme 2.

CHO), avoids the obtaintion of 1,4-bis(ferrocenyl)-ethenylbenzene as one of the major side-products of these types of reactions. The ferrocenyl–acetal complex so synthesized, can be transformed into the carboxaldehyde compound **2**, by simply reacting the acetal derivative in a solution of hydrochloric acid as has already been reported [10d].

Compound **3-(*E*,*E*)** can be obtained in a one pot reaction from a HEW reaction using *p*-xylenebis(diethylphosphonate) [12] ferrocenecarboxaldehyde and terephtaldehyde. In this reaction we avoid the formation of any *Z* isomer, since the HEW process unambiguously leads to the *E* isomers. Compound **3** can also be obtained in a one-pot reaction, by using (*E*)-1,2-bis(*p*-phenylcarboxaldehyde)ethene and [1-(triphenylphosphinomethyl)ferrocenyl]iodide in a WH reaction, giving rise to moderate yields of **3** although a mixture of the (*E*,*E*) and (*Z*,*E*) isomers were obtained. The bisaldehyde compound (*E*)-1,2-bis(*p*-phenylcarboxaldehyde)ethene, was obtained according to the method that we describe in Section 4.

In order to obtain push–pull heterobimetallic complexes from the ferrocenyl compounds obtained, we have coordinated compounds **4** and **5** to metal carbonyl fragments $M(CO)_5$ ($M = Cr, W$). The synthesis of these compounds is summarized in Scheme 3 (the coordination of **4** has already been reported and the resulting compounds characterized) [6]. These compounds decompose after several days in solution, but not decomposition was observed in the solid state.

In all cases, the vinyl protons of the *E* isomers appear as doublets with coupling constants of 16 Hz, in accord with the expected trans stereochemistry. The *Z* isomers show lower coupling constants for the vinyl protons (ca. 12 Hz), this being a good method of determining the stereochemistry of the compounds obtained. Besides, the effect of the electronwithdrawing acceptor group is also witnessed in the ^{1}H chemical shifts of the



Scheme 3.

substituted C_5H_5 ring. These signals appear at higher frequencies in those compounds with *E* conformation, where the electronic communication between the ferrocenyl and the electronaccepting group is more effective.

The IR spectra of the heterobimetallic compounds are virtually identical, indicating the presence of a metal pentacarbonyl moiety, the bands being readily assigned to the two A_1, B_2 and E modes for the pseudo C_{4v} metal center, by comparison with other monosubstituted metal carbonyl derivatives [14]. The ^{13}C-NMR clearly shows the two carbonyl inequivalent sites of the pentacarbonyl fragments, so confirming the proposed geometry of the compounds. Comparison of the IR spectra of the heterobimetallic compounds shows that the compounds containing W have lower values of ν(CO), meaning that W is more capable than Cr of reducing its electron density by π back-donation to CO.

Electrospray mass spectra were recorded using a Micromass Quattro LC instrument, using CH_3CN and/or CH_3OH as the mobile phase solvent. Cone voltage were typically varied from 15 to 90 V in order to investigate the effect of higher voltages on fragmentation pathways of parent ions. The peaks in the ESMS are identified by the most intense m/z value within the isotopic mass distribution. Isotope patterns were compared with theoretical patterns obtained using the MassLynx NT software package. In all cases there was good agreement between the experimental and calculated isotopic mass distribution.

2.2. Electronic spectra

The electronic absorption spectra of the new ferrocenyl nitrile compounds were taken in different solvents and the results are shown in Table 1. Electronic absorption spectra of these compounds show a maximum of two strong bands between 250 and 320 nm and between 370 and 470 nm. The higher energy band was assigned to the π–π* band according to the reported data in the literature for similar ferrocenyl compounds [7d,16]. The lower energy band is assigned to a MLCT band, this being strongly influenced by the nature of the ligand (chainlength, electron acceptor moiety) and metal coordinated fragment (($M(CO)_5$). This assignment is in accordance to the theoretical results reported by Barlow et al. and to other experimental results [7,16], although we are aware that some controversy about this assignation has been reported. For most ferrocene derivatives the charge transfer bands usually gains significantly in oscillator strength as the acceptor strength increases [7d,11c,15]. This band was found to increasingly red-shifted with increasing chain length, as expected for a lowering of the energy of the π* orbital of the ligand. Red shift is also achieved for the cases in which an electron-accepting moiety is coordinated to the ligand, as in complexes **9-(*E,E*)**, **9-(*E,Z*)**, **10-(*E,E*)**, **10-(*E,Z*)**, these changes being much more appreciable for the (E,E) isomers, according to their greater charge transfer capabilities. Thus, while compound **4-(*E*)** exhibits a λ_{max} at 329 nm, this value progressively shifts to longer wavelengths in going to **5-(*E,Z*)** 340 nm, to **5-(*E,E*)** 369 nm and finally to **6-(*E,E,Z*)** 380 nm. Similar trends are observed for other families of ferrocenyl phenylethynyl compounds [16]. The lower hypsochromic shifts for the *Z* configured isomers may be justified for their trend to disturb from coplanarity due to enhanced allylic strain [17]. The much weaker d–d transitions substantially overlap the MLCT bands and are not assigned.

Table 1
Electronic spectra data of ferrocenyl-nitriles

Compound	λ_{max} (nm, MLCT)				
	$CHCl_3$	Acetone	CH_2Cl_2	THF	MeOH
4-(*E*)	329	–	329	327	327
5-(*E,Z*)	340	339	340	341	345
5-(*E,E*)	369	364	368	364	364
6-(*E,E,Z*)	380	373	375	376	380
6-(*E,E,E*)	–	–	–	–	–
9-(*E,Z*)	345	349	340	343	341
9-(*E,E*)	380	378	382	383	364
10-(*E,Z*)	344	341	344	344	341
10-(*E,E*)	394	382	389	386	362

According to the tabulated UV–vis data (Table 2) the solvachromicities of the ferrocenyl(styryl)nitrile compounds are fairly small. This result is not surprising, since the CN group is not a powerful acceptor. For

Table 2
Cyclic voltammetric data for compounds **1**–**10**

Compound	$E_{1/2}$ (mV) (ΔE_p (mV)) Ferrocene-based	$E_{1/2}$ (mV) (ΔE_p (mV)) M [c]-based
Ferrocene	445 (105)	–
1	460 (70)	–
2-(*E*)	500 (105)	–
3-(*E*,*E*)	450 (95)	–
3-(*Z*,*E*)	460 (100)	–
4-(*E*) [a]	480 (80)	–
5-(*E*,*E*)	440 (70)	–
5-(*E*,*Z*)	445 (70)	–
6-(*E*,*E*,*E*) [d]	–	–
6-(*E*,*E*,*Z*)	420 (85)	–
7-(*E*) [a]	500 (70)	980 (66)
8-(*E*) [a]	495 (70)	1150 [b]
9-(*E*,*E*)	435 (80)	965 (70)
9-(*E*,*Z*)	450 (85)	965 (75)
10-(*E*,*E*)	435 (85)	965 [b]
10-(*E*,*Z*)	450 (70)	1160 [b]

[a] Data from Ref. [6].

[b] Irreversible peak, measured at 100 mV s^{-1}.

[c] M = Cr, W

[d] Not measured.

the heterobimetallic complexes **9-(*E*,*E*)**, **9-(*E*,*Z*)**, **10-(*E*,*E*)** and **10-(*E*,*Z*)**, the solvatochromic behavior is more important, so confirming the stronger electron-accepting capabilities of the metal-carbonyl units. This result gives us an idea of the dipole moments in the ground and in the excited states, which have a direct relation to hyperpolarizability. The charge transfer band λ_{max} shifts upon changing the solvent from CH_2Cl_2 to MeOH. These hypsochromic shifts mean that the dipole moment in the excited state is lower than in the ground state. In addition this effect is greater in the cases were all the double bonds are *E* [18].

2.3. Cyclic voltammetry

The electrochemical data obtained for the compounds studied are summarized in Table 2. All the complexes display the chemically reversible ferrocene/ferricinium couple in CH_2Cl_2. The peak to peak separation are, however, significantly greater than the ideal value of 60 mV s^{-1} for a fully reversible one-electron process. This may be due to a combination of uncompensated solution resistance and slightly slow electron-transfer kinetics. The half-wave potential of the ferrocenyl moieties for the aldehydes derivatives **2** and **3-(*E*,*E*)** are more anodic than that measured for ferrocene, meaning some degree of electron transfer between the iron center and the electron accepting aldehyde fragment. Similar anodic shift has also been reported for the nitrile derivative **4-(*E*)** [6]. However, the halfwave potential of the nitrile derivatives with longer conjugated chains are similar to that shown for ferrocene, compounds **5-(*E*,*Z*)** and **5-(*E*,*E*)** or even more lower, compound **6-(*E*,*E*,*Z*)** indicating that the oxidation is favored by the delocalization of the charge along the longer conjugated system of the ligand. This cathodic shift is larger for the waves in which the increase of the chain is achieved in a linear form (*E*-isomers).

Coordination of the neutral unit $M(CO)_5$, to the ferroceny nitrile ligands, does not have any significant effect on the redox potential of the ferrocene center. However, the coordination of this unit to the shorter chain ferrocenyl nitrile derivative **4-(*E*)** comes an increase of the redox potential for both Cr and W in agreement with an electron transfer in the direction $Fc \rightarrow M(CO)_5$. These results are in accordance to those reviewed by Heck et al. in which the redox shift depends in opposite directions of both the strength of the electron-accepting moiety and the length of the conjugated chain. [8]. The wave associated to the $M(CO)_5/[M(CO)_5]^+$ couple is reversible for the Cr case and irreversible for W, as seen in some other examples [6,7f]. The oxidation potential of the second step ascribed to the metal-carbonyl fragment depends on the metal present, this being higher for the W complexes compared to the Cr complexes.

3. Conclusions

In summary, a series of ferrocenyl-based oligomers have been obtained using Wittig and HEM reactions. These compounds proved to be good electronic messengers along the (up to 25 Å) conjugated chain, as seen from the data obtained from the cyclic voltammetry and electronic spectra. This gives an easy way that allows one to design suitable molecules for electron transfer studies and nonlinear optical studies. Through electronic spectroscopy and electrochemical studies we have shown that chain-lengthening and coordination of the compounds clearly influence the values of the reduction potential and the energies of the charge transfer bands in the electronic spectra.

4. Experimental

4.1. General details

All reactions were carried out under a nitrogen atmosphere using standard Schlenck techniques. Solvents for synthesis and electrochemical measurements were dried and degassed by standard methods before use. Chromatographic work was performed on silica gel 60 Å or neutral alumina columns.

Compound **2** was obtained according to literature methods [19]. Compounds **1**, $Cr(CO)_6$ and $W(CO)_6$ were purchased from Aldrich Chemicals and used without further purification.

NMR spectra were recorded on a Varian Innova 300 MHz and 500 MHz, using $CDCl_3$ as solvent unless otherwise stated. IR spectra were recorded on a Perkin–Elmer System 2000 FT-IR using NaCl pellets. Electronic absorption spectra were obtained on a UV-1603 Shimazdzu spectrophotometer. Elemental analyses were performed on a EA 1108 CHNS-O Carlo Erba Instruments. Cyclic voltammetry experiments were performed with a Echochemie pgstat 20 electrochemical analyzer. All measurements were carried out at room temperature (r.t.) with a conventional three-electrode configuration consisting of platinum working and auxiliary electrodes and a Ag/AgCl reference electrode containing aqueous 3 M KCl. The solvent in all experiments was CH_2Cl_2, which was obtained in HPLC grade. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate, synthesized by metathesis of tetrabutylammonium bromide and HPF_6, recrystallized from ethanol and dried under vacuum. $E_{1/2}$ values were determined as $1/2(E_{p,a}+E_{p,c})$, where $E_{p,a}$ and $E_{p,c}$ are the anodic and cathodic peak potentials, respectively. All potential reported are not corrected for the junction potential. Electrospray mass spectra were recorded using a Micromass Quattro LC instrument, using CH_3CN and/or CH_3OH as the mobile phase solvent. The samples were added to give a mobile phase of approximate concentration 0.1 mM. This solution was injected into the spectrometer via a Rheodyne injector fitted a 10 μl sample loop, and nitrogen was employed as a drying and nebulising gas.

4.2. Synthesis of (E)-1,2-bis(p-phenylaldehyde)ethene

To a solution of sodium hydride 60% dispersion in mineral oil (650 mg, 21 mmol) in THF (25 ml) it was added at r.t. 4-bromobenzyltriphenylphosphonium bromide (10 g, 20 mmol) in THF (100 ml). After stirring the reaction mixture for 1 h at r.t. was added *p*-bromebenzaldehyde (3.7 mg, 20 mmol) in THF (70 ml) and the resulting solution was stirred for 4 h. After removing the solvent under reduced pressure, the product was extracted with $CH_2Cl_2–H_2O–NH_4Cl$ and dried over Na_2SO_4. Purification by column chromatography on silica gel using hexane–AcOEt (9:1) as eluent afforded pure compound (*E*)-1,2-bis(*p*-phenylbromide)ethene. Yield: 70%. Then, to a solution of (*E*)-1,2-bis(*p*-phenylbromide)ethene (2.5 g, 7.4 mmol) in THF (75 ml) at − 78°C BuLi (8.1 ml, 22.2 mmol) was added and the reaction mixture stirred at − 78°C for 1 h and at 0°C for 2 h. After cooling again to − 78°C *N*-formylmorpholine (3.2 ml, 41 mmol) was added and stirred at r.t. overnight. After removing the solvent under reduced pressure, the product was extracted with CH_2Cl_2–HCl (5%) and dried over Na_2SO_4. Purification by column chromatography on silica gel using hexane–AcOEt (9:1) as eluent afforded pure compound (*E*)-1,2-bis(*p*-phenylaldehyde)ethene. Yield: 75%.

^{1}H-NMR (300 MHz, $CDCl_3$): δ 9.99 (s, 2H, CHO); 7.87 (d, 4H, $^3J_{H-H}=7.8$ Hz, C_6H_4); 7.66 (d, 4H, $^3J_{H-H}=7.8$ Hz, C_6H_4); 7.24 (s, 2H, CH=CH). ^{13}C-NMR (300 MHz, $CDCl_3$): δ 127.9, 130.8, 131.2 (10C, CH=CH and C_6H_4); 136.4, 142.9 (4Cq, C_6H_4); 192.0 (2C, CHO).

4.3. Synthesis of **3-(*Z,E*)** and **3-(*E,E*)**

4.3.1. Using (E)-1,2-bis(p-phenylaldehyde)ethene

To an ice-cold solution of (1-(triphenylphosphinomethyl)ferrocenyl]iodide (3 g, 5.1 mmol) in THF (50 ml) potassium *tert*-butoxide (850 mg, 7.6 mmol) was added and the resulting solution stirred for 30 min to form the ylide. The aldehyde (*E*)-1,2-bis(*p*-phenylaldehyde)ethene (2.5 ml, 20.4 mmol) was added and the resulting mixture stirred for ca. 24 h. After removing the solvent under reduced pressure, the product was extracted with $CH_2Cl_2–H_2O–NaHCO_3$ and purified by column chromatography on silica gel with hexane–CH_2Cl_2 (4:1). Recrystallization from CH_2Cl_2–hexane mixtures afforded pure compounds. Yields: 10% (for **3-(*Z,E*)**), 35% (**3-(*E,E*)**).

4.3.2. Using the Horner–Emmons–Wadsworth reaction

To an ice-cold solution of *p*-xylenebis(diethylphosphonate) (4.0 g, 10.6 mmol) in THF (75 ml) was added sodium hydride 60% dispersion in mineral oil (500 mg, 12.5 mmol) and the resulting solution stirred for 45 min at 0°C and 60 min at r.t. The aldehyde **1** (1.8 g, 8.4 mmol) was added at 0°C and the resulting solution stirred 5 h at r.t. Then, sodium hydride 60% dispersion in mineral oil (575 mg, 14.4 mmol) was added at 0°C and the reaction mixture stirred for 45 min. Finally, terephtaldehyde (1.5 g, 11.2 mmol) was added at 0°C and the reaction mixture stirred for 5 h at r.t. After removing the solvent under reduced pressure, the product was extracted with $CH_2Cl_2–H_2O–NaHCO_3$ and dried over $MgSO_4$. Purification by column chromatography on silica gel using hexane–CH_2Cl_2 (2:5) as eluent. Recrystallization from CH_2Cl_2–hexane mixtures afforded pure compound **3-(*E,E*)**. Yield: 40%.

^{1}H-NMR for compound **3-(*Z,E*)** (300 MHz, $CDCl_3$): δ 7.79 (d, 2H, $^3J_{H-H}=8.4$ Hz, C_6H_4); 7.26 (d, 2H, $^3J_{H-H}=8.4$ Hz, C_6H_4); 7.19 (d, 2H, $^3J_{H-H}=8.4$ Hz, C_6H_4); 7.08 (d, 2H, $^3J_{H-H}=8.1$ Hz, C_6H_4); 6.85 (d, 1H, $^3J_{H-H}=12.2$ Hz, CH=CH); 6.77 (d, 1H, $^3J_{H-H}=12.0$ Hz, CH=CH); 6.50 (d, 1H, $^3J_{H-H}=16.0$ Hz, CH=CH); 6.34 (d, 1H, $^3J_{H-H}=16.0$ Hz, CH=CH); 4.34 (s, 2H, C_5H_4); 4.25 (s, 2H, C_5H_4); 4.14 (s, 5H, C_5H_5). ^{13}C-NMR (300 MHz, $CDCl_3$): δ 67.8, 69.8 (4C, C_5H_4); 69.9 (5C, C_5H_5); 83.4 (1Cq, C_5H_4); 125.3, 125.7, 127.8, 129.6, 130.5, 130.9, 131.7, 133.0 (12C, CH=CH and C_6H_4); 132.4, 135.3, 138.8, 144.0 (4Cq, C_6H_4); 190.1 (1C, CHO). IR (cm^{-1}): 1670 (vs), 1654 (s), 1405 (w), 1273(w). Anal. Calc. for compound **3-(*Z*,*E*)**, $C_{27}H_{22}FeN$ ($M_w = 418.32$): C, 77.50; H, 5.30. Found: C, 77.33; H, 5.53%.

^1H-NMR for compound **3-(*E*,*E*)** (300 MHz, $CDCl_3$): δ 7.88 (d, 2H, $^3J_{H-H} = 8.1$ Hz, C_6H_4); 7.67 (d, 2H, $^3J_{H-H} = 8.4$ Hz, C_6H_4); 7.53 (d, 2H, $^3J_{H-H} = 8.4$ Hz, C_6H_4); 7.46 (d, 2H, $^3J_{H-H} = 8.4$ Hz, C_6H_4); 7.27 (d, 1H, $^3J_{H-H} = 16.2$ Hz, CH=CH); 7.15 (d, 1H, $^3J_{H-H} = 16.2$ Hz, CH=CH); 6.94 (d, 1H, $^3J_{H-H} = 16.2$ Hz, CH=CH); 6.71 (d, 1H, $^3J_{H-H} = 15.9$ Hz, CH=CH); 4.49 (t, 2H, $^3J_{H-H} = 1.8$ Hz C_5H_4); 4.32 (s, 2H, $^3J_{H-H} = 1.8$ Hz C_5H_4); 4.16 (s, 5H, C_5H_5). ^{13}C-NMR (300 MHz, $CDCl_3$): δ 67.7, 69.6 (4C, C_5H_4); 69.6 (5C, C_5H_5); 83.8 (1Cq, C_5H_4); 125.9, 126.7, 127.2, 127.4, 127.9, 128.4, 130.9, 132.5 (12C, CH=CH and C_6H_4); 135.5, 135.7, 138.8, 144.1 (4Cq, C_6H_4); 192.1 (1C, CO). IR (cm^{-1}): 1678 (vs), 1660 (s), 1452 (w), 1243(w), 1028(w), 811 (w). Anal. Calc. for compound **3-(*E*,*E*)**, $C_{27}H_{22}FeN$ ($M_w = 418.32$): C, 77.50; H, 5.30. Found: C, 77.10; H, 5.18%.

4.4. Synthesis of **5-(*E*,*Z*)**

To an ice-cold solution of *p*-[(triphenylphosphinomethyl)-benzonitrile] iodine (2.5 g, 5.5 mmol) in THF (75 ml) potassium *tert*-butoxide (539 mg, 4.8 mmol) was added and the resulting solution stirred for 30 min at 0°C and 45 min at r.t. The aldehyde **2-(*E*)** (1.6 g, 5.0 mmol) was added at 0°C and the resulting solution stirred overnight at r.t. After removing the solvent under reduced pressure, the product was extracted with CH_2Cl_2–H_2O–$NaHCO_3$ and dried over $MgSO_4$. The title compound was purified by column chromatography on silica gel using hexane–CH_2Cl_2 (1:1) as eluent. Recrystallization from CH_2Cl_2–hexane mixtures afforded pure compound **5-(*E*,*Z*)**. Yield: 45%. ^1H-NMR (500 MHz, $CDCl_3$): δ 7.52 (d, 2H, $^3J_{H-H} = 8.5$ Hz, C_6H_4); 7.38 (d, 2H, $^3J_{H-H} = 8.0$ Hz, C_6H_4); 7.30 (d, 2H, $^3J_{H-H} = 7.5$ Hz, C_6H_4); 7.15 (d, 2H, $^3J_{H-H} = 8.5$ Hz, C_6H_4); 6.87 (d, 1H, $^3J_{H-H} = 16.0$, CH=CH); 6.65 (d, 1H, $^3J_{H-H} = 16.0$, CH=CH); 6.71 (d, 1H, $^3J_{H-H} = 12.0$, CH=CH); 6.55 (d, 1H, $^3J_{H-H} = 12.0$, CH=CH); 4.45 (t, 2H, $^3J_{H-H} = 1.5$ Hz, C_5H_4); 4.29 (t, 2H, $^3J_{H-H} = 1.5$ Hz, C_5H_4); 4.14 (s, 5H, C_5H_5). ^{13}C-NMR (500 MHz, $CDCl_3$): δ 67.4, 69.6 (4C, C_5H_4); 69.6 (5C, C_5H_5); 83.3 (1Cq, C_5H_4); 110.1 (1C, CN); 125.6, 126.1, 126.7, 128.5, 129.0, 129.3, 133.1, 135.0 (12C, CH=CH and C_6H_4); 120.0, 135.1, 137.6, 140.1 (4Cq, C_6H_4). IR (cm^{-1}): 2207 (s), 1300 (w), 1117 (w). Anal. Calc. for compound **5-(*E*,*Z*)**, $C_{27}H_{21}FeN$ ($M_w = 415.32$): C, 78.10; H, 5.10; N, 3.37. Found: C, 78.12; H, 5.07; N, 3.39%. Electrospray MS. Cone 64 V. *m*/*z* (fragment): 415, M^+.

4.5. Synthesis of **5-(*E*,*E*)**

To an ice-cold solution of *p*-xylenebis(diethylphosphonate) (2.0 g, 5.3 mmol) in THF (75 ml) sodium hydride 60% dispersion in mineral oil (212 mg, 5.3 mmol) was added and the resulting solution stirred for 45 min at 0°C and 60 min at r.t. The aldehyde **1** (1.1 g, 5.0 mmol) was added at 0°C and the resulting solution stirred 5 h at r.t. Then, sodium hydride 60% dispersion in mineral oil (212 mg, 5.3 mmol) was added at 0°C and the mixture stirred for 45 min at r.t. Finally, 4-cyanobenzaldehyde (917.9 mg, 7.0 mmol) was added and the reaction mixture was stirred overnight at r.t. After removing the solvent under reduced pressure, the product was extracted with CH_2Cl_2–H_2O–$NaHCO_3$ and dried over $MgSO_4$. The title compound was purified by column chromatography on silica gel washing with hexane–CH_2Cl_2 (4:1) first and using hexane–CH_2Cl_2 (1:2) as eluent. Recrystallization from CH_2Cl_2–hexane mixtures afforded pure compound. Yield: 47%. ^1H-NMR (500 MHz, $CDCl_3$): δ 7.64 (d, 2H, $^3J_{H-H} = 8.0$ Hz, C_6H_4); 7.59 (d, 2H, $^3J_{H-H} = 8.0$ Hz, C_6H_4); 7.50 (d, 2H, $^3J_{H-H} = 8.0$ Hz, C_6H_4); 7.45 (d, 2H, $^3J_{H-H} = 8.0$ Hz, C_6H_4); 7.21 (d, 1H, $^3J_{H-H} = 16.5$, CH=CH); 7.10 (d, 1H, $^3J_{H-H} = 16.0$, CH=CH); 6.94 (d, 1H, $^3J_{H-H} = 16.0$, CH=CH); 6.71 (d, 1H, $^3J_{H-H} = 16.0$, CH=CH); 4.49 (s, 2H, C_5H_4); 4.32 (s, 2H, C_5H_4); 4.16 (s, 5H, C_5H_5). ^{13}C-NMR (500 MHz, $CDCl_3$): δ 67.4, 69.7 (4C, C_5H_4); 69.7 (5C, C_5H_5); 83.5 (1Cq, C_5H_4); 110.9 (1C, CN); 125.8, 126.4, 126.6, 127.2, 127.8, 128.4, 132.6, 132.9 (12C, CH=CH and C_6H_4); 119.5, 135.2, 138.9, 142.5 (4Cq, C_6H_4). IR (cm^{-1}): 2211 (s), 1590 (w), 967 (w). Anal. Calc. for compound **5-(*E*,*E*)**, $C_{27}H_{21}FeN$ ($M_w = 415.32$): C, 78.10; H, 5.10; N, 3.37. Found: C, 78.18; H, 5.00; N, 3.33%. Electrospray MS. Cone 84 V. *m*/*z* (fragment): 415, M^+.

4.6. Synthesis of **6-(*E*,*E*,*Z*)**

This compound was obtained following the general procedure described for compound **5-(*E*,*Z*)** and using the aldehyde **3-(*E*,*E*)** (2.1 g, 5.0 mmol) instead of **2-(*E*)**. The purification was made by column chromatography on silica gel using hexane–CH_2Cl_2 (2:1) as eluent. Yield: 25%. ^1H-NMR (500 MHz, $CDCl_3$): δ 7.53–7.37 (m, 10H); 7.14 (d, 2H, $^3J_{H-H} = 8.5$ Hz, C_6H_4); 7.10 (d, 1H, $^3J_{H-H} = 16.5$, CH=CH); 7.06 (d, 1H, $^3J_{H-H} = 16.5$, CH=CH); 6.90 (d, 1H, $^3J_{H-H} = 16.5$, CH=CH); 6.70 (d, 1H, $^3J_{H-H} = 16.0$, CH=CH); 6.74 (d, 1H, $^3J_{H-H} = 12.0$, CH=CH); 6.58 (d, 1H, $^3J_{H-H} = 12.0$, CH=CH); 4.48 (s, 2H, C_5H_4); 4.30 (s, 2H, C_5H_4); 4.15 (s, 5H, C_5H_5). ^{13}C-NMR (500 MHz, $CDCl_3$): δ 67.7, 69.9 (4C, C_5H_4); 69.9 (5C, C_5H_5); 84.0 (1Cq, C_5H_4); 111.2 (1C, CN); 126.3, 126.8, 127.1, 127.6, 128.0, 129.0, 129.7, 130.0, 130.2, 132.7, 133.6 (18C, CH=CH and C_6H_4); 119.6, 136.0, 136.3, 137.8, 138.2, 142.9 (6Cq, C_6H_4). IR

(cm^{-1}): 2218 (s), 1248 (w). Anal. Calc. for compound **6-(*E,E,Z*)**, $C_{35}H_{27}F_6FeN$ ($M_w = 517.45$): C, 81.20; H, 5.26; N, 2.71. Found: C, 81.84; H, 5.63; N, 2.73%. Electrospray MS. Cone 77 V. *m*/*z* (fragment): 517, M^+.

4.7. Syntheses of the compound ***6-(E,E,E)***

This compound was obtained following the general procedure described for compound **5-(*E,E*)** and using the aldehyde **2-(*E*)** (1.6 g, 5.0 mmol) instead of **1**. Purification was made by column chromatography on silica gel using hexane–CH_2Cl_2 (1:4) as eluent. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.64 (d, 2H, $^3J_{H-H} = 8.0$ Hz, C_6H_4); 7.58 (d, 2H, $^3J_{H-H} = 8.0$ Hz, C_6H_4); 7.43 (d, 2H, $^3J_{H-H} = 8.0$ Hz, C_6H_4); 7.34 (d, 2H, $^3J_{H-H} = 8.0$ Hz, C_6H_4); 7.32 (d, 2H, $^3J_{H-H} = 8.5$ Hz, C_6H_4); 7.26 (d, 2H, $^3J_{H-H} = 8.0$ Hz, C_6H_4); 7.19 (d, 1H, $^3J_{H-H} = 16.0$, CH=CH); 7.08 (d, 1H, $^3J_{H-H} = 17.0$, CH=CH); 6.88 (d, 1H, $^3J_{H-H} = 16.0$, CH=CH); 6.68 (d, 1H, $^3J_{H-H} = 16.0$, CH=CH); 6.62 (d, 1H, $^3J_{H-H} = 17.0$, CH=CH); 6.59 (d, 1H, $^3J_{H-H} = 17.0$, CH=CH); 4.47 (s, 2H, C_5H_4); 4.30 (s, 2H, C_5H_4); 4.15 (s, 5H, C_5H_5).^{13}C-NMR (500 MHz, $CDCl_3$): δ 67.6, 70.0 (4C, C_5H_4); 69.9 (5C, C_5H_5); 83.7 (1Cq, C_5H_4); 111.2 (1C, CN); 126.3, 127.2, 127.4, 127.6, 127.9, 130.0, 130.2, 131.4, 132.8, 133.0, 133.8 (18C, CH=CH and C_6H_4); 119.5, 135.8, 136.3, 137.7, 138.7, 142.6 (6Cq, C_6H_4). IR (cm^{-1}): 2211 (s), 1308 (w). Electrospray MS. Cone 76 V. *m*/*z* (fragment): 517, M^+.

4.8. Syntheses of the compounds ***9-(E,E)*** *and* ***9-(E,Z)***

Chromium hexacarbonyl (176 mg, 0.8 mmol) was dissolved in THF (30 ml) and the resulting solution was irradiated using a Hg lamp for 1 h. Compound **5-(*E,Z*)** (150 mg, 0.4 mmol) or compound **5-(*E,E*)** (150 mg, 0.4 mmol) were added to the yellow solution formed upon irradiation in order to obtain compounds **9-(*E,Z*)** or **9-(*E,E*)**, respectively. The reaction mixture was stirred for another 30 min, filtered to remove the solid, and the solvent was removed under reduced pressure. Purification by column chromatography on neutral alumina with CH_2Cl_2–hexane (1:1) afforded pure compounds **9-(*E,Z*)** yield 40% or **9-(*E,E*)** yield 60%.

^{1}H-NMR for compound **9-(*E,Z*)** (300 MHz, $CDCl_3$): δ 7.54 (d, 2H, $^3J_{H-H} = 8.4$ Hz, C_6H_4); 7.39 (d, 2H, $^3J_{H-H} = 8.4$ Hz, C_6H_4); 7.32 (d, 2H, $^3J_{H-H} = 8.4$ Hz, C_6H_4); 7.17 (d, 2H, $^3J_{H-H} = 8.1$ Hz, C_6H_4); 6.72 (d, 1H, $^3J_{H-H} = 16.2$ Hz, CH=CH); 6.49 (d, 1H, $^3J_{H-H} = 16.2$ Hz, CH=CH); 6.55 (d, 1H, $^3J_{H-H} = 12.0$ Hz, CH=CH); 6.38 (d, 1H, $^3J_{H-H} = 12.0$ Hz, CH=CH); 4.47 (t, 2H, $^3J_{H-H} = 1.8$ Hz, C_5H_4); 4.31 (t, 2H, $^3J_{H-H} = 1.8$ Hz, C_5H_4); 4.15 (s, 5H, C_5H_5). ^{13}C-NMR (300 MHz, $CDCl_3$): δ 67.9, 69.9 (4C, C_5H_4); 69.9 (5C, C_5H_5); 83.7 (1Cq, C_5H_4); 109.5 (1C, CN); 125.8, 126.4, 128.5, 129.8, 130.1, 130.4, 132.7, 132.9 (12C, CH=CH and C_6H_4); 129.1, 134.3, 138.3, 143.9 (4Cq, C_6H_4); 214.3 (4C, CO); 219.1 (1C, CO). IR (cm^{-1}): 2209 (s), 2074 (s), 1934 (vs). Anal. Calc. for compound **9-(*E,Z*)**, $C_{32}H_{21}FeNO_5Cr$ ($M_w = 607.37$): C, 63.30; H, 3.45; N, 2.31. Found: C, 61.7; H, 3.83; N, 2.29%.

^{1}H-NMR for compound **9-(*E,E*)** (500 MHz, $CDCl_3$): δ 7.64 (d, 2H, $^3J_{H-H} = 8.0$ Hz, C_6H_4); 7.57 (d, 2H, $^3J_{H-H} = 8.0$ Hz, C_6H_4); 7.51 (d, 2H, $^3J_{H-H} = 7.5$ Hz, C_6H_4); 7.46 (d, 2H, $^3J_{H-H} = 7.5$ Hz, C_6H_4); 7.24 (d, 1H, $^3J_{H-H} = 16.0$ Hz, CH=CH); 7.09 (d, 1H, $^3J_{H-H} = 16.5$ Hz, CH=CH); 6.95 (d, 1H, $^3J_{H-H} = 16.0$ Hz, CH=CH); 6.71 (d, 1H, $^3J_{H-H} = 15.5$ Hz, CH=CH); 4.49 (s, 2H, C_5H_4); 4.33 (s, 2H, C_5H_4); 4.16 (s, 5H, C_5H_5). ^{13}C-NMR (300 MHz, $CDCl_3$): δ 67.7, 69.9 (4C, C_5H_4); 69.9 (5C, C_5H_5); 83.7 (1Cq, C_5H_4); 108.7 (1C, CN); 125.8, 126.1, 126.8, 127.3, 127.9, 132.7, 133.0, 133.3 (12C, CH=CH and C_6H_4); 128.8, 135.2, 139.1, 143.4 (4Cq, C_6H_4); 214.4 (4C, CO); 219.7 (1C, CO). IR (cm^{-1}): 2213 (s), 2074 (s), 1942 (vs). Anal. Calc. for compound **9-(*E,E*)**, $C_{32}H_{21}FeNO_5Cr$ ($M_w = 607.37$): C, 63.30; H, 3.45; N, 2.31. Found: C, 62.6; H, 3.50; N, 2.32%. Electrospray MS. Cone 27 V. *m*/*z* (fragment): 607, M^+.

4.9. Syntheses of ***10-(E,E)*** *and* ***10-(E,Z)***

These compounds were obtained using the general procedure described for **9** but using tungsten hexacarbonyl (281.5 mg, 0.8 mmol) instead of chromium hexacarbonyl. Yield for compound **10-(*E,Z*)** 40% and for compound **10-(*E,E*)** 70%.

^{1}H-NMR for compound **10-(*E,Z*)** (300 MHz, $CDCl_3$): δ 7.57 (d, 2H, $^3J_{H-H} = 8.7$ Hz, C_6H_4); 7.45 (d, 2H, $^3J_{H-H} = 8.1$ Hz, C_6H_4); 7.32 (d, 2H, $^3J_{H-H} = 8.1$ Hz, C_6H_4); 7.16 (d, 2H, $^3J_{H-H} = 8.1$ Hz, C_6H_4); 6.90 (d, 1H, $^3J_{H-H} = 16.2$ Hz, CH=CH); 6.66 (d, 1H, $^3J_{H-H} = 16.2$ Hz, CH=CH); 6.78 (d, 1H, $^3J_{H-H} = 12.0$ Hz, CH=CH); 6.58 (d, 1H, $^3J_{H-H} = 12.0$ Hz, CH=CH); 4.47 (t, 2H, $^3J_{H-H} = 1.8$ Hz, C_5H_4); 4.32 (t, 2H, $^3J_{H-H} = 1.8$ Hz, C_5H_4); 4.15 (s, 5H, C_5H_5). ^{13}C-NMR (500 MHz, $CDCl_3$): δ 67.7, 69.9 (4C, C_5H_4); 69.9 (5C, C_5H_5); 83.7 (1Cq, C_5H_4); 108.7 (1C, CN); 125.9, 126.5, 128.2, 128.7, 129.9, 130.6, 133.3, 134.7 (12C, CH=CH and C_6H_4); 125.4, 134.9, 138.5, 144.6 (4Cq, C_6H_4); 197.0 (4C, CO); 200.7 (1C, CO). IR (cm^{-1}): 2073 (s), 1928 (vs). Anal. Calc. for compound **10-(*E,Z*)**, $C_{32}H_{21}FeNO_5W$ ($M_w = 739.23$): C, 52.00; H, 2.86; N, 1.89. Found: C, 52.03; H, 2.99; N, 1.91%.

^{1}H-NMR for compound **10-(*E,E*)** (500 MHz, $CDCl_3$): δ 7.68 (d, 2H, $^3J_{H-H} = 8.5$ Hz, C_6H_4); 7.65 (d, 2H, $^3J_{H-H} = 8.0$ Hz, C_6H_4); 7.52 (d, 2H, $^3J_{H-H} = 8.0$ Hz, C_6H_4); 7.47 (d, 2H, $^3J_{H-H} = 8.0$ Hz, C_6H_4); 7.27 (d, 1H, $^3J_{H-H} = 16.5$ Hz, CH=CH); 7.11 (d, 1H, $^3J_{H-H} = 16.5$ Hz, CH=CH); 6.95 (d, 1H, $^3J_{H-H} = 16.5$ Hz, CH=CH); 6.72 (d, 1H, $^3J_{H-H} = 16.0$ Hz, CH=CH); 4.49 (s, 2H, C_5H_4); 4.33 (s, 2H, C_5H_4); 4.16 (s, 5H, C_5H_5). ^{13}C-NMR (300 MHz, $CDCl_3$): δ 67.7, 70.1 (4C, C_5H_4); 69.9 (5C, C_5H_5); 83.7 (1Cq, C_5H_4); 108.5 (1C, CN);

125.8, 126.1, 126.8, 127.6, 128.1, 128.8, 133.7, 133.8 (12C, CH=CH and C_6H_4); 127.9, 134.9, 139.3, 143.9 (4Cq, C_6H_4); 196.8 (4C, CO); 200.5 (1C, CO). IR (cm^{-1}): 2075 (s), 1976 (sh), 1922 (vs). Anal. Calc. for compound **10-(*E*,*E*)**, $C_{32}H_{21}FeNO_5W$ ($M_w = 739.23$): C, 52.00; H, 2.86; N, 1.89. Found: C, 53.24; H, 2.74; N, 1.81%. Electrospray MS. Cone 30 V. m/z (fragment): 739, M^+.

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References

[1] For excellent recent reviews on ferrocene-based compounds, see: (a) A. Togni, T. Hayashi (Eds.), Ferrocenes: Homogeneous Catalysis – Organic Synthesis Materials – Science,VCH, Weinheim, Germany, 1995. (b) A. Togni, R.L. Halterman (Eds.), Metallocenes, Wiley-VCH, Weinheim, Germany, 1998. (c) N.J. Long, Metallocenes: A Introduction to Sandwich Complexes, Blackwell Science, Oxford, 1998.

[2] (a) J.P. Launay (Ed.), Molecular Electronics, Gauthier-Villars, Paris, 1991. (b) J.P. Launay, New J. Chem. 1 (1991) 97.

[3] (a) A.C. Ribou, J.P. Launay, K. Takashashi, T. Nihira, S. Tarutani, C.W. Spangler, Inorg. Chem. 33 (1994) 1325. (b) S. Woitellier, J.P. Launay, C.W. Spangler, Inorg. Chem. 28 (1989) 758.

[4] (a) A.C. Ribou, J.P. Launay, M.L. Sachtleben, H. Li, C.W. Spangler, Inorg. Chem. 35 (1996) 3735. (b) A. Hradsky, B. Bildstein, N. Schuler, H. Schottenberger, P. Jaitner, K.H. Ongania, K. Wurst, J.P. Launay, Organometallics 16 (1997) 392.

[5] (a) N.J.Long, A.J. Martin, R. Vilar, A.J.P. White, D.J. Williams, M. Younus, Organometallics 18 (1999) 4261. (b) S. Barlow, D. O'Hare, Chem. Rev. 97 (1997) 637. (c) Y. Zhu, O. Clot, O. Wolf, G.P.A. Yap, J. Am. Chem. Soc. 120 (1998) 1812. (d) O. Lavastre, L. Ollivier, P.H. Dixneuf, S. Sibandhit, Tetrahedron 51 (1996) 1683. (e) M.C.B. Colbert, J. Lewis, N.J. Long, P.R. Raithby, A.J.P. White, D.J. Williams, J. Chem. Soc. Dalton Trans. 99 (1997) 99. (f) O. Lavastre, M. Even, P.H. Dixneuf, A. Pacreau, J.P. Vairon, Organometallics 15 (1996) 1530.

[6] J. Mata, S. Uriel, E. Peris, R. Llusar, S. Houbrechts, A. Persoons, J. Organomet. Chem. 562 (1998) 197.

[7] (a) J.T. Lin, J.J. Wu, Ch. Sh. Li, Y.S. Wen, K.J. Lin, Organometallics 15 (1996) 5028. (b) A. Togni, G. Rins, Organometallics 12 (1993) 3368. (c) G. Doineau, G. Balavoine, T. Fillebeen-Khan, J.C. Clinet, J. Delaire, I. Ledoux, R. Loucif, G. Puccetti, J. Organomet. Chem. 421 (1991) 299. (d) I.S. Lee, S.S. Lee, Y.K. Chung, D. Kim, N.W. Song, Inorg. Chim. Acta 279 (1998) 243. (e) K.N. Jayaprakash, P.C. Ray, I. Matsuoka, M.M. Bhadbhade, V.G. Puranik, P.K. Das, H. Nishihara, A. Sarklar, Organometallics 18 (1999) 3851. (f) S. Sakanishi, D.A. Badrdwell, S. Couchman, J.C. Jeffrey, J.A. McCleverty, M.D. Ward, J. Organomet. Chem. 528 (1997) 35. (g) S. Barlow, H.E. Bunting, C. Ringham, J.C. Green, G.U. Bublitz, S.G. Boxer, J.W. Perry, S.R. Marder, J. Am. Chem. Soc. 121 (1999) 3715.

[8] J. Heck, S. Dabeck, T. Meyer-Fridrichsen, H. Wong, Coord. Chem. Rev. 190-192 (1999) 1217.

[9] (a) I.S. Lee, H. Seo, Y.K. Chung, Organometallics 18 (1999) 1091. (b) V. Cadierno, S. Conejero, M.P. Gamasa, J. Gimeno, I. Asselberghs, S. Houbrechts, K. Clays, A. Persoons, J. Borge, S. García-Granda, Organometallics 18 (1999) 582. (c) U. Behrens, H. Brussard, U. Hagenau, J. Heck, E. Hendrickx, J. Kornich, J.G.M. Van der Linden, A. Persoons, A.L. Spek, N. Veldman, B. Voss, H. Wong, Chem. Eur. J. 2 (1996) 98. (d) U. Hagenau, J. Heck, E. Hendrickx, A. Persoons, T. Schuld, H. Wong, Inorg. Chem. 35 (1996) 7863; 35 (1996) 7863. (e) R. Loucif-Saiba, J.A. Delaire, L. Bonazzola, G. Doisneau, G. Balavoine, T. Fillebeen-Khan, L. Ledoux, G. Puccetti, Chem. Phys. 167 (1992) 369. (f) S. Houbrechrts, K. Clays, A. Persoons, V. Cadierno, M.P. Gamasa, J. Gimeno, Organometallics 15 (1996) 5266.

[10] (a) G.G.A. Balavoine, J.C. Daran, G. Iftime, P.G. Lacroix, E. Manoury, A. Delaire, I.J. Maltey-Fanbton, K. Nakatani, Organometallics 18 (1999) 21. (b) M.M. Bhadbhade, A. Das, J.C. Jeffrey, J.A. McCleverty, J.A. Navas-Badiola, M.D. Ward, J. Chem. Soc. Dalton Trans. (1995) 2769. (c) K.R.J. Thomas, J.T. Lin, Y.S. Wen, J. Organomet. Chem. 575 (1999) 301. (d) H.E. Bunting, M.L.H. Green, S.R. Marder, M.E. Thompson, D. Bloor, P.V. Kolinsky, R.J. Jones, Polyhedron 11 (1992) 1489.

[11] (a) A. Houlton, J.R. Miller, J. Silver, N. Jassim, T.L. Axon, D. Bloor, G.H. Cross, Inorg. Chim. Acta 205 (1993) 67. (b) J.C. Calabrese, L. Cheng, J.C. Green, S.R. Marder, W. Tam, J. Am. Chem. Soc. 113 (1991) 7227. (c) A. Houlton, N. Jasim, R.M.G. Roberts, J. Silver, D. Cunningham, P. McArdle, T. Higgins, J. Chem. Soc. Dalton Trans. (1992) 2235.

[12] J.K. Lee, R.R. Schrock, D.R. Baigent, R.H. Friend, Macromolecules 28 (1995) 1966.

[13] (a) J. Boutagy, R. Thomas, Chem. Rev. 74 (1974) 87. (b) W.S. Jr. Wadsworth, Org. React. 25 (1997) 73. (c) B.E. Maryanoff, A.B. Reitz, Chem. Rev. 89 (1989) 863. (d) M.S. Paley, J.M. Harris, J. Org. Chem. 56 (1991) 368.

[14] (a) E. Peris, J.A. Mata, V.J. Moliner, J. Chem. Soc. Dalton Trans. (1999) 3898. (b) P.S. Bratterman, Metal Carbonyl Spectra, Academic Press, New York, 1975.

[15] (a) J.T. Lin, S.S. Sun, L. Lee, K.J. Lin, Y.F. Huang, Inorg. Chem. 34 (1995) 2323. (b) V. Alain, A. Fort, M. Barzoukas, C.T. Chen, M. Blanchard-Desce, S. Marder, J.W. Perry, Inorg. Chim. Acta 97 (1996) 43.

[16] (a) J.S. Schumm, D.L. Pearson, J.M. Tom, Angew. Chem. Int. Ed. Engl. 33 (1994) 1360. (b) R.P. Hsung, C.E.D. Chidsey, L.R. Sita, Organometallics 14 (1995) 4808.

[17] J.A. Mata, S. Uriel, R. Llusar, E.V. Peris, Organometallics 19 (2000) 3797.

[18] C. Runser, A. Fort, M. Barzoukas, C. Combellas, C. Suba, A.R. Thiebault Graff, J.P. Kintzinger, Chem. Phys. 193 (1995) 309.

[19] S. Toma, A. Gaplovsky, P. Elecko, Chem. Papers 39 (1985) 115.