

Synthesis and characterization of new ferrocenyl heterobimetallic compounds with high NLO responses

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Abstract

Several ferrocenyl based heterobimetallic compounds have been obtained and characterized, and their NLO responses have been measured. We find that the observed β values are among the highest of the organometallic based materials reported up to date.
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1. Introduction

In the last ten years, the incorporation of metals to NLO systems have given a new dimension to the study and design of new chromophores [1]. Although a large number of organometallic complexes have been studied, just a few examples can be found in which clear design criteria are applied for the optimization of the nonlinear responses [2]. It has been stated that the use of organometallic compounds in NLO has a wide fan of advantages [1] that make them appropriate in the field of non linear optics. One of these advantages is that the electronic properties of the metal fragment can be tuned, so that the NLO response can be modulated. The use of heterobimetallic organometallic complexes in which the electron-accepting and donating properties of two organometallic fragments are combined in order to obtain high first hyperpolarizabilities is rare, and only recently some examples have been reported [3]. The introduction of two metal centres in the NLO

chromophore can allow us to tune both, electron-donor and electron-acceptor fragments by modifying their electronic properties.

In the search of new combinations of organometallic fragments we have chosen a typical donor fragment (ferrocene), and a series of electron accepting moieties derived from $M(CO)_6$ ($M = Cr$ or Mo). The ferrocenyl ligands were prepared according to conventional organic synthesis, and we have developed a synthetic route to ligands with long conjugated chains. We have studied the electrochemical properties of our compounds and relate them to their NLO responses. These bimetallic compounds exhibit static hyperpolarizabilities up to 164×10^{-30} esu, the largest measured to date for ferrocenyl derivatives.

2. Experimental section

2.1. General details

All reactions were carried out under a nitrogen atmo-

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sphere 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 Alumina columns.

Compound **1** was obtained according to literature methods [4]. We report modified methods to the obtainment of compounds **2** [5], **5**, **8** and **9** [6] in which we have simplified the work up and improved the yields.

Proton-NMR spectra were recorded on a Varian Gemini 200 MHz, using CDCl_3 as solvent unless otherwise stated. IR spectra were recorded on a Perkin Elmer System 2000 FT-IR using NaCl pellets. Cyclic voltammetry experiments were performed with a ECHOCHEMIE PGSTAT 20 electrochemical analyzer. All measurements were carried out at room temperature 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 from sds. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate, obtained from Sigma or 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 potentials reported are not corrected for the junction potential.

2.2. NLO measurements

Details of the HRS set-up have been discussed previously [7,8]. All measurements are performed in chloroform and the known hyperpolarizability of para-nitroaniline in this solvent (23×10^{-30} esu) is used as a reference [9]. The samples are passed through a 0.45 μm filter for contaminated samples often produce spurious signals, and are checked for multiphoton fluorescence that can interfere with the HRS signal [10–12]. IR-laser pulses generated with an injection seeded, Q-switched Nd:YAG laser (Quanta-Ray GCR-5, 1064 nm, 10 ns pulses, 10 Hz) are focused into a cylindrical cell containing the solution (7 ml). The fundamental intensity is altered by rotation of a half-wave plate placed between crossed polarizers, and measured with a photodiode. An efficient condenser system is used to collect the light scattered at the harmonic frequency (532 nm) that is detected by a photomultiplier. Discrimination of the second-harmonic light from the fundamental light is accomplished by a low-pass filter and a 532 nm interference filter. Actual values for the intensities are retrieved by using gated integrators. In all experiments the incident light was vertically polarized along the z axis.

2.3. Syntheses of the ferrocenyl ligands **3**, **5** and **9**

To an ice-cold solution of (1-(triphenylphosphinomethyl)ferrocenyl)iodine (3 g, 5.1 mmol) in THF (50 ml) was added potassium tert-butoxide (850 mg, 7.6 mmol) and the resulting solution stirred for 30 min to form the ylide. The corresponding aldehyde, *t*-cyanamaldehyde (2.5 ml, 20.4 mmol for the synthesis of **3**), 4-pyridinecarboxaldehyde (1.5 ml, 15.3 mmol for the synthesis of **5**) and 4-cyanobenzaldehyde (1.2 g, 15.3 mmol for the synthesis of **9**), 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 and purified by column chromatography on silica gel with hexane/ CH_2Cl_2 (8:2) for compound **3** and hexane/ CH_2Cl_2 /acetone (12:8:1) for compounds **5** and **9** as eluent. Recrystallization from CH_2Cl_2 /hexane mixtures afforded pure compounds. Yields: 47% (for **3**), 60% (for **5**), 44% (for **9**). Proton-NMR spectrum for compound **3**: δ 7.41–7.18 (m, 5H, C_6H_5), 6.88–6.76 (m, 2H, $\text{CH}=\text{CH}$); 6.60–6.36 (m, 2H, $\text{CH}=\text{CH}$); 4.37 (s, 2H, C_5H_4); 4.25 (s, 2H, C_5H_4); 4.09 (s, 5H, C_5H_5); Proton-NMR spectrum for compound **5**: δ 8.45 (d, 2H, $^3J_{\text{H-H}} = 5.04$ Hz, $\text{C}_5\text{H}_4\text{N}$); 7.21 (d, 2H, $^3J_{\text{H-H}} = 5.88$ Hz, $\text{C}_5\text{H}_4\text{N}$); 7.06 (d, 1H, $^3J_{\text{H-H}} = 16.12$ Hz, $\text{CH}=\text{CH}$); 6.53 (d, 1H, $^3J_{\text{H-H}} = 16.08$, $\text{CH}=\text{CH}$); 4.43 (s, 2H, C_5H_4); 4.29 (s, 2H, C_5H_4); 4.09 (s, 5H, C_5H_5); Proton-NMR spectrum for compound **9**: δ 7.53 (d, 2H, $^3J_{\text{H-H}} = 8.43$ Hz, C_6H_4); 7.42 (d, 2H, $^3J_{\text{H-H}} = 8.36$ Hz, C_6H_4); 7.20 (CDCl_3); 6.96 (d, 1H, $^3J_{\text{H-H}} = 16.12$ Hz, $\text{CH}=\text{CH}$); 6.60 (d, 1H, $^3J_{\text{H-H}} = 16.14$ Hz, $\text{CH}=\text{CH}$); 4.43 (s, 2H, C_5H_4); 4.29 (s, 2H, C_5H_4); 4.09 (s, 5H, C_5H_5). Elemental Anal. Calc. for compound **3**, $\text{C}_{20}\text{H}_{18}\text{Fe}$, Mw = 314.21: C, 76.5; H, 5.8. Found: C, 76.6; H, 6.0. Elemental Anal. Calc. for compound **5**, $\text{C}_{17}\text{H}_{15}\text{FeN}$, Mw = 289.26: C, 70.6; H, 5.2; N, 4.8. Found: C, 71.1; H, 5.0; N, 4.8. Elemental Anal. Calc. for compound **9**, $\text{C}_{19}\text{H}_{15}\text{FeN}$, Mw = 313.18: C, 72.9; H, 4.8; N, 4.5. Found: C, 72.1; H, 5.0; N, 4.4.

2.4. Syntheses of **2** and **4**

$\text{Cr}(\text{CO})_6$ (500 mg, 2.3 mmol) and compound **1** (265 mg, 0.9 mmol) or compound **3** (283 mg, 0.9 mmol) were refluxed in buthyl ether (40 ml) overnight. After cooling the mixture to r.t., the solution was filtered and the solvent removed under reduced pressure. Purification by column chromatography on alumina with CH_2Cl_2 /hexane (4:1) afforded pure compounds **2** (Yield: 45%) and **4** (Yield: 57%). Proton-NMR spectrum for compound **2**: δ 6.82 (d, 1H, $^3J_{\text{H-H}} = 16.25$ Hz, $\text{CH}=\text{CH}$), 6.20 (d, 1H, $^3J_{\text{H-H}} = 16.16$ Hz, $\text{CH}=\text{CH}$); 5.47 (s, 5H, C_5H_5); 4.44 (s, 2H C_5H_4); 4.34 (s, 2H C_5H_4); 4.18 (s,

5H, C₅H₅); Carbon-NMR spectrum for compound **2**: δ 233.30 (3C, CO); 130.52 (1C, CH=CH); 121.24 (1C, CH=CH); 107.66 (1C, C₆H₅); 93.42 (2C, C₆H₅); 90.56 (1C, C₆H₅); 89.87 (2C, C₆H₅); 81.27 (1C, C₅H₄); 69.78 (2C, C₅H₄); 69.56 (5C, C₅H₅); 67.30 (2C, C₅H₄). Proton-NMR spectrum for compound **4**: δ 6.4–6.6 (m, CH=CH); 6.45 (d, 1H, $^3J_{\text{H-H}} = 16.16$ Hz, CH=CH); 6.05 (d, 1H, $^3J_{\text{H-H}} = 16.16$ Hz, CH=CH); 5.15–5.50 (m, 5H, C₆H₅); 4.37 (s, 2H C₅H₄); 4.27 (s, 2H C₅H₄); 4.18 (s, 5H, C₅H₅). Carbon-NMR spectrum for compound **4**: δ 233.24 (3C, CO); 134.83 (1C, CH=CH); 132.37 (1C, CH=CH); 125.31 (1C, CH=CH); 125.18 (1C, CH=CH); 107.13 (1C, C₆H₅); 82.03 (1C, C₅H₄); 69.46 (2C, C₅H₄); 69.21 (5C, C₅H₅); 67.21 (2C, C₅H₄). Elemental Anal. Calc. for compound **2**, C₂₁H₁₆FeO₃Cr, Mw = 424.20: C, 59.5; H, 3.8. Found: C, 59.3; H, 3.5. Elemental Anal. Calc. for compound **4**, C₂₃H₁₈FeO₃Cr, Mw = 450.24: C, 61.4; H, 4.0. Found: C, 61.2; H, 4.4.

2.5. Syntheses of **6** and **10**

Cr(CO)₆ (176 mg, 0.8 mmol) and Me₃NO (88.9 mg, 0.8 mmol) were dissolved in THF (20 ml) and the resulting solution was stirred for 20 min. Compound **5** (231 mg, 0.8 mmol) or compound **9** (250 mg, 0.8 mmol) was then added to the above solution for the preparation of **6** or **10**, respectively. The reaction mixture was stirred for another 20 min, the solution was filtered and the solvent removed under reduced pressure. Purification by column chromatography on alumina with CH₂Cl₂/hexane (1:1) afforded pure compounds **6** (Yield: 40%) and **10** (Yield: 20%). Proton-NMR spectrum for compound **6**: δ 8.34 (d, 2H, $^3J_{\text{H-H}} = 5.7$ Hz, C₅H₄N); 7.08 (d, 2H, $^3J_{\text{H-H}} = 5.9$ Hz, C₅H₄N); 7.13 (d, 1H, $^3J_{\text{H-H}} = 16.08$ Hz, CH=CH); 6.46 (d, 1H, $^3J_{\text{H-H}} = 16.1$, CH=CH); 4.45 (s, 2H C₅H₄); 4.35 (s, 2H, C₅H₄); 4.09 (s, 5H, C₅H₅); Carbon-NMR spectrum for compound **6**: δ 214.55 (1C, *trans* CO); 211.53 (4C, *cis* CO); 155.29 (2C, Py); 146.30 (1C, Py); 135.65 (2C, Py); 120.86 (2C, CH=CH); 80.96 (1C, C₅H₄); 70.52 (2C, C₅H₄); 69.54 (5C, C₅H₅); 67.85 (2C, C₅H₄); Proton-NMR spectrum for compound **10**: δ 7.52 (d, 2H, $^3J_{\text{H-H}} = 8.07$ Hz, C₆H₄); 7.41 (d, 2H, $^3J_{\text{H-H}} = 8.10$ Hz, C₆H₄); 6.96 (d, 1H, $^3J_{\text{H-H}} = 15.98$ Hz, CH=CH); 6.60 (d, 1H, $^3J_{\text{H-H}} = 16.12$, CH=CH); 4.43 (s, 2H, C₅H₄); 4.29 (s, 2H, C₅H₄); 4.09 (s, 5H, C₅H₅); Carbon-NMR spectrum for compound **10**: δ 219.41 (1C, *trans* CO); 214.05 (4C, *cis* CO); 143.31 (1C, C₆H₄); 132.78 (2C, C₆H₄); 128.97 (1C, C₆H₄); 126.20 (2C, C₆H₄); 123.95 (1C, CH=CH); 123.60 (1C, CH=CH); 107.86 (1C, CN); 81.71 (1C, C₅H₄); 70.10 (2C, C₅H₄); 69.89 (5C, C₅H₅); 67.53 (2C, C₅H₄). Elemental Anal. Calc. for compound **6**, C₂₂H₁₅NFeO₅Cr, Mw = 481.21: C, 54.9; H, 3.1; N, 2.9. Found: C, 54.3; H, 3.5; N, 3.1. Elemental Anal. Calc. for compound **10**, C₂₄H₁₅NFeO₅Cr, Mw = 505.23: C, 57.1; H, 3.0; N, 2.8. Found: C, 57.3; H, 3.4; N, 2.9.

2.6. Syntheses of **7**, **8** and **11**

Compounds **7**, **8** and **11** were prepared by the same general method than **6** and **10** from Mo(CO)₆ and W(CO)₆, respectively. Yield for **7**, 10%, yield for **8**, 63% and yield for **11**, 25%. Proton-NMR spectrum for compound **7**: δ 8.41 (d, 2H, $^3J_{\text{H-H}} = 6.23$ Hz, C₅H₄N); 7.08 (d, 2H, $^3J_{\text{H-H}} = 5.9$ Hz, C₅H₄N); 7.13 (d, 1H, $^3J_{\text{H-H}} = 16.08$ Hz, CH=CH); 6.46 (d, 1H, $^3J_{\text{H-H}} = 16.1$, CH=CH); 4.45 (s, 2H, C₅H₄); 4.35 (s, 2H, C₅H₄); 4.09 (s, 5H, C₅H₅); Carbon-NMR spectrum for compound **7**: δ 214.57 (1C, *trans* CO); 204.50 (4C, *cis* CO); 154.78 (2C, Py); 146.30 (1C, Py); 135.65 (2C, Py); 120.86 (2C, CH=CH); 80.96 (1C, C₅H₄); 70.52 (2C, C₅H₄); 69.54 (5C, C₅H₅); 67.85 (2C, C₅H₄); Proton-NMR spectrum for compound **8**: δ 8.54 (d, 2H, $^3J_{\text{H-H}} = 6.5$ Hz, C₅H₄N); 7.27 (d, 1H, $^3J_{\text{H-H}} = 16.5$ CH=CH); 7.23 (2H, $^3J_{\text{H-H}} = 6.6$ Hz, C₅H₄N); 6.49 (d, 1H, $^3J_{\text{H-H}} = 16.4$ Hz, CH=CH); 4.47 (s, 2H, C₅H₄); 4.37 (s, 2H, C₅H₄); 4.10 (s, 5H, C₅H₅); Proton-NMR spectrum for compound **11**: δ 7.56 (d, 2H, $^3J_{\text{H-H}} = 8.06$ Hz, C₆H₄); 7.47 (d, 2H, $^3J_{\text{H-H}} = 8.16$ Hz, C₆H₄); 7.04 (d, 1H, $^3J_{\text{H-H}} = 16.10$ Hz, CH=CH); 6.61 (d, 1H, $^3J_{\text{H-H}} = 16.02$, CH=CH); 4.45 (s, 2H, C₅H₄); 4.33 (s, 2H, C₅H₄); 4.11 (s, 5H, C₅H₅); Carbon-NMR spectrum for compound **11**: δ 199.92 (1C, *trans* CO); 196.11 (4C, *cis* CO); 143.45 (1C, C₆H₄); 132.85 (2C, C₆H₄); 125.95 (2C, C₆H₄); 125.01 (1C, C₆H₄); 123.18 (2C, CH=CH); 106.56 (1C, CN); 81.29 (1C, C₅H₄); 69.87 (2C, C₅H₄); 69.19 (5C, C₅H₅); 67.26 (2C, C₅H₄). Elemental Anal. Calc. for compound **7**, C₂₂H₁₅NFeO₅Mo, Mw = 525.15: C, 50.3; H, 2.9; N, 2.7. Found: C, 51.3; H, 3.4; N, 2.8. Elemental Anal. Calc. for compound **8**, C₂₂H₁₅NFeO₅W, Mw = 613.06: C, 43.1; H, 2.5; N, 2.3. Found: C, 43.7; H, 2.5; N, 2.1. Elemental Anal. Calc. for compound **11**, C₂₄H₁₅NFeO₅W, Mw = 637.08: C, 45.2; H, 2.4; N, 2.2. Found: C, 44.3; H, 2.3; N, 2.1.

3. Results and discussion

3.1. Synthesis and characterization of the ferrocenyl compounds

The new ferrocenyl compounds were prepared by conventional organic synthetic procedures (Wittig reactions), or modification of the literature methods. All the compounds were characterized by means of IR-, ¹H- and ¹³C-NMR spectroscopy and satisfactory microanalyses. The π bonded η^6 compounds (**2** and **4**) were obtained refluxing the corresponding ferrocenyl ligands (**1** or **3**) with chromium hexacarbonyl for 12 h in butyl ether. Fig. 1 shows the general procedure to the obtention of compounds **2**, **4**, **5**–**11**. The coordination of the ferrocenyl cyano and pyridyl derivatives were carried out by previously reacting Me₃NO with the correspond-

expected from the longer conjugated chain of **3**). The rest of the compounds show half wave potentials for the ferrocene center, that are higher than that shown for ferrocene, meaning that ferrocenyl ligands connected to electronegative/electron-accepting fragments show some electron transfer between the iron and the pyridyl or cyano fragments. Coordination to the metal carbonyl implies an additional increase on the half wave potential of the ferrocene center in all the cases, indicating that the carbonyl metal attached to the ferrocenyl ligands promotes an additional increase of the electron transfer in the direction $\text{Fe} \rightarrow \text{M}(\text{CO})_n$. On the other hand, the second oxidation step for **2** and **4** displays complete electrochemical irreversibility with an anodic peak potential $E_{\text{p,a}}$ showing a slight cathodic shift with respect to $E_{1/2}$ for $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$, in spite of the positive charge in **2**⁺ and **4**⁺.

In contrast, the cyclic voltammetric experiments for $\text{CpFe}(\eta^5\text{-C}_5\text{H}_4)\text{-CH=CH-py-Cr}(\text{CO})_5$ (**6**) show two electrochemical quasireversible oxidation waves. Both processes are coupled with a reduction on the reverse sweep. The peak separation, 75 and 77 mV, and the virtually equal peak currents suggest that we are observing two quasireversible one-electron oxidations. The half wave potential $E_{1/2}$ for **6**⁺/6 shows an anodic shift of 30 mV relative to that of **5**⁺/5 as expected based on the electron-withdrawing nature of the $(\text{C}_6\text{H}_5)\text{Cr}(\text{CO})_3$ moiety. Compounds **7** and **8** display complete electrochemical irreversibility for the oxidation of Mo and W respectively, as reported previously for **8** ([5]b).

The chromium based compound **10**, shows two electrochemical quasireversible oxidation waves. Both processes are coupled with a reduction on the reverse sweep. The related tungsten based compound **11**, displays complete electrochemical irreversibility for the oxidation of W. This result is consistent with those

Table 1
Cyclic voltammetric data for compounds **1–11**

Compound	$E_{1/2}(\text{V})$ (ΔE_{p} (mV)) Fe-based	$E_{1/2}(\text{V})$ (ΔE_{p} (mV)) M-based ^a
Ferrocene	0.446 (106)	—
1	0.440 (85)	—
2	0.481 (74)	0.808 ^b
3	0.436 (87)	—
4	0.448 (91)	0.784 ^b
5	0.498 (70)	—
6	0.520 (75)	0.928 (77)
7	0.518 (83)	1.110 ^b
8	0.530 (77)	1.125 ^b
9	0.482 (82)	—
10	0.499 (72)	0.981 (66)
11	0.495 (68)	1.146 ^b

^a M = Cr, Mo, W.

^b Irreversible peak, measured at 100 mV s^{−1}.

Table 2

Experimental nonlinear response of the compounds synthesised previously; ^a β and β_0 in 10^{-30} esu

Compound	λ_{max} (nm)	β	β_0^b
2	304	193	119
4	334	300	164
5	468	21	4
6	401	63	23
7	487	95	12
8	491	101	12
9	473	203	34
10	481	271	39
11	487	375	48

^a Measured in chloroform by the HRS method and calculated with respect to β of PNA in chloroform (23×10^{-30} esu). HRS at 1.06 mm. Values $\pm 15\%$.

^b Calculated from the two level model.

studies reported before where chromium and tungsten ferrocenyl derivatives show quasireversible and complete irreversible oxidation waves respectively [5,13].

3.3. NLO properties

The UV–vis spectra of compounds **1–11** show low absorption in the region where second harmonic is generated (1064 nm) in the solvent where the nonlinear response was studied by the hyper Rayleigh scattering method (chloroform). Table 2 shows the values of β obtained for compounds **1–11**. These values are comparable in magnitude to those obtained for the bimetallic cationic compounds reported by Heck et al. ([3]a,b). The simple two-level method allowed us to calculate the static hyperpolarizabilities, β_0 ; for compounds **7–11**, the differences between β and β_0 are rather large because the maximum of absorption of these compounds are relatively close to 532 nm. Since the molecules that we have studied display several optical transitions, the static hyperpolarizabilities given are only a crude estimation. In their estimations (two level model) we have only taken into account the transition closest to the harmonic frequency, and damping has been neglected. Compounds **2**, **4**, **6**, **7**, **8**, **10** and **11**, being a combination of two neutral fragments show the electron-accepting capability of the chromium carbonyl moiety through both π - and a σ -bonding to the electron donating ferrocene derivative. It is noteworthy pointing out that previous studies have shown that a series of $(\eta^6\text{-arene})\text{tricarboxylchromium}$ derivatives show low values of β ([2]d), while σ -bonded derivatives of $(\text{CO})_5\text{Cr}(p\text{-X-py})$ (X = H, NH₂, C₆H₅, CHO, COCH₃) gave interesting results [14]. Compound **9** shows a higher value of β than **5**, probably because of the longer chain separating the donor and acceptor fragments. As seen from Table 2, π -donation affords a much higher value of the hyperpolarizability than that shown of the ligands upon σ -donation. The result can

be interpreted in terms of the linkage to the carbonyl fragment. In the case of the π -bonded compounds (**2** and **4**), the orbitals participating in the conjugated delocalization of the charge are the same used in the formation of the bond to chromium. The lower increase of β in the σ -bonded complexes can be explained in terms of the role of the metal in lowering the energy of the pyridyl acceptor orbital and this way to increase the accepting properties of the pyridyl ligand [15].

There is a considerable increase in the value of β when we change the metal, in the order $W > Mo > Cr$, probably due to the decrease of the Pauling electronegativity in the same direction and to the higher backdonation capability of W compared to Cr and Mo. As we have previously mentioned, all the ferrocenyl-metalcarbonyl compounds that we report in the present work, show higher half wave potentials (based on the iron center), than that shown for ferrocene. We interpret this result as a consequence of a partial charge transfer to the metalcarbonyl fragment.

In summary, we have presented a series of heterobimetallic compounds showing large values of β . These compounds are easy-to-make, stable and soluble in most common organic solvents, showing low absorption in the second harmonic generation region. The electronic and optical properties of these compounds can be easily tuned by modifying the chainlength, bonding to the metal and change of the metal.

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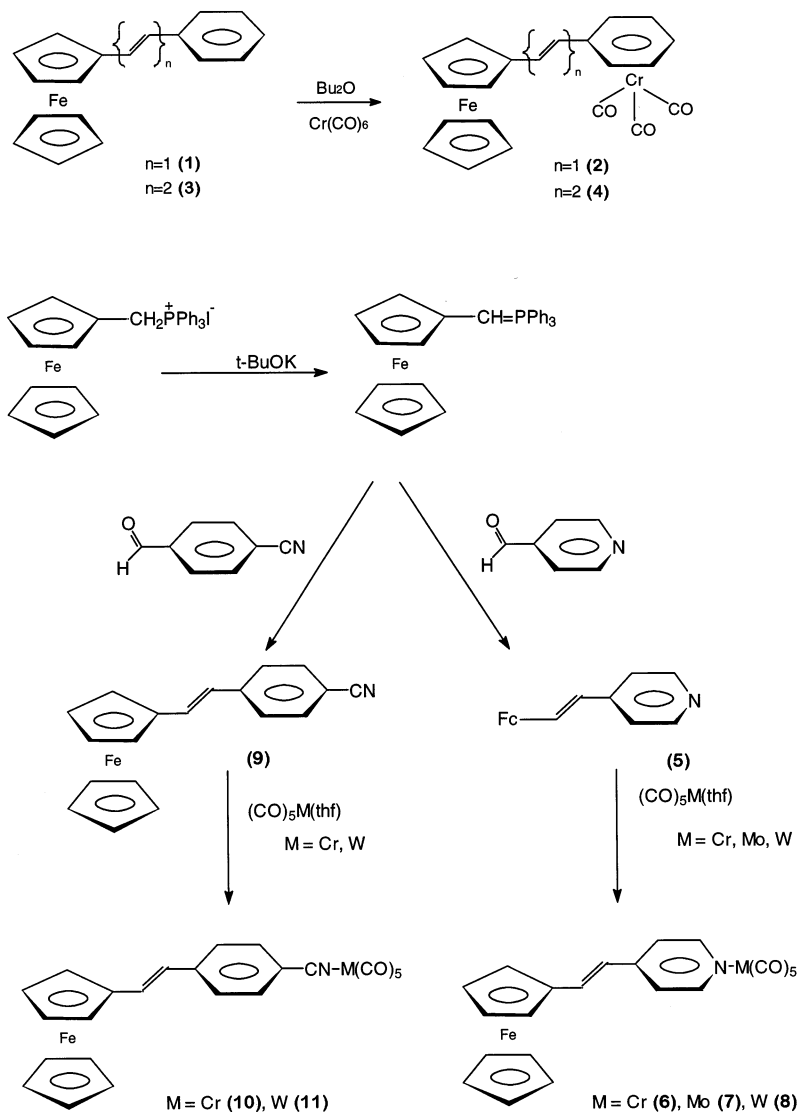


Fig. 1. Reaction scheme for the syntheses of compounds 2, 4, 5–11.

ing metal hexacarbonyl, and then adding the ferrocenyl ligand. This method showed better results than any other photochemical or thermal reaction used.

The pyridyl and cyano ferrocenyl ligands were obtained in moderate high yields, with high selectivities on the trans isomers, as stated in Section 2.

Comparison of the IR spectra of the σ -bonded cyano and pyridyl ferrocene derivatives (6, 7, 8, 10, 11) shows that the compounds containing W have lower values of $\nu(\text{CO})$, meaning that W is more capable than Cr and Mo of reducing its electron density by π back-donation to CO. As we comment in the NLO section, this fact supports the observation of the larger hyperpolarizabilities found for our compounds containing W. Similar results have been reported for group 6 metal Fischer type carbenes [14].

3.2. Cyclic voltammetry

Electrochemical data obtained for the compounds studied are summarized in Table 1.

Cyclic voltammetric investigations for the ferrocene derivatives $\text{CpFe}(\eta^5\text{-C}_5\text{H}_4)\text{-(CH=CH)-(C}_6\text{H}_5)$ (1), $\text{CpFe}(\eta^5\text{-C}_5\text{H}_4)\text{-(CH=CH)}_2\text{-(C}_6\text{H}_5)$ (3), $\text{CpFe}(\eta^5\text{-C}_5\text{H}_4)\text{-(CH=CH)-py}$ (5) and $\text{CpFe}(\eta^5\text{-C}_5\text{H}_4)\text{-(CH=CH)-(C}_6\text{H}_4\text{)-CN}$ (9) show a redox behavior analogous to the one observed for ferrocene, that is, an electrochemically quasireversible one-electron oxidation.

The half wave potential of the quasireversible wave for compounds 1 and 3 is slightly lower than that shown for ferrocene, indicating that the oxidation is favoured by the delocalization of the charge along the conjugated system of the ligand ($E_{1/2}(\text{3}) < E_{1/2}(\text{1})$), as