4 | Conclusions

Synthesis:

• New synthetic routes have been developed for the obtaining of a series of compounds based in polychlorotriphenylmethyl radicals connected to metallocene units (ferrocene or ruthenocene). Following this approach, radicals **1-5,** biradicals **7-9** and triradical **10** have been obtained and studied.

• Chemical, structural, magnetic, spectroscopic and electrochemical properties of the aforementioned radicals have been studied, proving that it is possible their tuning by changing the donor ability of the metallocence unit, the acceptor ability of the radical unit and the nature of the bridge. The donor ability of the metallocene unit has been modified by including methyl groups. The acceptor ability of the radical unit by varying the number of chlorines atoms onto the aromatic rings.

Magnetism:

• Magnetic properties of the monoradicals **1-5** have been studied by EPR and SQUID. From the magnetic susceptibility data we have found that monoradicals **1-3** and **5** present outsized values of magnetization at room temperature that exhibits field-dependence, fact that has been tentatively ascribed to significant orbital contributions of the Fe(III) fraction over the spin value.

• Magnetic properties of biradicals **7-9** have been studied by EPR and SQUID. From this data, it is concluded that the 1,1'-ferrocenylene bridge acts as a ferromagnetic coupler between the two radical units connected to it. When the ferrocene unit is substituted with methyl groups or it is changed for a ruthenocene unit, the magnetic exchange vanishes showing a paramagnetic behaviour in all the temperature range.

• The photoinduced isomerization of radicals *trans*-**3** to *cis*-**5** has been monitored by UV/Vis and EPR spectrosocopy and also followed by HPLC chromatography. From this study it is possible to conclude that a one-way photoinduced self-assembly process has been established. This represents an interesting example of a photomagnetic system based on a

supramolecular phenomenon in which a doublet species is converted into a singlet one. Such results have also been validated by ab-initio calculations.

Electronic Properties:

- Ferrocene-polychlorotriphenylmethyl radicals present intramolecular electron transfer phenomenon in solution and in solid state. As a consequence, they exhibit an intense broad near-IR band, which it is attributed to an intramolecular electron transfer transition from the ferrocenyl moiety to the PTM radical. The energy of the intramolecular electron transfer phenomena can be easily tuned by changing the substitutents of the donor or acceptor units or even the nature of the solvent.

- The study of intramolecular electron transfer phenomena in ferrocene-based polychlorotriphenylmethyl radicals allowed us to establish for the first time a novel valence tautomeric example combining an organic radical as acceptor unit and a ferrocene unit as the donor group.

- Picosecond time resolved absorption spectroscopy measurements for radicals **1** and **2** permitted us to monitor the charge separation state that confirms the presence of photoinduced electron transfer phenomena. The lifetime of such charge separation state decreases with increasing the polarity of the medium.

Nonlinear Optical Properties:

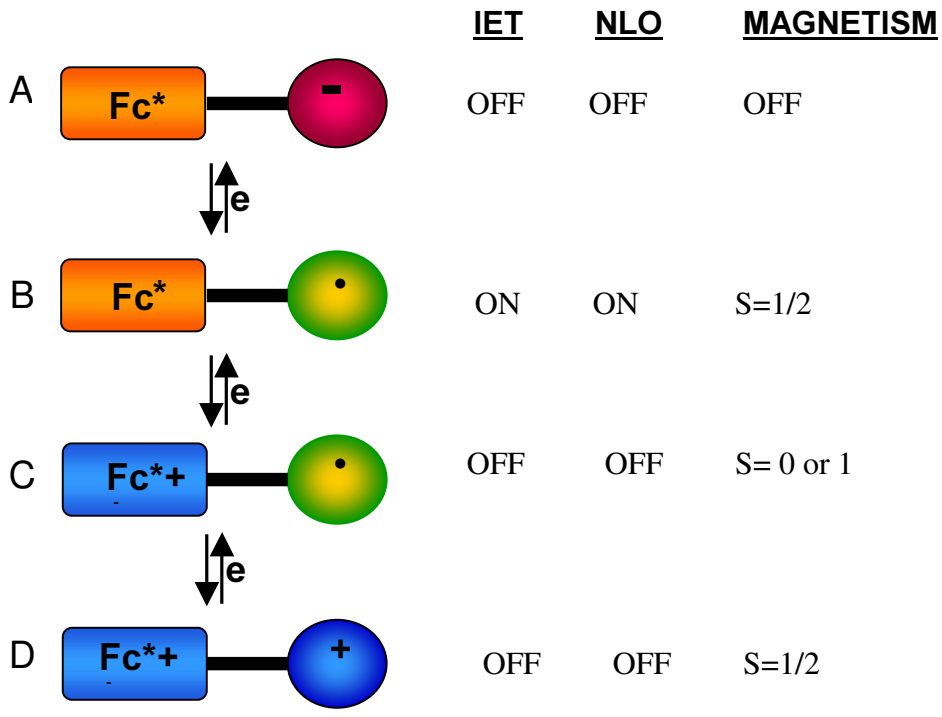
- Polychlorotriphenylmethyl radicals **30**-**35, 12** and **15** constitute a unique example of open-shell series that combines both, high NLO responses and good chemical, thermal, and photo-optical stabilities, thanks to their octupolar character.

- Ferrocene-based polychlorotriphenylmethyl radicals are push-pull systems exhibiting intense NLO responses that can be modulated at will simply tuning the donor and acceptor capabilities of the ferrocene and radical units.

New Perspectives

As, magnetic, NLO and IET phenomena are intrinsically present in the compounds presented in this thesis and considering the great interest in the development of molecular electronic devices that can be used as optical and/or magnetic data storage or processing media, it will be interesting the establishment of new multistate multifunctional molecular switching devices with these compounds based in a ferrocene unit connected to polychlortriphenymethyl radicals. Two kinds of molecular switching devices are expected: 1) *electrochemical* or 2) *photochemical*

1) *Electrochemical switch*:

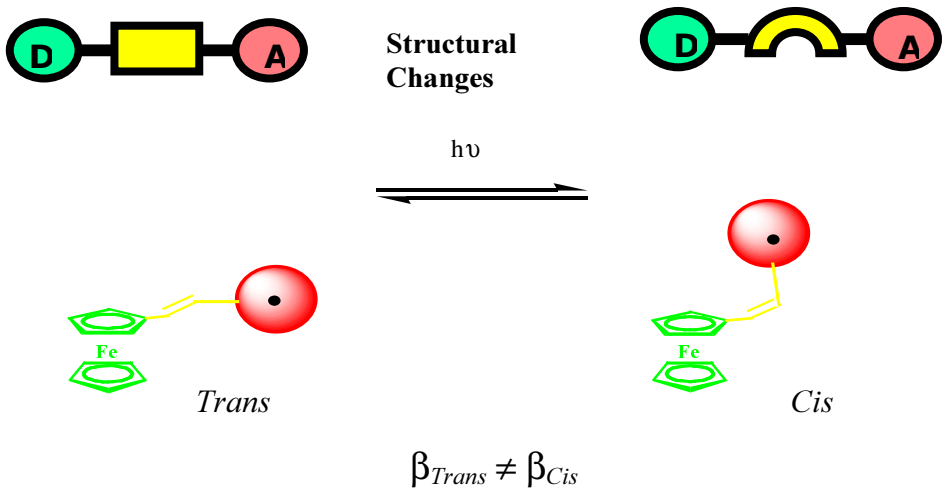


Using the redox properties of both, the ferrocene and radical units, it would be possible to establish an array of four states, with different electric, optical and magnetic properties that interconvert reversibly by an external electrochemical stimulus. Indeed, compound A, which is not expected to exhibit optical nor magnetic properties, can be oxidized to generate the ferrocene based radical B, which in addition to be a paramagnetic species must exhibit NLO responses as well as IET. Further oxidation of compound B would lead to a decrease of the NLO response of the complex since the ferricinium cation is not any more a donor species. However, the interest for complex C increases if we consider that both, the ferricinium cation and the radical unit, are open-shell species that are expected to be magnetically coupled through the vinylene bridge. Finally, oxidation of the radical unit of C to its corresponding cationic form will yield to a S=1/2 species like D with non NLO properties nor IET phenomena.

It is important to say that this fourtates array can be considered as an electrochromic system since all the complexes involved would exhibit different colours according with the presence of different chromophores. The colours tend to indicate the colour for each chormophore: violet for the anion, blue for the ferricinium, and dark green for the radical.

2) *Photochemical switch*

There is another strategy for a molecular switch, which can be used in a future. It can be applied in systems like the ones presented in this Thesis. For instance, in the case of the ferrocene schiff based trichlorotriphenylmethyl radicals **3** and **5** a photochemical isomerization has already been studied. The response for the *cis* and *trans* isomers for schiff base or vinylene bridge compounds, such as the ones presented throughout this Thesis, in front of the three properties here studied (magnetic, NLO and IET) must be very different. If we are able to reversibly photoisomerize such compounds, for instance, *in situ* in the HRS apparatus, we will be able to switch "on" and "off" at will the NLO response.



$\beta_{Trans} \neq \beta_{Cis}$

5 Experimental Part

5.1 INSTRUMENTS AND MATERIALS. SOLVENT AND REAGENTS.

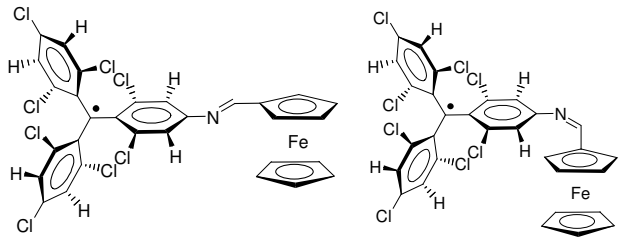
- *Elemental analysis* were obtained in the Servei d'anàlisis de la Universitat Autònoma de Barcelona (UAB).
- *UV-Vis and near-IR* were recorded using a Cary 5E Varian spectrophotometer.
- *IR spectrum* were recorded using a Perking Elmer spectrum one FT-IR Fourier transform spectrometer.
- *HPLC chromatography* was performed on a LC10-A Series spectrophotometer of Shimadzu equipped with a diode array detector (λ = 250-800nm), an external computer and a Perkin Elmer Series pump system. The inverse phase chromatographic columns were ODS-2 of Teknokroma.
- *Mass spectrometer*: Analytical Kompact LDI II from Kratos operating in pulsed ion extraction in positive mode and high power.
- *Electrochemical experiments* were performed with potenciostat Galvanostat 263A of EG&PAR, using a platinum wire as working electrode and a Ag/AgCl electrode as reference electrode. Anhydrous CH_2Cl_2 was freshly distilled over P_2O_5 under nitrogen. Commercial tetrabutylammonium hexafluorophosphate (Fluka, electrochemical grade) was used as the supporting electrolyte.
- *EPR spectra* were recorded on a Bruker ESP-300E spectrometer operating in the X-band (9.3 GHz). Signal-to-noise ratio was increased by accumulation of scans using the F/F lock accessory to guarantee a high-field reproducibility. Precautions to avoid undesirable spectral line broadening such as that arising from microwave power saturations and magnetic field over-modulation were taken. To avoid dipolar broadening, the solutions were carefully degassed three times using vacuum cycles with pure Argon. The g values were determined against the DPPH standard (g=2.0030). The program used to simulate the spectrum are WIN-EPR from Brucker Analytische Messtechnik Rheinstetten (Germany) and Sinfomia v.1.0 from Brucker Instruments Billerca, MA (USA).
- *SQUID:* Direct current (dc) magnetic susceptibility measurements were carried out on a Quantum Design MPMS SQUID susceptometer with a 55 KG magnet and operating in the range of 4-320K. All measurements were collected in a field of 10KG. Background correction data were collected from magnetic susceptibility measurements on the holder

capsules. Diamagnetic corrections estimated from the Pascal contents were applied to all data for determination of the molar paramagnetic susceptibilities of the compounds

- *Nuclear Magnetic Resonance (NMR) spectroscopy* measurements were carried out on a Bruker ARX 300MHz spectrometer using tetramethyl silane as intern reference.
- All solvents were reagent grade from SDS and were used as received and distilled otherwise indicated.
- All reagents, organic and inorganic, were of high purity grade and obtained from E. Merck, Fluka Chemie and Aldrich Chemical Co.

5.2 SYNTHESIS AND CHARACTERIZATION

5.2.1 Synthesis of (*trans*)-4-(ferrocenylimino)-2,6-(dichlorophenyl)bis(2,4,6-trichlorophenyl) methyl radical (3) and (*cis*)-4-(ferrocenylimino)- 2,6-(dichlorophenyl)bis(2,4,6-trichlorophenyl) methyl radical (5)



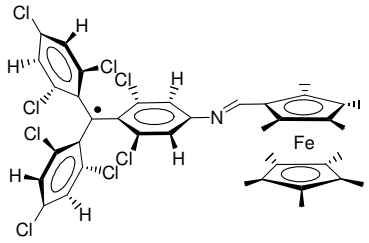
Reactants and Quantities:
200mg (0.37mmmol) of (4-amino-2,6 dichlorophenyl)bis(2,4,6-trichlorophenyl) methyl radical (**15**)
80mg (0.37mmol) of ferrocene monocarboxaldehyde
Molecular sieves
Toluene

Procedure: To a dry toluene solution of 200mg (0,37mmol) of (4-amino-2,6-dichlorophenyl)bis(2,4,6-trichlorophenyl)methyl radical, which was obtained as previously described,[1] was added 80mg of (0,37mg) ferrocene monocarboxaldehyde in the presence of molecular sieves. The mixture was heated up to 60ºC and stirred for 48h in the dark. The reaction is followed by silica thin layer chromatography first conditioned with a solution of 5% triethylamine (TEA), 72,5% carbon tetrachloride and 22,5% *n*-hexane and then eluted just with 75% carbonetetrachloride and 25% *n*-hexane. After removing the molecular sieves and evaporation of the solvent, a brown precipitate was obtained. This condensation reaction is not stereoselective; for this a mixture of *cis* (**5**) and *trans* (**3**) isomers was obtained. Compound **3** (50mg) was isolated as a dark brown microcrystalline material by crystallization from *n*-hexane with a yield of 20%, whereas 15mg of compound **5** was isolated as a dark green powder by flash chromatography, eluting with carbon tetrachloride, on a Florisil (magnesium silicate) column with a yield of 6%.

Characterization Data: [729.23 g/mol] *trans* (**3**): Anal. Calc. for $C_{30}H_{16}Cl_8FeN$: C, 49.4; H, 2.21; N, 1.90. Found C, 49.6; H, 1.8; N, 2.0 %. ν_{max}(KBr)/cm^{-1}: 3420, 2967, 2913, 1631, 1556, 1536, 1465, 1371, 1261, 1225, 1182, 1137, 1104, 1021, 858, 809. λ (methylcyclohexane)/nm (ε): 377 (20300), 409 (14900), 565 (1863). Cyclic Voltammetry in CH_2Cl_2 and tetrabutylammonium hydroxide as electrolyte: –0,661V, +0,609V and +1,054V vs Ag/AgCl. EPR (isotropic solution of toluene at 220K):

g=2,0030; hyperfine coupling constants: a(N)= 1,1837G; a($^{1}H_{meta}$)=1,0569G; a($^{1}H_{trans}$)=0,2453; a($^{13}C_{\alpha}$)=28,5G; a($^{13}C_{bridge}$)=12,5 and a($^{13}C_{ortho}$)=10,3G. Reverse phase HPLC: T=25ºC; Mobil phase: AcCN/THF; 70/30; flow: 1mL/min. Detectors at 220, 377, and 590nm: one peak at 7,9 min. EM-LDI-TOF (positive mode): m/z / amu/e- $M^{+\cdot}$: 729, $[M]^{+}$; 694, $[M-35]^{+}$; 659, $[M-70]^{+}$; 533, $[M-196]^{+}$. Crystallographic Data deposited to Cambridge Data Center as supplementary publication no. CCDC-147245 or see Chapter 6. *Cis* (**5**): Anal. Calc. for $C_{30}H_{16}Cl_8FeN$: C, 49.4; H, 2.21; N, 1.90. Found C, 49.8; H, 2.0; N, 2.2 %. ν_{max} (KBr)/ cm^{-1}: 3434, 2925, 2849, 1715, 1631, 1552, 1526, 1487, 1383, 1371, 1292, 1227, 1182, 1134, 1076, 1057, 926, 858, 817, 788. λ (methylcyclohexane)/nm (ε): 377 (23300), 407 (13600), 578 (2940). Cyclic Voltammetry in CH_2Cl_2 and tetrabutylammonium hydroxide as electrolyte: –0,669V, +0,723V and +1,056V vs Ag/AgCl. EPR (isotropic solution of toluene at 160K): zero field splitting parameters: |D'|=25,2 G, |E'|= 0. Reverse phase HPLC: T=25ºC; Mobil phase: AcCN/THF; 70/30; flow: 1mL/min. Detection at 220, 377, and 590nm one peak at 6,7min. EM-LDI-TOF (positive mode): m/z / amu/e- $M^{+\cdot}$: 729, $[M]^{+}$; 694, $[M-35]^{+}$; 659, $[M-70]^{+}$; 533, $[M-196]^{+}$.

5.2.2 Synthesis of (*trans*)-4-(nonamethylferrocenylimino)-2,6-dichlorophenyl)bis(2,4,6-trichlorophenyl)methyl radical (4)



Reactants and quantities:

500mg (0.936mmol) of (4-amino-2,6-dichlorophenyl)bis(2,4,6-trichlorophenyl)methyl radical (**15**)

318mg (0.936mmol) of nonamethylferrocene monocarboxaldehyde

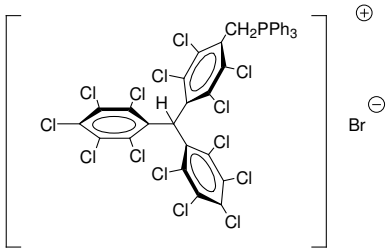
Molecular sieves

Toluene

Procedure: To a dry toluene solution of 500mg (0,936mmol) (4-amino-2,6-dichlorophenyl)bis(2,4,6-trichlorophenyl)methyl radical, which was obtained as previously described,[1] was added 318mg (0,936mg) nonamethylferrocene monocarboxaldehyde in the presence of molecular sieves. The mixture was heated up to 60ºC and stirred for 24h in the dark. The reaction is followed by silica thin layer chromatography first conditioned with a solution of 5% TEA, 72,5% carbon tetrachloride and 22,5% *n*-hexane and then eluted with a solution of 75% carbontetrachloride and 25% *n*-hexane. After removing the molecular sieves and evaporation of the solvent, a brown precipitate was obtained. Due to the high steric hindrance just the trans isomer of **4** was found in the reaction products. Finally, by a basic-alumina chromatography from carbon tetrachloride, a dark brown microcrystalline powder of **4** with a yield of 20% was obtained.

Characterization: [856.18 g/mol] Anal. Calc. for $C_{39}H_{34}Cl_8FeN$: C, 54.7; H, 3.97; N, 1.63. Found C, 54.48; H, 4.48; N, 1.73 %. νmax (KBr)/cm^{-1}: 3435, 2923, 2850, 1716, 1631, 1555, 1523, 1454, 1370, 1288, 1183, 1137, 1075, 1024, 857, 809, 562. $\lambda(CH_2Cl_2$/nm (ε): 378 (31200), 593 (5600), 900 (600). Cyclic Voltammetry in CH_2Cl_2 and tetrabutylammonium hydroxide as electrolyte: -0.59V, +0.233V, and +1.121V vs. Ag/AgCl. EM-LDI-TOF (positive mode): m/z / amu/e-: M^{+}: 935, $[M]^{+}$; 900, $[M-35]^{+}$; 865, $[M-70]^{+}$.

5.2.3 Synthesis of bis[pentachlorophenyl]-[4-methyltriphenylphosphonium-2,3,5,6-tetrachlorophenyl] methane bromide (17)[2]



Reactants and quantities:

3g [3.66mmol] of bis(pentachlorophenyl)(4-(bromomethyl)-2,3,5,6-tetrachlorophenyl)methane **16**[3]

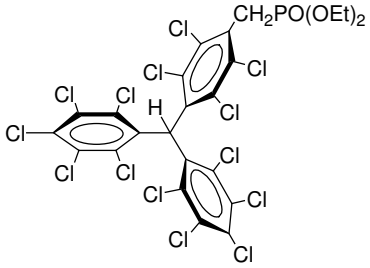
1.5g [5.718mmol] of triphenylphosphine (PPh_3)

210mL of benzene

Procedure: A solution of 3g (3.66mmol) of bis(pentachlorophenyl)(4-(bromomethyl)-2,3,5,6-tetrachlorophenyl)methane **16** and 1.5g (5.718g) of triphenylphosphine in 210mL of benzene was allowed to reflux for 20h. The resulting product, which precipitates from the reaction solution, was filtered off and washed with benzene several times. The solvent was distilled off under reduced pressure to yield 3.91 g of pure **17** with 92.1 % yield

Characterization Data: [1151.64 g/mol]. Calc Anal. For: $C_{38}H_{18}BrCl_{14}P.C_6H_6$: C, 45.85; H, 2.10; Found C, 45.44; H, 2.34. FT-IR (KBr, ν in cm^{-1}): 1585, 1480, 1435, 1370, 1295, 1110, 995, 840, 810, 755, 685, 495. UV-Vis-NIR (THF, λ_{max} in nm (ε)): 305(1530), 294(1406), 275(7800), 219(14000) ^{1}H-NMR ($CDCl_3$, TMS): 5.85 (d,2 H, J=5.85Hz), 6.90 (d, 1 H, J=1.90Hz), 7.33 (s, 6 H), 7.70(m, 15H).

5.2.4 Synthesis of bis[pentachlorophenyl][4-diethylphosphonate-2,3,5,6-tetrachlorophenyl] methane (20)[2]



Reactants and quantities:

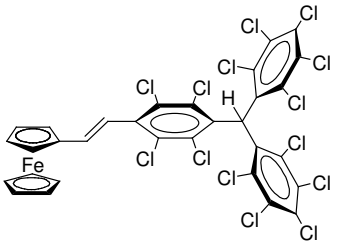
2g [2.44mmol] of bis(pentachlorophenyl)(4-(bromomethyl)-2,3,5,6-tetrachlorophenyl)methane **16**

4mL [23mmol] of triphenylphosphite

Procedure: A solution of 2g (2.44mmol) of bis(pentachlorophenyl) (4-(bromomethyl)-2,3,5,6-tetrachlorophenyl)methane **16** and 4mL (23mmol) of triphenylphosphite was left under reflux for 2h at 155ºC. After this time, 25mL of water was added and the reaction was kept under reflux for another 30min. The reaction mixture was extracted with 4 portions of 25mL of chloroform. The organic layer was washed with 20mL of water, dried with sodium sulfate and evaporated under reduced pressure. The product was purified by chromatography (Silica Gel, 3*35 cm, hexane) to yield 1.8g of **20** in a 84% yield.

Characterization Data: [876.704 g/mol]. Anal. Elemental Calc. For: $C_{24}H_{13}Cl_{14}O_3P$: C, 32.9; H, 1.49; Found C, 32.80; H, 1.50. FT-IR (KBr, ν in cm^{-1}): 2988, 2931, 2909, 2869, 1532, 1478, 1443, 1391, 1370, 1339, 1298, 1264, 1163, 1135, 1097, 1054, 1026, 968, 856, 809, 688, 668, 648, 634, 557, 518, 495. ^{1}H NMR ($CDCl_3$): δ=7.01 (1 H), 4.04 (q, J=7.10 Hz, 4H), 3.77 (d, J=22.54 Hz, 2H), 1.27 (t, J=7.10 Hz, 6H); UV/Vis (THF): λ (ε)= 302 (1170), 293 (1130), 250 (32 596), 222 (105 730) nm.

5.2.5 Synthesis of (*trans*)-4-ferrocenylvinylene-2,3,5,6-(tetrachlorophenyl)bis(pentachlorophenyl) methane (18)



Reactants and quantities:
44mg [360.0 μmol] of potassium-*tert*-butoxide
385mg [331.93 μmol] of Wittig-salt (**17**)
142mg [663.86 μmol] of ferrocenecarboxaldehyde
THF 10mL

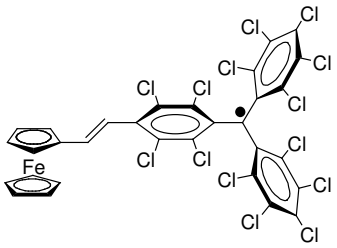
Procedure: **Wittig reaction**

Potassium-*tert*-butoxide [44 mg, 360.0 μmol] and the triphenylphosphonium wittig salt **17** (385 mg, 331.93 μmol) were suspended in approximately 10 ml of dry THF. The yellow ylide suspension that formed immediately was stirred for 75 minutes. Then the ferrocene carboxaldehyde (142 mg, 663.86 μmol) was added and the system was stirred for another 60 h.

The reaction mixture was quenched with 5 ml of HCl (2 N, in water), extracted with 4 portions of 25 mL of chloroform. The organic layer was washed with 20mL of water and dried with sodium sulfate. The solvent was distilled off under reduced pressure, and the product was purified by chromatography (Silica Gel, 3*35 cm, hexane/ether, 1/1) to yield 165 mg of **18**. Yield of 53%.

Characterization Data: [936.63 g/mol] Elemental Anal. Calc. For: $C_{31}H_{12}Cl_{14}Fe$: C, 39.8; H, 1.29; Found C, 39.70; H, 1.29. m.p.: 167-168ºC. FT-IR (KBr, ν in cm^{-1}): 2954, 2924, 2855, 1655, 1633, 1363, 1337, 1298, 1242, 1136, 1107, 958, 809, 531, 481. UV-Vis-NIR (CH_2Cl_2, λmax in nm (ε)): 304 (10037), 383 (1999),466 (1140). MS (EI, 70eV): m /z: 936 $M^{+\bullet}$(0.1%), 901(-Cl;0.01%), 815(-Fe(C_5H_5),0.05%), 739(-Fe(C_5H_5)$_2$, C, 2 H,2%). ^{1}H-NMR ($CDCl_3$, TMS): 4.22(s,5 H,cyclopentadienyle unsubst.), 4.38(s,2H,cyclopentadienyle subst.), 4.49(s,2H,cyclopentadienyle subst.), 6.66 (d,1 H,J=16.23Hz, vinyle), 6.91 (d,1 H,J=16.23Hz, vinyle), 7.03 (s,1 H,methane). Crystallographic Data deposited to Cambridge Data Center as supplementary publication no. CCDC 191556 or see Chapter 6.

5.2.6 Synthesis of *(trans)*-4-ferrocenylvinyl-2,3,5,6-(tetrachlorophenyl)bis (pentachlorophenyl) methyl radical (1)



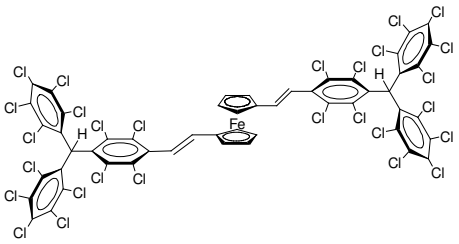
Reactants and quantities:
160 mg [171 μmol] of **18**
130μL [200 μmol] of tetrabutylammoniumhydroxide (40% in water,1.5M)
53.6mg [220 μmol] *p*-chloranil
25mL THF

Procedure: tetrabutylammonium hydroxide (40% in water, 1.5 M, 130 μL, 200 μmol) was added to a solution of **18** (160 mg, 171 μmol) in 25 ml of THF. The solution, which turned into purple immediately was stirred at ambient temperature for 4 h. Subsequently 53.6mg [220 μmol] of *p*-

chloranil were added and stirring was continued for another 35 min. The solvent was distilled off under reduced pressure, and the product was purified by flash chromatography (Silica Gel, 1*45 cm, hexane). Yield 83.2%.

Characterization Data: [935.61 g/mol] Calc. Elemental Analysis for $C_{31}H_{11}Cl_{14}Fe$: C, 39.7; H, 1.18; Found C, 39.70; H, 1.20. Cyclic Voltammogram in CH_2Cl_2 and tetrabutylammonium hydroxide as electrolyte: $E_{½}$ = 0.587 V; $E_{½}$ = -0.177V. FT-IR (KBr, ν in cm^{-1}): 3400, 2923, 2853, 1623, 1508, 1464, 1337, 1319, 1261, 1107, 1045, 1029,1001, 959, 817, 735, 712, 652, 561, 530, 478, 419. UV-Vis-NIR (THF, λmax in nm (ε)): 290 (14006), 386 (26572), 444 (11400), 940 (1350). UV-VIS-NIR (CH_2Cl_2λmax in nm (ε)): 291 (12871), 386 (21143), 442 (9024), 936 (848). MS (EI): m / z 936 $M^{+\bullet}$(25%), 902 (-Cl,16%), 866 (-2 Cl,12%), 832 (-3 Cl,4%),739 (-Fe(C_5H_5)$_2$, C, 2 H,9%). EPR (toluene/$CHCl_3$:1/1): g=2.0035, a($^1H_1$)= 1.77 G, a ($^1H_2$) = 0.57 G, a ($^{13}C_\alpha$) ≅ 29.75 G, a($^{13}C_{arom}$) ≅ 11.0 G. Crystallographic Data deposited to Cambridge Data Center as supplementary publication no. CCDC 191557 or see Chapter 6.

5.2.7 Synthesis of (*trans-trans*)-1,1'-ferrocenyldivinylene-bis[2,3,5,6-(tetrachlorophenyl)bis (pentachlorophenyl)] methane (23)

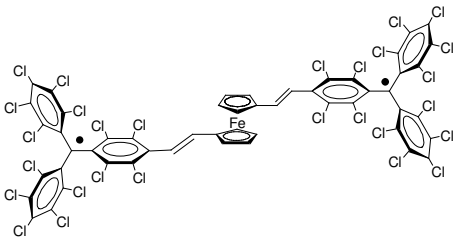


Reactants and quantities:
46 mg potassium-*tert*-butoxide [376.4 μmol]
395mg [340.44μmol] of **17**
39 mg [160.0 μmol] of 1,1'-ferrocenedicarboxaldehyde
10mL THF

Procedure: Potassium-*tert*-butoxide [46 mg, 376.4 μmol] and wittig salt **17** (395 mg, 340.44 μmol) were suspended in approximately 10 ml of dry THF. The yellow ylide suspension that formed immediately was stirred for 70 minutes. Then the 1,1'-ferrocenedicarbxbaldehyde (39 mg, 160 μmol) was added and the system was stirred for another 72 h. The reaction mixture was quenched with 5 ml of HCL (2 N, in water), extracted with 4 portions of 25 ml of chloroform. The organic layer was washed with 20mL of water, dried with sodium sulfate and evaporated under reduced pressure. The solvent was distilled off under reduced pressure and the product was purified by chromatography (silica 40*2.5 cm, hexane, chloroform). Yield 53.3%

Characterization Data: [1687.21 g/mol]; Elemental Anal. Calc. For $C_{52}H_{14}Cl_{28}Fe$: C, 37.02; H, 0.84; Found C, 37.06; H, 0.72**.** FT-IR (KBr, ν in cm^{-1}): 2925, 1634, 1533, 1369, 1338, 1299, 1241, 1138, 1045, 960, 810, 715, 685, 649, 531, 479. ^{1}H-NMR ($CDCl_3$, TMS): 4.44(s,4 H,cyclopentadienyle subst.), 4.51 (s,4H,cyclopentadienyle subst.), 6.69 (d,2H,J=16.2Hz,vinyle), 6.94 (d,2H,J=16.2Hz, vinyle), 7.03(s,1 H, methane)

5.2.8 Synthesis of 1,1'-(*trans-trans*)- ferrocenyldivinylene-bis[2,3,5,6-tetrachlorophenyl-bis(pentachlorophenyl)methyl] diradical (7)



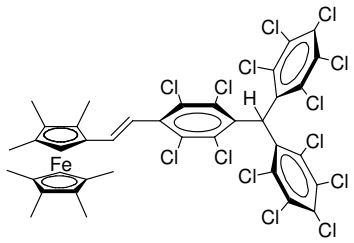
Reactants and quantities:
133 mg [78.8 μmol] of **23**
131µL[197.0 μmol] of tetrabutylammoniumhydroxide (40% in water, 1.5 M)
53.6 mg [220.0 μmol] of *p*-chloranil
THF 15 mL

Procedure: tetrabutylammonium hydroxide (40% in water, 1.5 M, 131 µl, 197 μmol) was added to a solution of **23** (133 mg, 78.8 µmol) in 15 ml of THF. The solution, which turned into purple immediately, was stirred at ambient temperature for 4 h. Subsequently *p*-chloranil (53.6 mg, 220 µmol) was added and stirring was continued for another 35 min.

The solvent was distilled off under reduced pressure and the product was purified by chromatography (silica 40*2.5 cm, hexane, chloroform) to yield 82 mg of a prepurified product. A second chromatography (silica 40*2.5 cm, hexane: carbon tetrachloride, 1:1) gave 60 mg of pure **7.** Yield 45.2 %. The product is crystallized from C_6H_6

Characterization Data: [1685.19 g/mol]. Elemental Anal. Calc. For $C_{52}H_{12}Cl_{28}Fe$: C, 41.80; H, 1.40; Found C, 42.20; H, 1.65; Cyclic Voltammetry in CH_2Cl_2 and tetrabutylammonium hydroxide as electrolyte: $E_{½}$ = +0.666 V; $E_{½}$ = -0.181V vs. Ag/AgCl. m.p.: decomposition at T > 165ºC. FT-IR (KBr, ν̃ cm^{-1}): 2923, 2853, 1716, 1623, 1507, 1465, 1337, 1319, 1261, 1156, 1119, 1046, 959, 945, 869, 817, 735, 712, 699, 652, 561, 530, 475, 417. UV-Vis-NIR (THF, λmax in nm (ε)): 286 (22341), 387 (44881),442 (18519), 920 (1980). ESR (toluene/$CHCl_3$:1/1): g = 2.0027, a ($^1H_1$) = 0.80G, a ($^1H_2$) = 0.30 G, a ($^{13}C_\alpha$) ≅ 13.0G, a ($^{13}C_{arom}$) ≅ 6G.

5.2.9 Synthesis of (*trans*)-4- nonamathylferrocenylvinylene-2,3,5,6-(tetrachlorophenyl)bis(pentachlorophenyl) methane (21)



A) Wittig reaction
Reactants and quantities:
143.87mg [1.28mmol] of potassium-*tert*-butoxide
1.241g [1.10mmol] of **17**
400mg [1.17mmol] of nonamethylferrocene carboxaldehyde
10mL THF

Procedure: Potassium-*tert*-butoxide [143.87mg, 1.28mmol] and the wittig salt **17** (1.241g, 1.10mmol) were suspended in approximately 10 ml of dry THF. The yellow ylide suspension that formed immediately was stirred for 70 minutes. Then the nonamethylferrocene carboxaldehyde (400 mg, 1.17mmol) was added and the system was stirred for another 72 h.
The reaction mixture was quenched with 5 ml of HCL (2 N, in water), extracted with 4 portions of 25 mL of chloroform. The organic layer was washed with 20mL of water, dried with sodium sulfate and

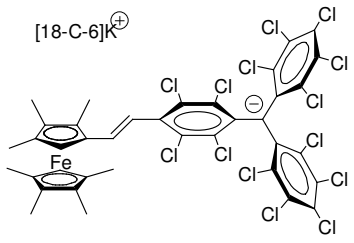
evaporated under reduced pressure. The solvent was distilled off under reduced pressure and the product was purified by chromatography (silica 40*2.5 cm, hexane, chloroform. Yield: 50mg (4%).

B) Wittig-Horner-Emmons reaction

Reactants and quantities:
636.7mg [0.726mmol] of the phosphonate **20**
189.9 mg [1.69mmol] of potassium-*tert*-butoxide
271.46 mg [0.799 mmol] of nonamethylferrocenecarboxaldehyde
10mL THF

Procedure: The phosphonate **20** (636.7mg, 0.726 mmol) was suspended in approximately 17 mL of dry THF under argon. The solution was cooled down to –78°C and then potassium-*tert*-butoxide [189.9mg, 1.69mmol] was added. The orange-yellow ylide suspension that is formed immediately was stirred for 15min. Then the temperature was increased to 0°C with an ice bath and finally the nonamethylferrocenecarboxaldehyde (271.46mg, 0.799mmol) dissolved in 5mL of THF was added slowly and the system was stirred for another 60 hours at room temperature.
The reaction mixture was quenched with 5 ml of HCL (2 N, in water), extracted with 4 portions of 25 mL of chloroform. The organic layer was washed with 20mL of water, dried with sodium sulfate and evaporated under reduced pressure. The product was purified by chromatography (silica Gel, 3*35cm, hexane/ether, 1/1) to yield 700mg of **7**. Yield of 90%.
Characterization Data: [1062.87 g/mol] Elemental Anal. Calc. For $C_{40}H_{30}Cl_{14}Fe.1/2C_6H_{14}$: C, 46.7; H, 3.37; Found C, 46.52; H, 3.43; Cyclic Voltammetry in CH_2Cl_2 and tetrabutylammonium hydroxide as electrolyte: $E_{½}$ = 0.090 V vs. Ag/AgCl; FT-IR (KBr, ν in cm^{-1}): *trans*: 2954, 2922.7, 2854.25, 1624, 1536, 1451, 1423, 1373, 1299, 1241, 1135, 1028, 972, 809, 716, 683, 648, 529, 468. *Cis*: 2954, 2922.7, 2854.25, 1668, 1618, 1536, 1451, 1423, 1373, 1299, 1241, 1135, 1028, 972, 809, 716, 683, 648, 529, 468. UV-Vis-NIR (CH_2Cl_2, λ_{max} in nm (ε)): 304 (5533), 338 (5872), 519 (990) EM-LDI-TOF (negative mode): *m/z* / amu/e^- $M^{+\bullet}$ 1063, $[M]^-$; 1028, $[M-35]^-$; 992, $[M-71]^-$; 957, $[M-106]^-$; 870, 822, 679,481, 311, [M-752]. ^{1}H-NMR ($CDCl_3$): δ 7.01 (s, 1H), 6.92 (d, J = 16.6Hz, 1H), 6.65 (d, J = 16.6Hz, 1H), 1.90 (s, 6H), 1.75 (s, 6H), 1.65 (s, 15H).

5.2.10 Synthesis of (*trans*)-4-nonamathylferrocenylvinylene-2,3,5,6-(tetrachlorophenyl)bis(pentachlorophenyl) methyl anion (22)



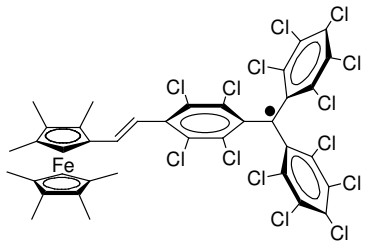
Reactants and quantities:
350mg [329.4µmol] of **21**
98.12mg [372.18µmol] of 18-Crown-6
201.44mg [3.59mmol] of potassium hydroxide
30mL CH_2Cl_2

Procedure: 350mg of compound **21** (329.4µmol) were suspended in approximately 10 mL of dry CH_2Cl_2 under argon. The 18-Crown-6 (98.12mg, 372.18µmol) was added and finally a dry powder of potassium hydroxide (201.44mg, 3.59mmol) was added to the solution which was left with strong stirring for 24 hours. The excess of potassium hydroxide was filtrated and washed with CH_2Cl_2 and

the solvent was evaporated under reduced pressure. Finally the product was cleaned with hexane several times**.** Yield: 89%

Characterization Data: [1365.27 g/mol] Elemental Anal. Calc. For $C_{40}H_{29}Cl_{14}Fe$ + $C_{12}H_{24}O_6K$: C, 45.75; H, 3.91; Found C, 45.6; H, 3.75. FT-IR (KBr, ν in cm^{-1}): 2913, 2857, 2066, 1972, 1631, 1472, 1453, 1373, 1352, 1335, 1283, 1249, 1107, 962, 838, 721, 663, 687, 649, 612, 584, 530, 523. UV-Vis-NIR (CH_2Cl_2, λmax in nm (ε)): 531 (31365) EM-LDI-TOF (positive mode): *m/z* / amu/e^- $M^{-\bullet}$: 1061, $[M]^-$; 1026, $[M-35]^-$; 991, $[M-70]^-$; 956, $[M-100]^-$;303, $[M-758]^-$; Cyclic Voltammetry in CH_2Cl_2 and tetrabutylammonium hydroxide as electrolyte: $E_{½}$ = -187mV , $E_{½}$ = 129mV, $E_{½}$ = aprox.1800mV vs Ag/AgCl .

5.2.11 Synthesis of (*trans*)-4-nonamathylferrocenylvinylene-2,3,5,6-(tetrachlorophenyl)bis(pentachlorophenyl) methyl radical (2)

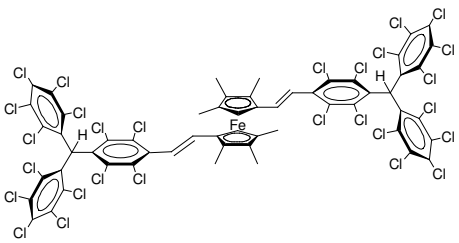


Reactants and quantities:
40mg [29.3μmol] of the methyl anion **22**
5.70mg [29.3μmol] of $AgBF_4$
10mL of CH_2Cl_2

Procedure: 40mg of the methyl anion **22** [40mg, 29.3μmol] were suspended in approximately 10 mL of dry CH_2Cl_2 (passed through activated alumina in order to deactivate the acidic point of the solvent) under argon in strict inert conditions (previous vacuum-argon at –70ºC). The $AgBF_4$ (5.70mg, 29.3μmol) was added and after a few minutes the color of the solution changed form violet to dark-brown and gray precipitate was formed (Agº). The solution was left with strong stirring for 30min. The solution was filtered and washed with CH_2Cl_2 and dissolved and filtered again with hexane. Without further purification the solvent was evaporated under reduced pressure. Yield: 70%

Characterization Data: [1061.86 g/mol] Anal. Calc. For: $C_{40}H_{29}Cl_{14}Fe$: C, 45.24; H, 2.75; Found C, 45.5 ; H, 2.85. FT-IR (KBr, ν in cm^{-1}): 2901, 1612, 1505, 1474, 1420, 1375, 1351, 1335, 1262, 1108, 1084, 1029, 965, 838, 816, 736, 712, 667, 652, 530. UV-Vis-NIR (CH_2Cl_2, λ_{max} in nm (ε)): 346 (7415), 385 (11405), 497 (4004), 661 (2046), 1506 (965.5). EM-LDI-TOF (positive mode): *m/z* / amu/e^- $M^{-\bullet}$: 1061, $[M]^-$; 991, $[M-70]^-$; 956, $[M-105]^-$; 371, 303, 287, 242, 215. Cyclic Voltammetry in CH_2Cl_2 and tetrabutylammonium hydroxide as electrolyte: -0.4V, 0.09V vs. Ag/AgCl. EPR (toluene/$CHCl_3$:1/1): two different signals with different g values. Crystallographic Data deposited to Cambridge Data Center as supplementary publication no. CCDC 191558 or see Chapter 6.

5.2.12 Synthesis of (*trans-trans*)-1,1'-octamethylferrocenyldivinylene-bis[2,3,5,6-(tetrachlorophenyl)bis (pentachlorophenyl)] methane (24)

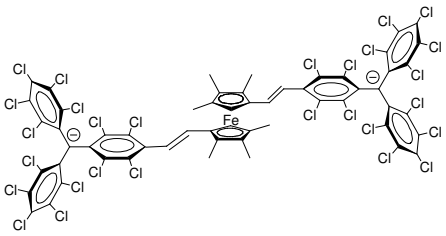


Wittig-Horner-Emmons reaction
Reactants and quantities:
900mg [1.026mmol] of the phosphonate **20**
268.38mg [2.39mmol] of potasium-*tert*-butoxide
200mg [0.564mmol] of octamethylferrocene-1,1´-biscarboxaldehyde
10ml THF

Procedure: 900mg of the phosphonate **20** (1.026mmol) were suspended in approximately 10mL of dry THF under argon. The solution was cooled down to –78°C and then potassium-*tert*-butoxide [268.38mg, 2.39mmol] was added rapidly. The orange-yellow suspension that is formed immediately was stirred for 15min. Then the temperature was increased to 0° C with and ice bath and finally a octamethylferrocenebiscarboxaldehyde (200mg, 0.564mmol) THF solution was added dropwise and the system was stirred for another 60 hours at room temperature.
The reaction mixture was quenched with 5 ml of HCL (2 N, in water), extracted with 4 portions of 25 mL of chloroform. The organic layer was washed with 20mL of water, dried with sodium sulfate and evaporated under reduced pressure. The product was purified by chromatography (silica Gel, 3*35cm, hexane/$CHCl_3$, 10/1). Yield: 67%

Characterization Data: [1799.428 g/mol] Elemental Anal. Calc. For $C_{60}H_{30}Cl_{28}Fe$: C, 40.05; H, 1.68; Found C, 40.1; H, 1.71. FT-IR (KBr, ν in cm^{-1}): 2920, 2347, 1843, 1733, 1716, 1698, 1624, 1554, 1541, 1535, 1456, 1370, 1336, 1298, 1269, 1239, 1136, 1118, 1027, 973, 874, 837, 809, 714, 682, 671, 663, 649, 612, 529, 489, 468. UV-Vis-NIR (CH_2Cl_2, λ_{max} in nm (ε)): 305 (22928), 326 (23471), 498 (3841) EM-LDI-TOF (positive mode): *m/z* / amu/e^- $M^{-\bullet}$: 1799, $[M]^-$; 1764, $[M-35]^-$; 1728, $[M-71]^-$; 1692, $[M-107]^-$; 1658, $[M-141]^-$. ^{1}H-NMR ($CDCl_3$): δ 6.99 (s, 2H), 6.96 (d, J = 16.6Hz, 2H), 6.62 (d, J = 16.6Hz, 2H), 1.94 (s, 12H), 1.79 (s, 12H).

5.2.13 Synthesis of (*trans-trans*)-1,1'-octamethylferrocenyldivinylene-bis[2,3,5,6-(tetrachlorophenyl)bis(pentachlorophenyl)] methane bisanion (25)

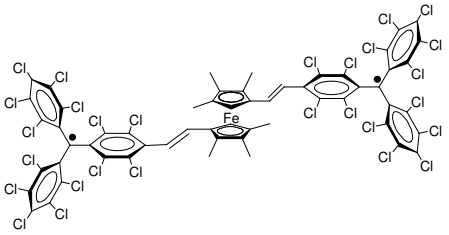


Reactants and quantities:
100mg [55.6µmol] of **24**
33.11mg [125.6µmol] of 18-Crown-6 Ether
68.6mg [1.222mmol] of potassium hydroxide
15mL CH_2Cl_2

Procedure: 100 mg (55.6mmol) of **24** were suspended in approximately 15 mL of dry CH_2Cl_2 under argon. The 18-Crown-6 Ether (33.11mg, 125.6mmol) was added and finally a dry powder potassium hydroxide (68.6g, 1.222mmol) was also added to the solution which was left with strong stirring for 24 hours. The excess of potassium hydroxide was filtrated off and washed with CH_2Cl_2 and the solvent was evaporated under reduced pressure. Finally the product was cleaned with hexane several times. Yield: 55%

Characterization Data: [2404.2476 g/mol] Elemental Anal. Calc. For: $C_{60}H_{28}Cl_{28}Fe$ + $C_{24}H_{48}K_2O_{12}$: C, 41.96; H, 3.19; Calc with 2 hexane; C, 44.7, H, 4.07, Found C, 44.83; H, 4.35; FT-IR (KBr, ν in cm^{-1}): 2899, 1973, 1631, 1606, 1505, 1472, 1454, 1370, 1351, 1282, 1248, 1108, 964, 837, 806, 721, 687, 661, 648, 612, 582, 523, 470 UV-Vis-NIR (CH_2Cl_2, λmax in nm (ε)): 291 (sh) (13628), 341 (sh) (9988), 533 (31779) EM-LDI-TOF (positive mode): *m/z* / amu/e^- $M^{-\bullet}$: 1797, $[M]^-$; 1762, $[M-35]^-$; 1727, $[M-70]^-$; 1691, $[M-106]^-$; 1658, $[M-139]^-$; 1621, $[M-176]^-$; 1587, $[M-210]^-$; 1551,$[M-246]^-$; 697, $[M-1100]^-$; 677, $[M-1120]^-$; 667, $[M-1130]^-$; 417, $[M-1380]^-$; 339, $[M-1458]^-$; 303, $[M-1494]^-$.

5.2.14 Synthesis of (*trans-trans*)-1,1'-octamethylferrocenyldivinylene-bis[2,3,5,6-(tetrachlorophenyl)bis(pentachlorophenyl)] methyl diradical (8)

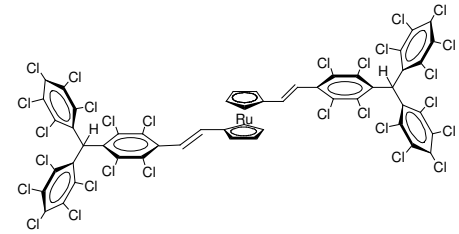


Reactants and quantities:
71mg [28.5µmol] of the bis-anion **25**
15.379mg [79μmol] of $AgBF_4$
15mL of CH_2Cl_2

Procedure: 71mg of the bis-anion **25** [28.5µmol] were dissolved in approximately 15mL of dry CH_2Cl_2 (passed through activated alumina in order to deactivate the acidic point of the solvent) under argon in strict inert conditions (previous vacuum-argon at –70ºC). Then $AgBF_4$ (15.379mg, 79μmol) was added. After 10 minutes the color of the solution changed form violet to dark-brown and a grey precipitate was formed (Agº). The solution was left with strong stirring for 30min. The solution was filtered and washed with CH_2Cl_2 and dissolved and filtered again with hexane. Without further purification the solvent was evaporated under reduced pressure. Yield: 30%

Characterization Data: [1797.415 g/mol] Elemental Anal. Calc. For: $C_{60}H_{28}Cl_{28}Fe$: C, 40.09; H, 1.57; Found C,41.2,H,2. UV-Vis-NIR (CH_2Cl_2, λmax in nm (ε)): 281 (14380), 336(10311), 369 (13443), 386 (20937), 411 (10856), 567 (1618), 822 (686). EM-LDI-TOF (positive matrix): *m/z* / amu/e^- $M^{-\bullet}$: 1797, $[M]^-$; 1762, $[M-35]^-$; 1727, $[M-70]^-$; 1691, $[M-106]^-$; 1658, $[M-139]^-$; 1621, $[M-176]^-$; 371, $[M-1426]^-$; 322, $[M-1475]^-$; 303, $[M-1494]^-$. Cyclic Voltammetry in CH_2Cl_2 and tetrabutylammonium hydroxide as electrolyte: -0.171V and +0.280V vs. Ag/AgCl.

5.2.15 Synthesis of (*trans-trans*)-1,1'-ruthenocenyldivinylene-bis[2,3,5,6-tetrachlorophenyl-bis(pentachlorophenyl)] methane (26)



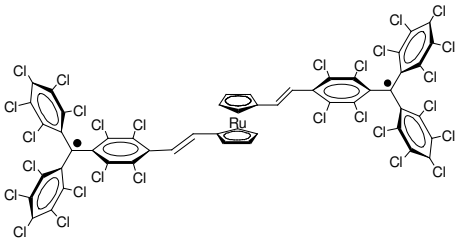
Reactants and quantities:
997,16mg [1.137mmol] of phosphonate **20**
297.4mg [2.65mmol] of the potassium-*tert*-butoxide
179.71mg [0.625mmmol] of ruthenocenebiscarboxaldehyde
15mL THF

Procedure: 997.16mg of the phosphonate **20** (1.137mmol) were dissolved in approximately 15mL of dry THF under argon. The solution was cooled down to –78°C and then potassium-*tert*-butoxide [297.4mg, 2.65mmol] was added rapidly. The orange-yellow suspension that is formed immediately was stirred for 15min. Then the temperature was increased to 0° C with and ice bath and finally the ruthenocenecarboxaldehyde (179.71mg, 0.625mmol) was added dropwise and the system was stirred for another 24 hours at room temperature.

The reaction mixture was quenched with 10 ml of HCL (1 N, in water), extracted with 4 portions of 25mL of chloroform. The organic layer was washed with 20mL of water, dried with sodiumsulfate and evaporated under reduced pressure. The product was purified by chromatography (silica Gel, 3*35cm, hexane/ether, 1/1). Yield: 60%.

Characterization Data: [1732,438 g/mol]. Elemental Anal. Calc. For $C_{52}H_{14}Cl_{28}Ru$: C, 36.05; H, 0.81;Calc with 2.4%hexane; C, 37.20, H, 1.10, Found C, 37.74; H, 1.02. Solubility: highly insoluble in ether, ethylacetate, hexane and chlorated solvents. FT-IR (KBr, ν in cm^{-1}): 2953, 2925, 2853, 1636, 1534, 1464, 1368, 1338, 1321, 1299, 1272, 1240, 1137, 1041, 959, 863, 809, 714, 694, 684, 673, 661, 648, 529, 517, 503, 461. UV-Vis-NIR (CH_2Cl_2, λ_{max} in nm (ε)): 312 (23810), 354 (sh) (15561) EM-LDI-TOF (positive, mode): *m/z* / amu/e^- $M^{-\bullet}$: 1732, $[M]^-$; 1696 $[M-36]^-$; 1661, $[M-71]^-$; 1625, $[M-107]^-$; 1590, $[M-142]^-$; 1554, $[M-178]^-$; 1519, $[M-213]^-$; 994, $[M-738]^-$; 959, $[M-773]^-$; 923, $[M-809]^-$; 673, $[M-1059]^-$; 639, $[M-1093]^-$; 604, $[M-1128]^-$; 567, $[M-1165]^-$; 531, $[M-1201]^-$; 496, $[M-1236]^-$; 460, $[M-1272]^-$; 425, $[M-1307]^-$; 389, $[M-1343]^-$; 354, $[M-1378]^-$; 316, $[M-1416]^-$; 288, $[M-1444]^-$; 270, $[M-1462]^-$; 256, $[M-1476]^-$; 242, $[M-1490]^-$. Cyclic Voltammetry in CH_2Cl_2 and tetrabutylammonium hydroxide as electrolyte: one highly irreversible wave at 1,13V vs. Ag/AgCl. ^{1}H-NMR ($CDCl_3$): 6.98 (s, 2H), 6.77 (d, 16.4Hz, 2H), 6.60 (d, 16.4Hz, 2H), 4.87 and 4.70 (pseudo t, 4+4H).

5.2.16 Synthesis of (*trans-trans*)-1,1'-ruthenocenyldivinylene-bis[2,3,5,6-tetrachlorophenyl-bis(pentachlorophenyl)] methyl radical (9)

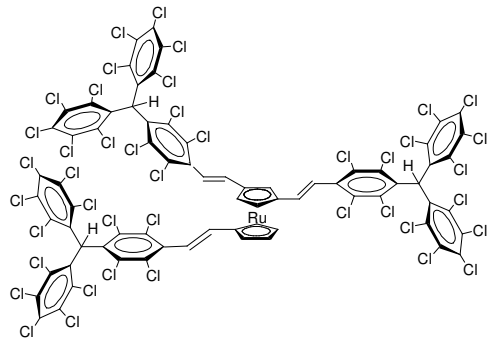


Reactants and quantities:
200 mg [115 μmol] of **26**
192.4μL [289 μmol] of tetrabutylammoniumhydroxide (40% in water, 1.5M)
70.96mg [288 μmol] of *p*-chloranil
25mL THF

Procedure: tetrabutylammoniumhydroxide (40% in water, 1.5 M, 192.4 μL, 115 μmol) was added to a solution of **26** (200 mg, 115 μmol) in 25 ml of THF. The solution, which turned into purple immediately was stirred at ambient temperature for 3.5 h. Subsequently *p*-chloranil was added and stirring, was continued for another 35 min. The solvent was distilled off under reduced pressure and the product was purified by flash chromatography (Silica Gel, 1*45 cm, hexane/$CHCl_3$, 1/1). Yield: 86%

Characterization Data: [1730.422g/mol] Elemental Anal. Calc. For $C_{52}H_{12}Cl_{28}Ru$: C, 36.1; H, 0.70; Calc with 2.2%hexane; C, 37.0; H, 1.0. Found C, 37.14; H, 1.04. FT-IR (KBr, ν in cm^{-1}): 2952, 2923, 2852, 1628, 1509, 1463, 1337, 1319, 1260, 1226, 1156, 1118, 1042, 1025, 958, 944, 929, 867, 816, 759, 735, 711, 698, 652, 661, 558, 505, 529, 460. UV-Vis-NIR (CH_2Cl_2, λmax in nm (ε)): 284 (sh) (21130), 377 (sh) (33500), 387 (50575), 449 (14390), 696 (3500) EM-LDI-TOF (positive mode): *m/z* / amu/e^- $M^{-\bullet}$: 1730, $[M]^-$; 1694 $[M-36]^-$; 1659, $[M-71]^-$; 1623, $[M-107]^-$; 1588, $[M-142]^-$; 1552, $[M-178]^-$; 1516, $[M-214]^-$; 1481, $[M-249]^-$; 1445, $[M-285]^-$; 992, $[M-738]^-$; 956, $[M-774]^-$; 921, $[M-637]^-$; 886, $[M-844]^-$; 706, $[M-1024]^-$; 672, $[M-1058]^-$; 637, $[M-1093]^-$; 601, $[M-1129]^-$; 567, $[M-1163]^-$; 534, $[M-1196]^-$; 496, $[M-1234]^-$. Cyclic Voltammetry in CH_2Cl_2 and tetrabutylammonium hydroxide as electrolyte: two electrons reversible reduction wave at –148mV and one electron reversible oxidation wave at 715mV. ESR (toluene/$CHCl_3$:1/1): g=2.0030, ^{1}Ha=1.6G, ^{1}Ha=0.65G; at 60K: L_{wx}=8, L_{wy}=8, L_{wz}=10, g_x=2.0030, g_y=2.0028, g_z=2.0024. |*D*'|=52; |*E*'|=0.

5.2.17 Synthesis of (*trans-trans-trans*)-1,1',3-ruthenocenyltrivinylene-tris[2,3,5,6-tetrachlorophenyl-bis(pentachlorophenyl)] methane (27)

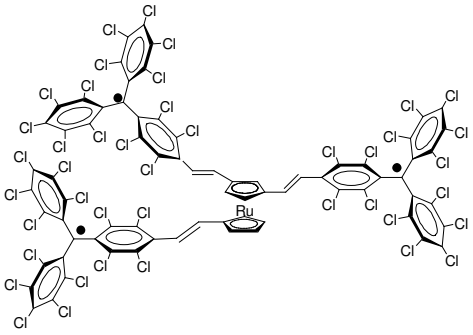


Reactants and quantities:
641.68 mg [0.732mmol] of phosphonate **20**
188.914 mg [1.683mmol] of potassium-*tert*-butoxide
100mg [0.317mmmol] of ruthenocenetriscarboxaldehyde
15mL THF

Procedure: 641.68mg of phosphonate **20** (0.732mmol) were dissolved in approximately 10mL of dry THF under argon. The solution was cooled down to –78°C and then potassium-*tert*-butoxide [188.914mg, 1.683 mmol] was added rapidly. The orange-yellow suspension that is formed immediately was stirred for 15min. Then the temperature was increased to 0° C with and ice bath and finally a ruthenocene triscarboxaldehyde (100mg, 0.317mmol) was added dropwise and the system was stirred for another 24 hours at room temperature. The reaction mixture was quenched with 10 ml of HCL (1 N, in water), extracted with 4 portions of 25 mL of chloroform. The organic layer was washed with 20mL of water, dried with sodium sulfate and evaporated under reduced pressure. The product was purified by chromatography (silica Gel, 3*35cm, hexane/$CHCl_3$, 1/1). Yield: 35%

Characterization Data: [2483,027 g/mol] Elemental Anal. Calc. For $C_{73}H_{16}Cl_{42}Ru$: C, 35.31; H, 0.65;Calc with 5.7%hexane; C, 38.10, H, 0.75, Found C, 38.62; H, 1.38. Solubility: insoluble in hexane, ethyl ether, ethyl acetate and soluble in THF, toluene, $CHCl_3$. FT-IR (KBr, ν in cm^{-1}): 2924, 2853, 1637, 1532, 1459, 1449, 1369, 1338, 1298, 1239, 1206, 1189, 1138, 1119, 1041, 958, 862, 809, 715, 684, 648, 612, 560, 529. EM-LDI-TOF (positive mode): *m/z* / amu/e^- $M^{-\bullet}$: 2483, $[M]^-$; 2447 $[M-36]^-$; 2412, $[M-71]^-$; 2377, $[M-106]^-$; 2342, $[M-141]^-$; 2304, $[M-179]^-$; 2235, $[M-248]^-$; 2199, $[M-284]^-$; 2163, $[M-320]^-$; 2129, $[M-354]^-$; 2093, $[M-390]^-$; 1790, $[M-693]^-$; 1752, $[M-731]^-$; 706, $[M-1777]^-$; 671, $[M-1812]^-$; 637, $[M-1846]^-$; 603, $[M-1129]^-$; 568, $[M-1915]^-$; 532, $[M-1951]^-$. Cyclic Voltammetry in CH_2Cl_2 and tetrabutylammonium hydroxide as electrolyte: one highly irreversible wave at 1,2V vs. Ag/AgCl. ^{1}H-NMR ($CDCl_3$): 6.98 (s, 2H), 6.97 (s, 1H), 6.78 (d, 16.23Hz, 3H), 6.66 (d, 16.23Hz, 3H), 5.22, 5.01, 4.85, 4.75 (pseudo t, J<3Hz).

5.2.18 Synthesis (*trans-trans-trans*)-1,1',3-ruthenocenyltrivinylene-tris[2,3,5,6-tetrachlorophenyl-bis(pentachlorophenyl)] methyl triradical (10)



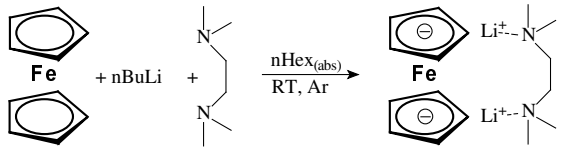
Reactants and quantities:
80 mg [32.2 μmol] of **27**
80.55μL [120.8μmol] of tetrabutylammoniumhydroxide (40% in water, 1.5M)
29.71 mg [120.8 μmol] of *p*-chloranil
25mL THF

Procedure: tetrabutylammonium hydroxide (40% in water, 1.5 M, 80.55 μL, 120.8 μmol) was added to a solution of **27** (80 mg, 32.2 μmol) in 25 ml of THF. The solution, that turned into purple immediately was stirred at ambient temperature for 3.5 h. Subsequently *p*-chloranil was added and stirring was continued for another 35 min. The solvent was distilled off under reduced pressure and the product was purified by flash chromatography (Silica Gel, 1*45 cm, hexane/$CHCl_3$, 3/1). Yield: 80%.

Characterization Data: [2480.003 g/mol] Elemental Anal. Calc. For $C_{73}H_{13}Cl_{42}Ru$: C, 35.36; H, 0.528;Calc with 5.4%hexane; C, 37.9H, 1.30, Found C, 37.88; H, 1.35. FT-IR (KBr,ν in cm^{-1}): 2954, 2924, 2853, 2382, 2326, 1727, 1627, 1509, 1464, 1376, 1337, 1319, 1259, 1157, 1120, 1042, 956, 943, 867, 816, 736, 711, 652, 529. UV-Vis-NIR (CH_2Cl_2, λ_{max} in nm (ε)): 275 (30393), 387(72296), 443 (20437), 675 (4706). EM-LDI-TOF (positive mode): *m/z* / amu/e^- $M^{-\bullet}$: 2481, $[M+1]^-$; 2407 $[M-73]^-$; 2338, $[M-142]^-$; 2300, $[M-180]^-$; 2268, $[M-212]^-$; 2230, $[M-250]^-$; 2197, $[M-283]^-$; 1390, $[M-1090]^-$; 1353, $[M-1127]^-$; 1317, $[M-1163]^-$; 1280, $[M-1200]^-$; 1244, $[M-1236]^-$; 1208, $[M-1272]^-$; 1172, $[M-1308]^-$; 706, $[M-1774]^-$; 671, $[M-1809]^-$; 637, $[M-1843]^-$; 603, $[M-1877]^-$; 568, $[M-1912]^-$; 532, $[M-1948]^-$.Cyclic Voltammetry in CH_2Cl_2 and tetrabutylammonium hydroxide as electrolyte: one reversible reduction wave of three electrons at –169mV and one reversible oxidation wave of one electron at 839mV vs. Ag/AgCl. ESR (toluene/$CHCl_3$: 1/1): signal at half field and third field.

5.3 SYNTHESIS OF METALLOCENE[4]

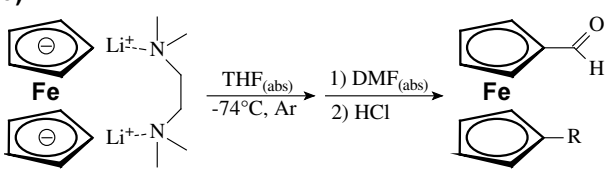
5.3.1 Synthesis of Dilithioferrocen - TMEDA (28)[5]



Reactants and quantities:
32.3 g [0.183mol] of ferrocene
69.3mL [0.459mol] of TMEDA
190mL (0.380mol) of *n*-BuLi 2M in *n*-pentane
200mL hexane

Procedure: Because of the highly pyrophoric product the synthesis must be performed under strict inert conditions (Schlenk-technique). Dry powder of ferrocene (32.3g, 0.183mol) was suspended in 200ml of dry hexane and stirred vigorously for half a hour. Then 69.3mL TMEDA (0.459 mol) were added at once and agitation was continued for a hour. 190mL of *n*-BuLi (2.0M in *n*-Pentan, 0.380mol) were added drop wise during 30min. A homogeneous suspension was formed and left with intensive agitation for 4 hours. The reaction products were filtered with a Schlenk-filter (porosity 3), cleaned four times with *n*-hexane and dried under vacuum. Yield: 38.4g of a yellow, highly pyrophoric powder.

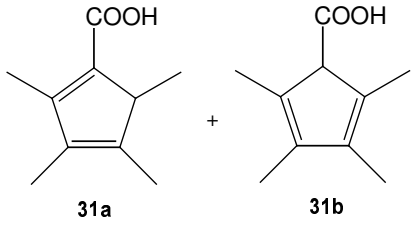
5.3.2 Synthesis of Ferrocenemonoaldehyde (R=H) (29) and Ferrocen -1,1´-dicarbaldehyde (R=CHO) (30)[5]



Procedure: 9.20g (29.3 mmol) of dilithioferrocene - TMEDA adduct **28** in 100mL of dry THF were cooled down to -80°C. The yellow-orange suspension was stirred for 30min. 6.00mL DMF (5.66g, 77.5mmol) were added and agitation continued for 15min, after this time the cooling bath was removed. The THF solvent was distilled off at ambient temperature. Then the solid reaction mixture was quenched with 75mL 14% HCl whereby the colour changed to dark red. The crude products were extracted 4 times with 150mL CH_2Cl_2, the organic phase was washed one time with 100 mL 14% HCl and water; the crude solid product was washed three times with 50mL *n*-Hexane to remove traces of ferrocene. The mixture of mono- and dialdehyde was separated and purified by column chromatography (eluent: first *n*-Hex/ Et_2O, then Et_2O). Yield: Ferrocene-monoaldehyde (R=H) **29**: 2.29g (35.9 %); Ferrocene -1,1´-dicarbaldehyde (R=CHO) **30**: 4.32g (60.9 %)

Characterization Data: Ferrocenealdehyde **29**: $C_{11}H_{10}FeO$ [214.05]; TLC: Rf: 0.84 (SiO_2/ Et_2O); FT-IR (KBr,ν in cm^{-1}): 3089, 2834, 2763, 1680vs, 1454, 1410, 1389, 1369, 1359, 1331, 1244, 1200, 1107, 1034, 1024, 1003, 843, 823, 742, 619, 592, 526, 499, 480, 457; ^{1}H-NMR ($CDCl_3$): 9.95 (s, 1H, CHO), 4.81 (t, 2H, Cp), 4.60 (t , 2H, Cp), 4.29 (s, 5H, Cp); Ferrocene-1,1´-dicarbaldehyde **30**: $C_{12}H_{10}FeO_2$ [242.06]; TLC: Rf: 0.59 (SiO_2 / Et_2O); FT-IR (KBr,ν in cm^{-1}): 3117, 3100, 3093, 2830, 2766, 1682vs, 1452, 1412, 1381, 1371, 1331, 1244, 1209, 1036, 1026, 987, 829, 740, 613, 592, 522, 488, 461, 434; ^{1}H-NMR ($CDCl_3$): 9.90 (s, 2H, CHO), 4.81 (t, 4H, Cp), 4.62 (t, 4H, Cp); ^{13}C- NMR ($CDCl_3$): 192.7 (CHO), 80.2, 74.1, 70.8 (Cp)

5.3.3 Synthesis of 2,3,4,5-Tetramethylcyclopenta-1,3-diene-1-carboxylic acid (31a) and 2,3,4,5-Tetramethylcyclopenta-2,4-diene-1-carboxylic acid (31b)[6]



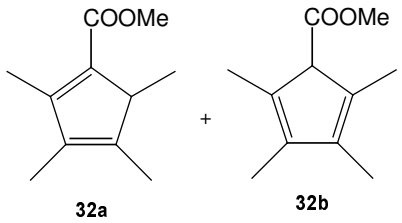
Reactants and quantities:

5.40 g [44.19 mmol] of 1,2,3,4-tetramethylcyclopenta-1,3-diene (Aldrich, 85% 1,3 isomer)
22.2 mL [44.0 mmol] of nBuLi (2.0M solution in pentane)
dry THF 200mL
50 mL of a saturated NH_4Cl solution
100 mL of diethyl ether

Procedure: A 22.2 mL (44.0 mmol) amount of 2.0 M *n*BuLi (solution in pentane) was added to a solution of 5.40 g (44.19mmol) of 1,2,3,4-tetramethylcyclopenta-1,3-diene (5) in 200 mL of dry THF at -20 °C. The mixture was stirred during 16 h and allowed to warm to 25 °C. The resulting thick white suspension was then cooled to -78 °C. At this temperature gaseous CO_2 was bubbled through the suspension during 2.5 h and the reaction mixture was allowed to warm to room temperature, while still maintaining CO_2 bubbling. After 30 min 50mL of a saturated NH_4Cl solution and 100mL of diethyl ether were added. The organic layer was separated and washed with brine, dried over $MgSO_4$, and evaporated in vacuum. The remaining pale yellow solid was dissolved in a minimum amount of warm diethyl ether and 2.2 g of **31a** (confirmed by X-Ray crystallography) crystallized during one day. A second crop of white product could be obtained by treating the pale yellow oily product with hexane. Yield: 6.41 g (66%) in total of **31a** and **31b** (as a ca. 6:1 mixture of 31a,b; confirmed by ^{1}H-NMR)

Characterization Data: [166.22 g/mol] $C_{10}H_{14}O_2$: **31a**: ^{1}H-NMR ($CDCl_3$,TMS): 12.5 (s broad, 1H, COO*H*), 3.03 (m, 1H, C*H*), 2.28 (d, 3H,CH_3), 1.90, 1.80 (2 s, each 3H, CH_3) 1.23 (s, 3H,CH_3); ^{13}C-NMR ($CDCl_3$, TMS): 170.6 (COOH), 159.5, 151.3, 135.5, 131.2 (C=C), 49.6 (*C*HCH$_3$), 14.7, 14.0, 12.4, 10.6 (*C*H$_3$); MS m/z 166 (M+, 100%), 151, 121, 107, 45, 28, 15. **31b**: ^{1}H-NMR ($CDCl_3$): 12.5 (s broad, 1H, COO*H*), 3.53 (m, 1H, C*H*), 1.91 (s, 6H, CH$_3$), 1.80 (m, 6H, CH_3); ^{13}C-NMR ($CDCl_3$) : 178.7 (COOH), 138.3, 130.8 (CdC), 62.8 (*C*HCOOH), 12.2, 11.4 (*C*H3).

5.3.4 Synthesis of 1-(Methoxycarbonyl)-2,3,4,5-tetramethylcyclopenta-1,3-diene (32a) and 1-(Methoxycarbonyl)-2,3,4,5-tetramethylcyclopenta-2,4-diene (32b)[6]



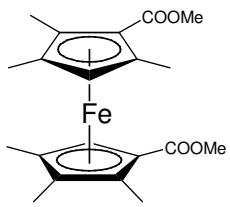
32a 32b

Reactants and quantities:
6.00 g mixture of the carboxylic acids **31a,b** (36.1 mmol)
6.94 g trimethyloxonium tetrafluoroborate (46.92 mmol)
Dichloromethane 250mL
8.17 mL diisopropylethylamine (46.92 mmol)

Procedure: A 6.00 g (36.1 mmol) amount of a mixture of the carboxylic acids **31a,b** was added to a suspension of 6.94 g (46.92 mmol) of trimethyloxonium tetrafluoroborate in 250 mL of dry dichloromethane at 0 °C. During 5 min 8.17mL (46.92 mmol) of diisopropylethylamine was added slowly. The mixture was allowed to warm to 20 °C and stirred for 22 h. Thereafter 20mL of 1M HCl was added, and the organic layer was separated, washed with a saturated $NaHCO_3$ solution and dried over $MgSO_4$. The solvent was removed in vacuum and the remaining pale yellow oil was distilled at 130-140°C and 8 mbar. Yield: 4.87 g (75%) of a colorless oil (ca. 6:1 mixture of **32a,b**, as determined by ^{1}H NMR).

Characterization Data: [180.25] Elemental Anal. Calc for $C_{11}H_{16}O_2$ (mixture of 32a,b): C, 73.30; H, 8.95. Found: C, 73.25; H, 8.82. 32a: ^{1}H-NMR ($CDCl_3$): 3.70 (s, 3H, OCH_3), 3.02 (m, 1H, *H*CCH$_3$), 2.25 (d, J 2.2Hz, 3H, CH$_3$), 1.88 and 1.80 (both m, each 3H, C=CCH_3), 1.17 (d, J 7.5 Hz, 3H, HCCH_3); ^{13}C-NMR ($CDCl_3$): 165.5 (C=O), 156.7, 149.3, 135.1, 131.8 (C=C), 50.47 (*C*H), 49.53 (O*C*H$_3$), 14.68, 13.71, 12.23, 10.59 (CH$_3$); MS m/z 180 (M+), 165, 149, 133, 121 (100%), 105, 91, 77.; 32b**:** ^{1}H-NMR ($CDCl_3$): 3.70 (s, 3H, OCH$_3$), 1.80 and 1.69 (br s, each 6H, C=CCH_3), signal for HCCOO overlapping with OCH$_3$ signal of 7a; ^{13}C-NMR ($CDCl_3$) 174.0 (C=O), 146.0, 138.4 (C=C), 64.2 (CH), 50.0 (O*C*H$_3$),12.57, 10.16 (*C*H$_3$).

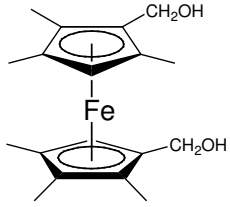
5.3.5 Synthesis of 1,1′-Bis(methoxycarbonyl)-2,2′,3,3',4,4',5,5'-octamethylferrocene (33)[6,7,8]



Reactants and quantities:
4.87 g methyl carboxylate **32a,b** (27.02 mmol)
4.54ml diisopropylamine (32.42mmol)
16.9ml nBuLi (2M in pentane) (33.78mmol)
2.74 g anhydrous $FeCl_2$ (21.6 mmol)
121 mg Fe powder (2.16 mmol)
THF 250 mL

Procedure: A solution of 4.87 g (27.02mmol) of the methyl carboxylate **32a,b** in 150 mL of dry THF was treated with 100 mL of a freshly prepared LDA solution at -78 °C (4.54ml diisopropylamine (32.42mmol) was mixed with 16.9ml nBuLi (2M in pentane, 33.78mmol) at -78 °C in 100mL of dry THF, 1h of stirring). The mixture was stirred during 1 h at this temperature while it turned slowly from yellow to red. After this time 2.74 g (21.6 mmol) of anhydrous $FeCl_2$ was added, together with 121 mg (2.16 mmol) of Fe powder (reduction of adventitious traces of $FeCl_3$). The suspension was stirred and allowed to warm slowly to 20 °C during 24h. A 200 mL volume of a saturated NH_4Cl solution was added, and the organic layer was washed with brine and dried over $MgSO_4$. The solvent was removed in vacuo, and the remaining solid was purified by flash chromatography over silica gel (4*20cm, eluent: ethyl acetate / hexanes (1:10)). Yield: 3.9 g (69%) of a red crystalline solid.
Characterization Data: [414.32] Elemental Anal. Calcd for $C_{22}H_{30}O_4Fe$: C, 63.78; H, 7.30. Found: C, 63.81; H, 7.41. ^{1}H-NMR ($CDCl_3$): 3.76 (s, OCH_3), 1.91, 1.66 (both s, CH_3). ^{13}C-NMR ($CDCl_3$): 172.5 (C=O), 84.8, 83.8 (CpC), 67.77 (Cp ipsoC), 10.54, 8.86 (CH_3). ; MS: m/z 414 (M+, 100%), 383, 355, 235, 147.

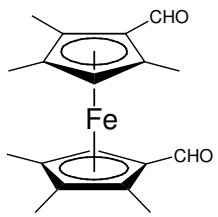
5.3.6 Synthesis of 1,1'-Bis(hydroxymethyl)-2,2',3,3',4,4',5,5'-octamethylferrocene (34)[6]



Reactants and quantities:
3.78 g methyl ester **33** (9.123 mmol)
1.472 g $LiAlH_4$ (38.77 mmol)
dryTHF 500 mL

Procedure: A 3.78 g (9.123 mmol) amount of the methyl ester **33** in 300 mL of dryTHF was treated with 1.472 g (38.77 mmol) of $LiAlH_4$ at 0 °C. The suspension was stirred for 22 h while warming it slowly to 25 °C. Thereafter, 20 mL of a saturated solution of NH_4Cl were cautious added.
The mixture was extracted with diethyl ether (250 mL), dried with $MgSO_4$, and filtered over Celite. The solvent was removed in vacuum, and the remaining solid was crystallized from acetone to separate from incomplete reduction product. Yield: 2.07 g (63.3%) of a yellow microcrystalline solid.
Characterization Data: [321.46] Elemental Anal. Calc. for $C_{20}H_{30}O_2Fe$: C, 67.04; H, 8.44. Found: C, 67.03; H, 8.20.^{1}H-NMR (DMSO-d6): 4.24 (t, JHH: 4.3 Hz, 2H, OH), 4.07 (d, JHH: 4.2 Hz, 4H, CH_2), 1.65, 1.61 (both s, 24H, CH_3). ^{13}C-NMR (DMSO-d6): 80.6, 79.1, 78.8 (CpC), 55.6 (CH_2), 9.28, 9.17 (CH_3).; MS: m/z 358 (M+), 340 (100%), 134, 119.

5.3.7 Synthesis of 2,2',3,3',4,4',5,5'-Octamethylferrocene-1,1'-dicarbaldehyde (35)[6]



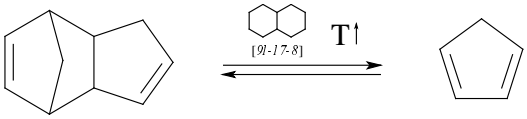
Reactants and quantities:
1.77 g dialcohol **34** (4.94 mmol)
9.8 g manganese dioxide (113 mmol), freshly prepared
Dichloromethane 600 mL

Procedure: A suspension of 1.77 g (4.94 mmol) of dialcohol **34** and 9.8 g (113 mmol) of manganese dioxide in 600 mL of dry dichloromethane was stirred during 18 h. Then, the mixture was filtered

through Celite and the solvent evaporated in vacuum. The residue was purified by flash chromatography over silica gel/ethyl acetate: hexanes (1:3). Yield: 1.346 g (76.9%) as red crystalline solid.

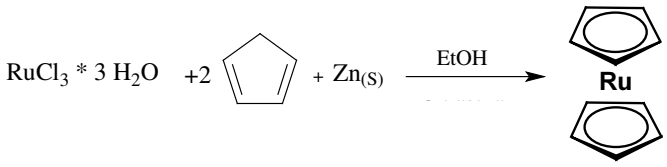
Characterization Data: [354.27] Elemental Anal. Calcd for $C_{20}H_{26}O_2Fe$: C, 67.81; H, 7.40. Found: C, 67.73; H, 7.41. ^{1}H-NMR ($CDCl_3$):10.00 (s, 2H, CHO), 1.96, 1.74 (both s, each 12H, CH_3). ^{13}C-NMR ($CDCl_3$): 196.5 (CHO), 87.1, 84.4 (CpC), 72.7 (Cp ipsoC), 9.34, 9.00 (CH_3). MS: m/z 354 (M+, 100%), 326, 297, 203, 174, 119.

5.3.8 Synthesis of Cyclopentadiene CpH (thermal Cracking of DiCp) (36)[5]



Procedure: 800ml Decalin (cis/trans Decahydronaphthalin) and 500ml Dicyclopentadien were warmed to 40ºC. The CpH distilled through a Vigreux-column and was collected in an ice-cooled flask containing 50g of $CaCl_2$(s).

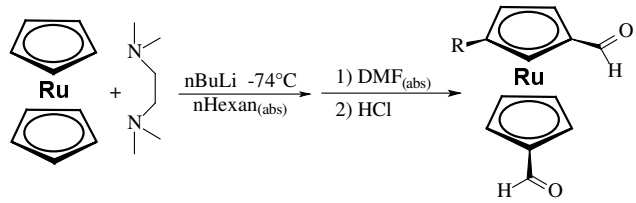
5.3.9 Synthesis of Ruthenocene (37)[5]



Procedure: In a 2.0 L flask 5.21g (19.93mmol) $RuCl_3$-Trihydrat is suspended in 1000mL of EtOH. Then 100ml (1.21mol, 80.0g) of cyclopentadiene were added and agitated. Then 52g (0.80mol) of $Zn_{(S)}$ are added slowly (H_2 – is generated). The reaction was warmed to 40ºC and agitated during half an hour. The solvent was removed under vacuum. The remaining solid (Zn, $ZnCl_2$) was digested two times with 100mL Toluene , and the organic phase was passed over celite and evaporated Yield: 4.216g (91.5 %) yellow powder.

Characterization Data: $C_{10}H_{10}Ru$ [231.26 g/mol]. FT-IR (KBr,ν in cm^{-1}):[9] 3083 (ν_{CH}, w); 1406 (ν_{CC}, s); 1261 (m); 1101 (ν_{CC}, vs); 1063 (m); 1051(m); 1001 (δ_{CH}, vs); 864 (s); 810 (π_{CH}, vs); 447 ^{1}H-NMR ($CDCl_3$) ^{1}H: δ 4.53 ppm

5.3.10 Synthesis of Ruthenocene-1,1´-dicarboxaldehyde (R=H, 38) and Ruthenocene-1,3,1´-tricarbaldehyd (R=CHO, 39)[5]



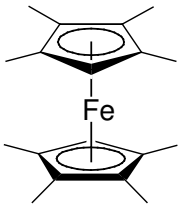
Procedure: 5.00g (21.65mmol) of Ruthenocene **(8a)** were suspended in 300mL of dry *n*-hexane under an argon atmosphere and stirred for 30min. Then 4.90mL (3.77g, 32.5mmol) of tetramethyl-ethylendiamine (TMEDA) were added and the mixture was agitated for further 15 min. Then 43.3mL of *n*-BuLi (2.0 M in *n*-Pentan, 86.6mmol) were added dropwise during 15 min. The reaction mixture was warmed to 40ºC for 30min and finally left with stirring overnight at room temperature. During this time a pale yellow precipitate was formed which was washed two times with 10 mL of dry *n*-hexane. The yellow solid was suspended in 60mL of dry n-hexane and 6.7mL of dry DMF (6.33g, 86.6

mmol) in 80ml of dry Et_2O were added dropwise under vigorous stirring during 15min; then 150mL of 5M HCl were added all at once. The mixture was extracted three times with 300mL of CH_2Cl_2. The organic phase was washed with a saturated solution of NaCl and dried. The crude product was chromatographied (SiO_2 (30*4 cm), eluent: first Et_2O/nHexane (1:1) and then just Et_2O) to obtain 1.75g (28.2% yield) of **38** and 1.35g (19.8%) of **39** as a yellow powders.

Characterization Data: 38: [287.28g/mol] $C_{12}H_{10}O_2Ru$. IR (KBr): 3102, 2959, 2929, 2873, 2828, 2803, 2778, 2763, 2728, 2710, 1688 (ν_{CO}, vs), 1449, 1377, 1242, 1034, 835, 744, 613, 520, 455, 412; NMR ($CDCl_3$) ^{1}H: 9.69 (2H, s, -CHO), 5.16 (2H, "t", CpH), 4.91 (2H, "t", CpH) ^{13}C: 189.7 (CHO); 85.6 (Cquart.), 72.5, 75.8 (CCp-H)

39: $C_{13}H_{10}O_3Ru$ [315.29] IR (KBr): 3099, 2963, 2919, 2873, 2778, 1690 (ν_{CO}, vs), 1460, 1435, 1369, 1231, 1148, 1121, 1034, 862, 742, 617, 540, 505, 470; MS (EI) (40eV, 200°C) (m/e, % Int.): 314 (100%, M^+-H); 286 (45%, M^+-CO); 259 (46%, M^+- 2CO); 231 (88%, M^+-3CO); 204 (43%); 166 (53%, RuCp). NMR ($CDCl_3$): ^{1}H: δ 9.72 (2H, s, CHO), 9.66 (1H, s, CHO), 5.67 (1H, s, Cp), 5.42 (2H, d, Cp); 5.25 (2H, t, Cp), 4.99 (2H, t, Cp). ^{13}C: 189.1(1CHO), 188.8 (2CHO), 87.9 ($2C_{quart.}$), 86.5($1C_{quart.}$), 77.0, 75.1, 74.0 (each $2C_{Cp}$), 72.9 ($1C_{Cp}$)

5.3.11 Synthesis of 1,1´,2,2´,3,3´,4,4´-octamethylferrocene (40)[10]

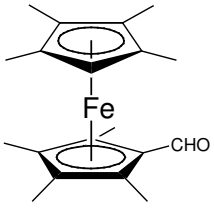


Quantities:

1,2,3,4-tetramethyl-1,3-cyclopentadiene	2.47g (20.2mmol)
n-Buthyllithium (2.5M in Hexane)	8.9mL (22.2mmol)
$FeCl_2$	1.40g (11.1mmol)

Procedure: To a solution of 1,2,3,4-tetramethyl-1,3-cyclopentadien in 100ml of dry THF cooled to –70ºC was added n-Buthyllithium dropwise during a few minutes. The mixture was allowed to warm up and was stirred further 30min at ambient temperature. After addition of ferrous chloride the suspension was stirred for 15 hours. Subsequently the black solution was gently refluxed for 5h, the THF was removed under vacuum and the residue was extracted with 50mL water and 15mL diethyl ether. The organic phase was dried with Na_2SO_4 and evaporated to yield 2.37g (78.6%) of an orange microcrystalline product which is not very stable on air. Melting point : 235ºC (fast heating).

5.3.12 Synthesis of Formyl-1´,2,2´,3,3´,4,4´,5-octamethylferrocene (41)[11]



Quantities:

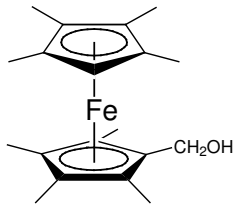
1,1´,2,2´,3,3´,4,4´-octamethylferrocene	**40** 2.00g (6.71mmol)
Phosporous oxychloride	5.0mL, 9.27g (60.5mmol)
N,N-dimethylformamide	3.0mL, 3.13g (42.8mmol)

Procedure: To a solution of the octamethylferrocenecarbaldehyd in 50mL of dry $CHCl_3$ under inert conditions were added phosphorous oxychloride and dimethylformamide. The deep red solution was stirred vigorously and heated to 50-60ºC for 6h hours. After cooling to ambient temperature the

mixture was quenched with 200 mL water and stirring was continued for additional 30 min. The mixture was extracted three times with a total of 200 mL of diethylether, the combined organic layers were washed two times with 50 mL water, with 30 mL saturated NaCl solution, dried with Na_2SO_4. TLC control (silica, n-hexane/ether 1:1) revealed that no further purification was needed. Finally, the solvent was evaporated. Yield: 1.74 g (79.5%) of a dark red solid, stable on air (mp.: 234-5ºC).

Characterization Data: $C_{19}H_{26}FeO$ [326.26 g/mol]. FT-IR (KBr ν in cm^{-1}): 3060, 2903,1665, 1028, 862, 825, 793, 684, 627, 615, 524, 509, 462 ^{1}H-NMR ($CDCl_3$, TMS): 10.05 (s,1 H, CHO), 3.84 (1H, s, CH), 2.03 (s, 6H, $2CH_3$), 1.83 (s, 6H, $2CH_3$), 1.68 (s, 6H, $2CH_3$), 1.64 (s, 6H, $2CH_3$); ^{13}C-NMR ($CDCl_3$, TMS): 195.5 (CHO), 71.3 (Cp), 11.0, 9.79, 9.47, 9.2 (8* $-CH_3$)

5.3.13 Synthesis of 1-hydroxymethyl-1´,2,2´,3,3´,4,4´,5-octamethylferrocene (42)[11]



Quantities:

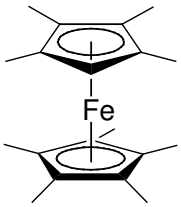
Formyl-1´,2,2´,3,3´,4,4´,5-octamethylferrocene **41** 1.50g (4.60mmol)

Lithium-triethylborohydride (1M in THF) 5.03 mL, 0.536g (5.06mmol)

Procedure:A solution of Formyl-1´,2,2´,3,3´,4,4´,5-octamethylferrocene in 40 mL of dry THF was cooled to –45ºC and Lithium-triethylborohydride (Superhydride) was added all at once. The color of the solution changed immediately from red to yellow-orange. After warming up for 30 min the solvent was evaporated and the residue was extracted with 50 mL water and 100mL diethylether. The organic phase was dried with Na_2SO_4 and the solvent was removed. Because of the air-sensitivity of the product it was not purified further. Yield 1.41 g (93%) yellow solid.

Characterization Data: $C_{19}H_{28}FeO$ [328.28 g/mol]. FT-IR (KBr, ν in cm^{-1}): 3295b, 3058, 2857, 1425, 1379, 1229, 1090, 1076, 1028, 993, 823, 812, 702, 688, 561, 509, 486; ^{1}H-NMR ($CDCl_3$, TMS): 4.34 (d, 2 H, CH_2), 3.32 (1H, s, CH), 1.79, 1.71, 1.68, 1.63 (s, 24, $8CH_3$); ^{13}C-NMR ($CDCl_3$, TMS): 80.8, 80.5, 80,4 79.6 (Cp), 70.2 (CpH), 58.2 (CH_2), 11.3, 9.71, 9.46, 9.4 (8* $-CH_3$)

5.3.14 Synthesis of 1,1´,2,2´,3,3´,4,4´,5-nonamethylferrocene (43)[11]



Quantities:

1-hydroxymethyl-1´,2,2´,3,3´,4,4´,5-octamethylferrocene
1.20 g (3.65 mmol)

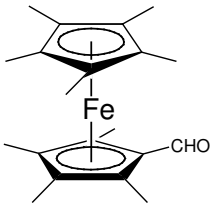
HBF_4*Et_2O (54 % in Et_2O) 1.26 mL (9.14 mmol)

$LiB(C_2H_5)_3H$ (1.0 M in THF) Superhydrid

Procedure: The 1-hydroxymethyl-1´,2,2´,3,3´,4,4´,5-octamethylferrocene was dissolved in 50 mL of dry Et_2O and cooled to –30 ºC under an Argon atmosphere. HBF_4 was added via a syringe, and the mixture was stirred. The color changed from yellow to orange and a flaky precipitate was formed which was filtered off under Argon, washed with 50 mL cold (-30 ºC) Et_2O to remove traces of HBF_4 and the Superydride was added via a syringe. The color of the reaction changes to yellow whereas

the solid precipitate was dissolved slowly under release of gaseous hydrogen. After 15min the mixture was extracted with 200mL Et_2O and 150mL water (both saturated with Argon), the organic phase was separated, washed with 150 mL of water, dried over Na_2SO_4, filtrated and evaporated to yield a yellow, air-sensitive powder which was used immediately in the following reaction. Yield calculated for quantitative reaction: 1.143g.

5.3.15 Synthesis of formyl-1´,2,2´,3,3´,4,4´,5,5-´nonamethylferrocene(44)[11]



Quantities:

1,1´,2,2´,3,3´,4,4´,5-nonamethylferrocene **43**	1.143 (3.65mmol)
Phosporous oxychloride	3.0mL, 5.02g (32.8mmol)
N,N-dimethylformamide	1.7mL, 1.61g (22.7mmol)

Procedure: To a solution of the nonamethylferrocene in 50mL of dry $CHCl_3$ under inert conditions were added phosphorous oxychloride and dimethylformamide. The deep red solution was stirred vigorously and heated to 50-60ºC for 6h hours. After cooling to ambient temperature the mixture was quenched with 200 mL water and stirring was continued for additional 30 min. The mixture was extracted three times with a total of 200 mL of diethylether, the combined organic layers were washed two times with 50 mL water, with 30 mL saturated NaCl solution, dried with Na_2SO_4. TLC control (silica, n-hexane/ether 1:1) revealed that no further purification was needed. Finally, the solvent was evaporated. Yield: 1.12 g (90.0%) of a dark red solid, stable on air (mp.: 234-5ºC).

Characterization Data: $C_{20}H_{28}FeO$ [340.29 g/mol]. ^{1}H-NMR ($CDCl_3$, TMS): 9.95 (s, 1H, C*H*O), 1.97, 1.76 (s, each 6H, 4*CH_3), 1.64 (s, 15H Cp*Me*$_5$); ^{13}C-NMR ($CDCl_3$, TMS): 195.7 (*C*HO), 86.0, 82,7 (*Cp*Me$_4$), 80.6 (*Cp*-Me$_5$), 72.5 (*Cp*-CHO), 9.3 (Cp*Me*$_5$), 8.9 (Cp*Me*$_4$)

REFERENCES

1. Teruel, L.; Viadel, ll.; Carilla, J.; Fajarí, Ll.; Brillas, E.; Sañé, J.; Rius, J.; Juliá, L. *J. Org. Chem*., *61*, **1996**, 6063.
2. Rovira, C.; Ruiz- Molina, D.; Elsner, O.; Vidal-Gancedo, J.; Bonvoisin, J.; Launay, J.-P.; Veciana, J., *Chem. Eur. J.*, **2001**, *7*, 240
3. Ballester, M.; Veciana, J.; Riera, J.; Castañer, J.; Rovira, C.; Armet, O., *J. Org. Chem*., *51***, 1986**, 2472.
4. All metallocenes have been synthesized by Christian Sporer in the Institut für Allgemeine, Anorganische und Theoretische Chemie of the Innsbruck University.
5. (a) G. G. A. Balavoine , G. Doisneau , T. Fillebeen-Kahn *J. Organomet. Chem.* **1991***, 412* , 381-382 (b) R. Sanders , U. T. Mueller-Westerhoff *J. Organomet. Chem.* **1996**,*512* , 219-224 (c) U. T. Mueller-Westerhoff , Z. Yang , G . Ingram *J. Organomet. Chem.* **1993**,*463* , 163-167
6. Hobi, M.; Ruppert, O.; Gramlich, V. and Togni, A. *Organometallics* **1997**, *16*, 1384-1391
7. Gonsalves, K.; Zhan-ru, L.; Rausch, M. D. J. Am. Chem. Soc. 1984, 106, 3862. and Rausch, M. D.; Ciappenelli, D. J. *J. Organomet. Chem.* **1967**, *10*, 127.
8. The addition of iron powder to ferrous and/or ferric chloride to generate “active” FeCl2 in the synthesis of ferrocenes *has been previously reported. See: (a) King, R. B.; Bisnette, M. B. J. Organomet.Chem.* ***1967****, 8*, 287. (b) Phillips, L.; Lacey, A. R.; Cooper, M. K. *J. Chem. Soc., Dalton Trans*. **1988,** 1383. (c) For practical reasons, no experiments using the isolated THF adduct of FeCl2 have been carried out. See: Aresta, M.; Nobile, C. F.; Petruzzelli, C. *Inorg. Chem*. **1977**, *16*, 1817.
9. K. Nakamoto “Infrared and raman spectra of inorganic and coordination compounds “ 3th Ed. **1978** J. Wiley & Sons
10. Schmitt, G.; Oezman, S. *Chemiker Zeitung*, **1976,** *100*, 143
11. Zou C., Wrighton M. S.; *J. Am. Chem. Soc*., **1990,** *112*, 7578-7584