Synthesis of Soluble 1,3-Bridged Ferrocene-Acetylene Polymers and the Divergent-Convergent Synthesis of Defined Oligomers

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A –CH_2NMe_2 group attached to ferrocene can be used as an *ortho*/*ortho*-directing group to selectively synthesize 1,2,3-substituted ferrocenes, which are used as starting materials for novel 1,3-linked ferrocene polymers and oligomers. The Sonogashira coupling reaction of 1-(I),2-(CH_2NMe_2)-ferrocene with HC≡$CSiEt_3$ results in 1-(C≡$CSiEt_3$),2-(CH_2NMe_2)-ferrocene (**1b**), which – following an *ortho*-lithiation/iodination sequence – is converted into 1-(I),2-(CH_2NMe_2),3-(C≡$CSiEt_3$)-ferrocene (**1d**). Removal of the –$SiEt_3$ protective group yields 1-(I),2-(CH_2NMe_2),3-(C≡CH)-ferrocene, which can be polymerized under Sonogashira conditions to yield a soluble, bimodal ferrocene-acetylene polymer of M_W = 3700/7100 and M_n = 4272. To understand the properties of the polymer better and to evaluate the effect of 1,3-substitution on the electronic communication between the metal centers, a divergent-convergent approach was used to synthesize defined di-, tri- and tetranuclear ferrocenes. Accordingly, **1d** was cross-coupled with 1-(CH_2NMe_2),2-(C≡CH)-ferrocene to give [2-(CH_2NMe_2)-ferrocene-1-yl]-C≡C-[2-(CH_2NMe_2),3-(C≡$CSiEt_3$)-ferrocene-1-yl] (**2a**). Removal of the protective group in **2a** led to [2-(CH_2NMe_2)-ferrocene-1-yl]-C≡C-[2-(CH_2NMe_2),3-(C≡CH)-ferrocene-1-yl] (**2b**), which was treated with [1-(I),2-(CH_2NMe_2)-ferrocene-3-yl]-C≡C-[2-(CH_2NMe_2),3-(C≡$CSiEt_3$)-ferrocene-1-yl] (**2c**) to result in the corresponding tetrameric ferrocene (**4a**).

Introduction

Organic polymers such as polypyrrole, poly(*p*-phenylene),[1] polythiophene,[2] poly(*p*-phenylenevinylene)[3][4] or -ethynylene[5] display interesting properties like photo- and electroluminescence and conductivity, which are useful in antistatic coatings, battery materials or blue-light photo diodes.[6][7] Organometallic polymers could offer all of this and even more as the metal may impart unusual magnetic, electronic and optical properties on such materials.[8][9] Prominent in this field are ferrocene polymers,[10] which either consist of an organic backbone to which ferrocenyl groups are attached (e.g. polyvinylferrocene) or of 1,1′-ferrocenediyl groups in the polymer backbone; other metallocenes have been used less frequently.[11] One breakthrough in the synthesis of soluble, high molecular weight ferrocene polymers has been the discovery of an ROP-type coupling of strained ferrocenophanes by Manners and coworkers.[12] Despite the progress made recently, virtually all known ferrocene polymers, with a few (mostly poorly soluble) exceptions,[13] still suffer from two basic disadvantages: typically the different ferrocene units are linked by electronically insulating bridges that only allow electrostatic interactions between the different metal centers and, in addition, most often 1,1′-ferrocenediyl units are used as repeat units.

It is quite obvious that ferrocene polymers are more likely to display exceptional properties when the different metal centers are coupled intimately through suitable unsaturated bridging units.[14][15] We therefore decided to initiate a program aimed at synthesizing novel types of soluble 1,3-linked ferrocenediyl polymers.

Results and Discussion

Synthesis

A few 1,3-substituted ferrocenes have been described in the literature,[16] but starting from ferrocene itself, it is difficult to selectively introduce two substituents in the 1,2- or 1,3-positions of ferrocene. We therefore reasoned that it should be easier to synthesize 1,3-substituted ferrocenes by using an *ortho*/*ortho*-directing group to obtain 1,2,3-substituted ferrocenes instead.[17] In this respect the $-CH_2NMe_2$ unit in $FcCH_2NMe_2$ appears to be a suitable group for directed *ortho*/*ortho* metallation[18] and appears very convenient as $FcCH_2NMe_2$ is commercially available or can be synthesized at low cost.[19] Another advantage of $FcCH_2NMe_2$ is that the amine can be quaternized easily to give $-NMe_3^+$, which happens to be a good leaving group in nucleophilic substitution reactions.[20]

The reaction of $FcCH_2NMe_2$ first with *n*BuLi and then with iodine leads to the known 1-(I),2-(CH_2NMe_2)-ferrocene (**1a**),[21] which was coupled with HC≡$CSiEt_3$ in a Sonogashira-type reaction[22][23] to produce 1-(C≡$CSiEt_3$),2-(CH_2NMe_2)-ferrocene (**1b**) (yield > 90%) (Scheme 1).[24]

Compound **1b** can be deprotonated regioselectively with *n*BuLi at the other *ortho* position (with respect to the $-CH_2NMe_2$ unit) to yield, after reaction with iodine,

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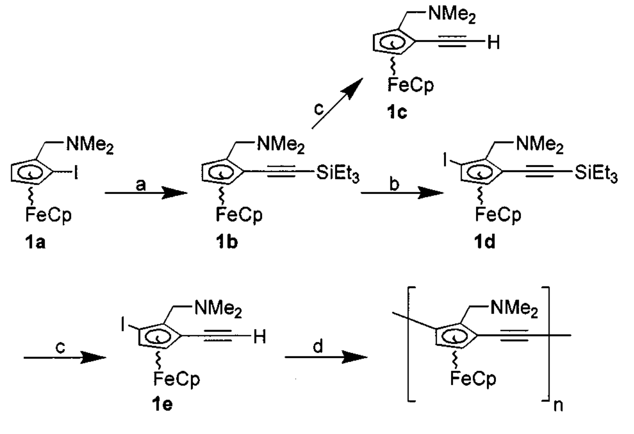
Scheme 1. a: $PdCl_2(PPh_3)_2$, CuI, $HCCSiEt_3$, solvent iPr$_2$NH, reflux; b: 1. BuLi, 0°C, Et_2O, 2 h, 2. $+I_2$, -78°C; c: nBu$_4$N$^+$F$^-\cdot 3\ H_2O$; d: $PdCl_2(PPh_3)_2$, CuI, solvent iPr$_2$NH, reflux

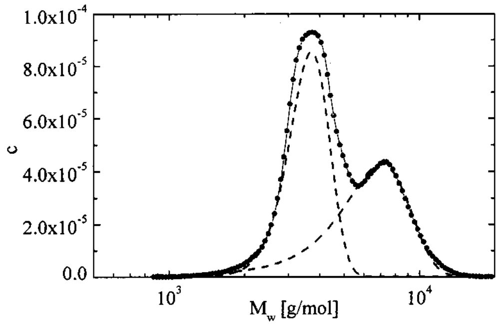


the 1,2,3-substituted ferrocene 1-(I),2-(CH_2NMe_2),3-($C{\equiv}CSiEt_3$)-ferrocene (**1d**) (yield 66%). This reaction works very well for the $-SiEt_3$-protected acetylene, but only gives low yields (ca. 20%) of the respective 1,2,3-substituted ferrocene with an $-SiMe_3$-protected acetylene. Obviously, the latter protecting group is not entirely stable towards nBuLi. Cleavage of the $-SiEt_3$ protective group in **1b** or **1d** is easily effected with aq. 50% KOH or nBu$_4$N$^+$F$^-\cdot 3\ H_2O$ to produce the respective 1-($C{\equiv}CH$),2-(CH_2NMe_2)-ferrocene (**1c**) and 1-(I),2-(CH_2NMe_2),3-($C{\equiv}CH$)-ferrocene (**1e**) in 75−80% yield.

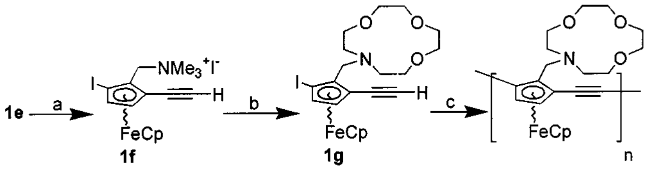
The 1,2,3-substituted ferrocene **1e** has two functional groups that can be coupled under Sonogashira conditions to form a dark red, glassy material (> 90% yield). This mixture was purified by flash chromatography and gave low molecular weight oligomers and a polymeric fraction. An attempted determination of the molecular mass of the latter material by standard GPC techniques was not successful, since an affinity-type chromatographic separation was observed. Obviously, this is caused by the polar nature of this material. We therefore had to resort to GPC-LALLS (gel-permeation chromatography/low-angle laser-light scattering) in an extremely polar mobile phase (DMF, 0.1 M guanidinium hydrochloride) to suppress affinity-type interactions with the stationary phase. With this method a characteristic bimodal molecular-weight distribution with $M_W = 3700$ and 7100 was found (Figure 1). This polymer is highly soluble in polar solvents (CH_2Cl_2, $CHCl_3$), which may appear surprising given its rigid backbone. In this respect it should, however, be noted that the polymer formed is a diastereomeric mixture with random orientations of the CpFe units with respect to the polymer backbone. This may be a disadvantage with respect to the characterization of the low molecular weight oligomers, but should not unfavorably influence the electronic properties of the polymers. On the other hand this disorder could very well be responsible for the good solubility of these materials.

Another advantage of the $-CH_2NMe_2$ group is that it can be functionalized easily by alkylation, followed by reaction of the quaternary ammonium salt with various nucleophiles (see Scheme 2). We have tested this by treating **1e** with MeI to give [1-($C{\equiv}CH$),2-(CH_2NMe_3)-ferrocene]$^+$I$^-$ (**1f**) (yield 91%). This salt was treated with aza-12-crown-4 to produce the crown ether substituted monomer (1-$C{\equiv}CH$),[2-CH_2(aza-12-crown-4)]-ferrocene (**1g**) (yield 29%), which was polymerized under Sonogashira coupling conditions to give a redox-active crown ether polymer. This polymer is potentially attractive as the utility of such materials as electro-active sensors for metal ions has been demonstrated by Bäuerle,[25] Garnier[26] and Swager.[27] The dark-red mixture of oligomers and polymers was separated by flash-chromatography. The GPC-LALLS investigation of this polymer initially suggested much higher molecular weights ($M_W = 61000$, $M_n = 58000$), but the strong tailing of the GPC traces casts some doubt on these results, and may very well be the result of an aggregation process involving several polymer molecules. It is interesting in terms of chain-termination reactions that the oligomeric fractions from both polymerizations display vinylic resonances in the ^{1}H-NMR spectrum. The same phenomenon was also observed in related coupling reactions of mononuclear complexes of sterically more demanding acetylene derivatives of chiral FcCH(Me)NMe$_2$.[28]

Figure 1. Molecular weight distribution of the 1,3-ferrocene-acetylene polymer as determined by GPC-LALLS

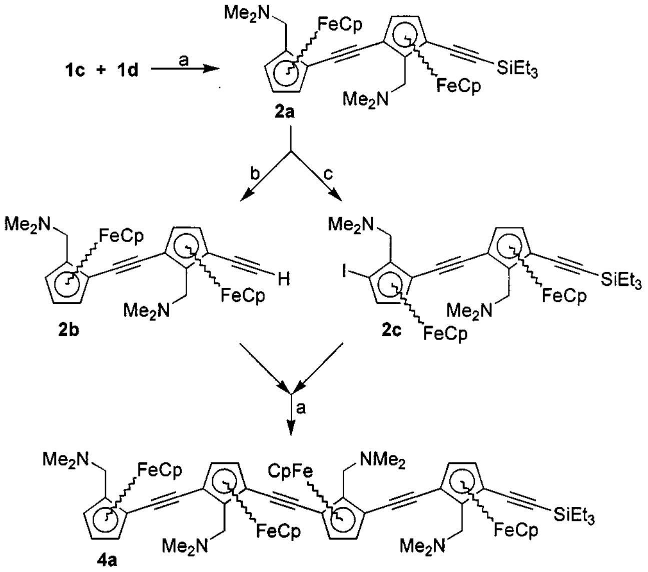


Scheme 2. a: MeI; b: aza-12-crown-4, CH_3CN reflux; c: $PdCl_2(PPh_3)_2$, CuI, solvent iPr$_2$NH, reflux



In order to better understand the electronic properties of the polymeric materials we have prepared defined oligomers using a divergent-convergent approach, which has been used successfully by Tour et al.[29] and Moore et al.[30] in the synthesis of related oligothiophenes and oligoethynylarenes. Starting from **1c** and **1d** a Sonogashira coupling generates [2-(CH_2NMe_2)-ferrocene-1-yl]-$C{\equiv}C$-[2-(CH_2NMe_2),-3-($C{\equiv}CSiEt_3$)-ferrocene-1-yl] (**2a**) (yield > 90%) (Scheme 3). This batch was split and the first half used for a lithiation/iodination sequence resulting in [2-(CH_2NMe_2),3-(I)-ferrocene-1-yl]-$C{\equiv}C$-[2-(CH_2NMe_2),3-($C{\equiv}CSiEt_3$)-ferrocene-1-yl] (**2c**) (yield 65%), while the remaining **2a** was deprotected with $nBu_4N^+F^- \cdot 3\ H_2O$ to give [1-(CH_2NMe_2)-ferrocene-2-yl]-C≡C-[2-(CH_2NMe_2),3-(C≡CH)-ferrocene-1-yl] (**2b**) (yield 80%). Both **2b** and **2c** were then coupled according to the Sonogashira protocol to give the tetramer [2-(CH_2NMe_2)-ferrocene-1-yl]-C≡C-[2-(CH_2NMe_2)-ferrocene-1,3-diyl]-C≡C-[1-(CH_2NMe_2)-ferrocene-1,3-diyl]-C≡C-[2-(CH_2NMe_2),3-(C≡$CSiEt_3$)-ferrocene-1-yl] (**4a**) (yield 73%). The highly polar nature of this tarry, red material caused tailing and repeated chromatography was necessary to obtain analytically pure samples since **4a** could not be recrystallized. These purification problems also were the reason why we did not attempt to extend our synthetic procedure to the octameric ferrocene.

Scheme 3. a: $PdCl_2(PPh_3)_2$, CuI, $HCCSiEt_3$, solvent iPr_2NH, reflux; b: $nBu_4N^+F^- \cdot 3\ H_2O$; c: 1. + BuLi, 0°C, Et_2O, 2 h, 2. + I_2, −78°C



In order to be able to compare the influence of the substitution pattern (1,3- or 1,1′-) on the electronic properties of the ferrocene-acetylenes, we synthesized the two trinuclear ferrocenes **3a** and **3b** (Scheme 4). Both complexes only differ in that **3a** has a 1,3-substituted ferrocene core, while **3b** has a 1,1′-substituted ferrocene unit. The coupling reaction of **1a** and **2b** gave **3a**, while the respective coupling of 1,1′-diiodoferrocene and **1c** produced **3b**, both in yields of around 75%. A closer investigation of these compounds should provide evidence of the better electronic delocalization of the ring with the 1,3-substitution pattern than that with the 1,1′-positions.

NMR Spectroscopy

The ^1H-NMR spectra of the mononuclear ferrocenes are straightforward, while those of the oligomers are characterized by more complex spin systems. For example the number of $-N(CH_3)_2$ resonances found ($\delta = 2.20-2.35$ in **4a**), correspond to the number of diastereomers, e.g. four lines in **2a**. Accordingly, the large number of $-N(CH_3)_2$ resonances in **4a** reflects the large number of diastereomers (Figure 2, top). The fact that the $-CH_2-$ groups have diastereotopic protons in the 1,2,3-substituted species leads to another complex set of resonances that usually appear in two groups ($\delta = 3.48-3.53$ and $\delta = 3.65-3.81$ in **4a**). The C_5H_5 resonances of the unsubstituted cyclopentadienyl ring are typically split into no more than two resonances, while those of the C_5H_2 unit in 1,2,3-substituted cyclopentadienyl rings are observed as a group of signals at low field ($\delta = 4.38-4.45$ in **4a**) with respect to C_5H_5. In between these two signals, the characteristic resonances of the *ortho*-H (hydrogen atom next to $-CH_2NMe_2$ in 1,2-substituted ferrocenes) can be found at $\delta = 4.26$ (in **4a**).

Scheme 4. a: $PdCl_2(PPh_3)_2$, CuI, $HCCSiEt_3$, solvent iPr_2NH, reflux

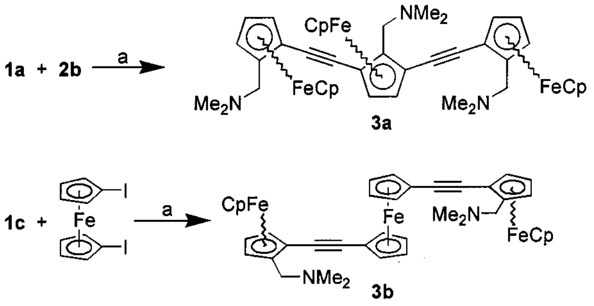
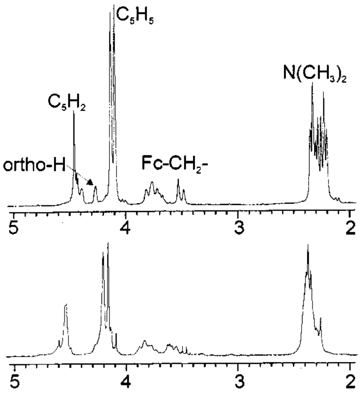


Figure 2. ^1H-NMR spectra of the tetramer **4a** (top) and polymer I (bottom)



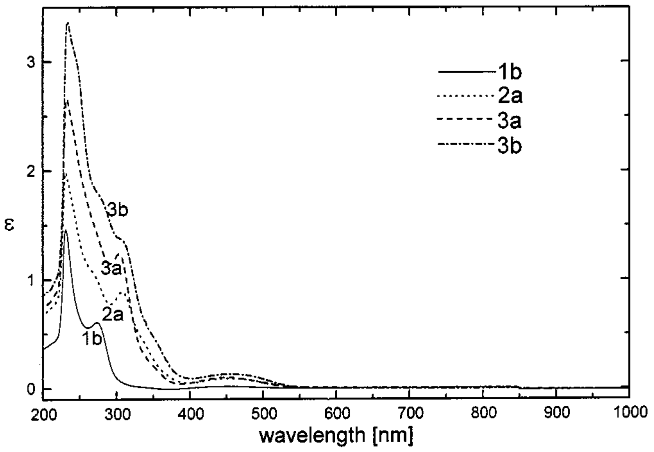
With this knowledge in mind the ^1H-NMR spectrum of polymer I can be understood. The typical signals of the tetramer are found (in broadened form) in the polymer, reflecting the large number of different microenvironments for each functional group. Most striking in the spectrum of the polymer is the apparent absence of the *ortho*-H, since an ideal polymer entirely consists of 1,2,3-substituted ferrocenes.

The ^{13}C-NMR spectra of the oligomers are complicated and it is difficult to extract useful information; there are simply too many lines that show up more readily in the ^{13}C-NMR spectra due to their larger signal dispersion. However, again it is possible to distinguish different groups of signals for the different chemical units (CH_3, CH_2, cyclopentadienyl ring and −C≡C− groups).

UV/Vis Spectroscopy

The UV/Vis spectra of ferrocene and its derivatives are characterized by two weak bands around 325 nm and 440 nm, which are both attributed to d-d transitions.[31] Any perturbation of the electronic structure of the ferrocenes, i.e. conjugation within a conjugated chain, should lead to a bathochromic shift of the respective UV/Vis transitions. Consequently, the UV/Vis spectra of our ferrocenes were measured (Figure 3) and the characteristic d-d transition proved to be quite informative: **1b**: λ_{max} = 441 nm (ε [L/M·cm] = 206); **2a**: 452 (850); **3a**: 456 (1220); **3b**: 448 (926); **4a**: 466 (1560); polymer: 468 nm. The long-wavelength shift and the stronger extinction of **3a** vs. **3b** support the idea of a better electronic delocalization in the 1,3-linked species.

Figure 3. UV/Vis spectra of the mononuclear **1b**, the dinuclear **2a** and the trinuclear ferrocenes **3a** and **3b** (10^{-4} M in CH_2Cl_2)



Cyclic Voltammetry

To complement the UV/Vis studies and in order to better understand the degree of electronic communication between the ferrocene units in the oligomers and polymers described here,[32] we attempted to determine the redox potentials of these compounds. However, the electrochemical experiments performed with the aminoferrocenes **1−4** were not very successful and we were only able to observe reversible electron-transfer processes with mononuclear ferrocenes when the cyclic voltammetric experiments were carried out at low temperatures (T = −20°C).

The respective studies of the ferrocene oligomers **2−4**, however, were rather disappointing as we could not observe reversible or at least quasi-reversible electron-transfer processes. Despite testing several solvents (acetonitrile, acetone, dichloromethane, dimethylformamide) under varying conditions, the voltammograms of the dimers and higher oligomers were complicated by numerous extremely broad redox waves (deposition on the electrode surface?) and/or a number of additional unexplained waves. In the case of the polymers the cyclic voltammogram consists of several uncharacteristic broad humps, from which we could not extract any meaningful information. These observations may be rationalized in the light of recent results by Robinson, Simpson et al.[33] who investigated the electrochemistry of related 2,2′′-bis(1-dialkylamino)-1,1′′-ferrocenes. In their study it was found that oxidation processes involving binuclear dialkylamino-ferrocenes are complicated by amine oxidation as well as oxidatively induced protonation and deprotonation processes. The fact that the former compounds are closely related to our binuclear ferrocenes might serve as an explanation for the problems experienced by us. Nonetheless, the disappointing electrochemistry of these compounds must be viewed as a major drawback.

Summary and Conclusions

We have shown that the $-CH_2NMe_2$ group can be used as an *ortho*/*ortho*-directing substituent in ferrocene chemistry to allow easy access of 1,2,3-substituted ferrocenes. This synthetic route was used to prepare 1-(I),2-(CH_2NMe_2),3-(C≡CH)-ferrocene, which can be polymerized in a Sonogashira-type coupling reaction to yield a soluble, bimodal 1,3-linked ferrocene-acetylene polymer of M_w = 3700/7100. Starting from 1-(I),2-(CH_2NMe_2),3-($C{\equiv}CSiEt_3$)-ferrocene, defined ferrocene oligomers were also available through a divergent-convergent synthesis to give a tetrameric ferrocene-acetylene.

By studying model compounds with ferrocene-acetylene substituents in either the 1,3- or the 1,1′-position it was shown, by the more pronounced bathochromic shift of the ferrocene d-d transitions in the former compound, that the electronic communication in 1,3-linked ferrocenes is better than in 1,1′-linked species and it is therefore proposed that the 1,3-linked ferrocene polymers will display superior intermetallic electronic communication as compared to their 1,1′-linked relatives. Unfortunately, it was not possible to further support this by electrochemical experiments since all oligonuclear 1,2,3-substituted compounds derived from $FcCH_2NMe_2$ described here do not display reversible electron-transfer processes.

In conclusion the $-CH_2NMe_2$ unit attached to ferrocene is very useful for synthetic transformations and should allow the synthesis of a variety of 1,2,3-substituted ferrocenes. It is, however, a major drawback of this functional group in terms of redox reactions that the electrochemistry of ferrocenes with several $-CH_2NMe_2$ groups is not straightforward.

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Experimental Section

General: Commercially available solvents and reagents were purified according to literature procedures. − Chromatography was performed on silica gel MN60. − NMR spectra were recorded at 300 K with a Bruker Avance (^{1}H NMR 200 MHz, ^{13}C NMR 50.3

MHz,). ^{1}H-NMR signals were referenced to residual ^{1}H impurities in the solvent and ^{13}C-NMR signals to the solvent signals: $CDCl_3$ ($\delta = 7.26$, $\delta = 77.0$), C_6D_6 ($\delta = 7.16$, $\delta = 128.0$), CD_3CN ($\delta = 1.93$, $\delta = 1.30$). For the purpose of ^{1}H-NMR signal assignment CpH denotes a proton attached to the sp^2-carbon atom of cyclopentadiene or to the carbon atom of a ferrocene η^5-cyclopentadienyl ring. − Mass spectra: Finnigan MAT 3800. − IR spectra were recorded with a Bruker IFS-25 in $CHCl_3$ solution. − UV/Vis spectra were recorded with a JASCO-UV-570 spectrometer in CH_2Cl_2 solution. − Elemental analyses: Mikroanalytisches Laboratorium der Chemischen Laboratorien, Universität Freiburg. For several compounds, especially for the oligomeric and polymeric materials, we could not obtain analytically pure samples due to phosphorus-based impurities from the catalyst,[34] which proved difficult to remove by chromatography. Recrystallisation of the oily, highly viscous materials was not possible. All chromatographic purifications were performed on alumina-N deactivated with 10% water. − Gel-permeation chromatography with a low-angle laser-light scattering detector was performed in dimethylformamide/0.1 M guanidinium chloride solvent using a Milton-Roy type KMX 6 detector, a Knauer HPLC-PUMP 64, a Pharmacia LKB VWM 2141 UV meter and Waters 10^3-10^5 Å columns. The calibration of the hydrodynamic volumina/molecular mass was routinely performed with polystyrene standards (PSS, PL) in THF.

1-(I),2-(CH$_2$NMe$_2$)-ferrocene (**1a**): Modified from the literature procedure.[21] To a solution of [(dimethylamino)methyl]ferrocene (21.5 g, 0.100 mol) in diethyl ether (300 ml) was added *n*BuLi (50 ml, 0.125 mol). After stirring for 4 h at room temp., the reaction mixture was cooled to −78°C and a solution of I_2 (30.5 g, 0.120 mol) in THF (75 ml) added dropwise. The solution was slowly allowed to warm to room temp. during approx. 1 h. After stirring for further 15 min, the reaction mixture was added to water (500 ml) to extract LiI. The organic layer was separated and the water extracted once more with diethyl ether. The combined organic extracts were dried with $MgSO_4$, filtered and concentrated to dryness. The residue was purified by flash chromatography (alumina-B, $CHCl_3$). The solvents were evaporated to yield the product as dark-red oil, which slowly solidified upon standing, yield 24.0 g (65%), red oily crystals. − ^{1}H NMR ($CDCl_3$): $\delta = 2.25$ [s, 6 H, $N(CH_3)_2$], 3.38 (s, 2 H, CH_2), 4.11 (s, 5 H, CpH), 4.22 ("t", *J* = 1.8 Hz, 1 H, CpH), 4.31 (br., 1 H, CpH), 4.43 (br., 1 H, CpH). − ^{13}C NMR ($CDCl_3$): $\delta = 43.56$, 57.55, 69.94, 70.27, 71.89, 73.05, 75.57, 80.62.

1-(C≡CSiEt$_3$),2-(CH$_2$NMe$_2$)-ferrocene (**1b**): To a deoxygenated solution of 1-(I),2-(CH$_2$NMe$_2$)-ferrocene (4.80 g, 13 mmol) and (triethylsilyl)acetylene (1.82 g, 13 mmol) in diisopropylamine (75 ml) were added $(Ph_3P)_2PdCl_2$ (92 mg, 0.13 mmol) and CuI (49 mg, 0.72 mmol). The reaction mixture was heated under reflux for 18 h, filtered, the precipitate washed with diethyl ether and the volatiles evaporated to dryness. The remaining red oily product was almost pure and used as such for the subsequent reactions, yield 4.60 g (92%), red liquid. − ^{1}H NMR ($CDCl_3$): $\delta = 0.62$ (q, *J* = 5.7 Hz, 6 H, $SiCH_2$), 1.06 (t, *J* = 5.5 Hz, $SiCH_2CH_3$), 2.21 [s, 6 H, $N(CH_3)_2$], 3.50 (s, 2 H, CH_2), 4.11 (s, 5 H, C_5H_5), 4.15 ("t", *J* = 1.9 Hz, 1 H, CpH), 4.29 (cm, 1 H, CpH), 4.43 (cm, 1 H, CpH). − ^{13}C NMR ($CDCl_3$): $\delta = 4.60$, 6.61, 44.75, 56.95, 66.89, 68.09, 70.42, 70.63, 71.25, 85.65, 90.13, 104.63. − IR: $\tilde{\nu} = 2147$ cm^{-1}. − $C_{21}H_{31}FeNSi$ (381.42): calcd. C 66.13, H 8.19, N 3.67; found C 66.02, H 7.95, N 3.70.

1-(C≡CH),2-(CH$_2$NMe$_2$)-ferrocene (**1c**): A solution of 1-(C≡CSiEt$_3$),2-(CH$_2$NMe$_2$)-ferrocene (8.30 g, 0.88 mmol) in CH_3OH (10 ml) was treated with aqueous KOH (1 ml, 50%) and stirred under nitrogen for 1 h. The volatiles were evaporated, water was added and the residue extracted with diethyl ether. The ethereal layer was separated, dried with $MgSO_4$, filtered and concentrated. The remaining oil was purified by chromatography (cyclohexane/ethyl acetate, 10:1), yield 4.80 g (73%), red oil. − ^{1}H NMR ($CDCl_3$): $\delta = 2.21$ [s, 6 H, $N(CH_3)_2$], 2.82 (s, 1 H, ≡CH), 3.48 (s, 2 H, CH_2), 4.14 (s, 5 H, C_5H_5), 4.16 ("t", *J* = 2 Hz, 1 H, CpH), 4.29 (m, 1 H, CpH), 4.45 (m, 1 H, CpH). − ^{13}C NMR: $\delta = 44.80$, 57.03, 65.62, 68.09, 70.55, 71.53, 75.70, 81.84, 85.81. − $C_{15}H_{16}FeIN$ (393.0): calcd. C 45.84, H 4.10, N 3.56; found C 45.26, H 4.42, N 3.29.

1-(C≡CSiEt$_3$),2-(CH$_2$NMe$_2$),3(I)-ferrocene (**1d**): A solution of 1-(C≡CSiEt$_3$),2-(CH$_2$NMe$_2$)-ferrocene (4.60 g, 12.1 mmol) in diethyl ether (75 ml) was treated with BuLi (6.0 ml, 15 mmol) at −78°C and slowly warmed to room temp. After stirring for 1 h, the reaction mixture was cooled to −78°C and a solution of I_2 (3.05 g, 12.0 mmol) in THF (10 ml) added dropwise and then the reaction mixture was slowly warmed to room temp. After stirring for further 15 min, the reaction mixture was added to water (100 ml) and the LiI extracted. The organic layer was separated and the water extracted once more with diethyl ether. The combined organic extracts were dried with $MgSO_4$, filtered and concentrated to dryness. The remaining oil was purified by flash chromatography (cyclohexane/ethyl acetate, 10:1), yield 4.0 g (66%), red oil. − ^{1}H NMR ($CDCl_3$): $\delta = 0.65$ (q, *J* = 7.9 Hz, 6 H, $SiCH_2$), 1.05 (t, *J* = 8 Hz, 9 H, CH_3), 2.28 [s, 6 H, $N(CH_3)_2$], 3.40−3.62 (m, 2 H, NCH_2), 4.10 (s, 5 H, C_5H_5), 4.46−4.52 (m, 2 H, CpH). − ^{13}C NMR ($CDCl_3$): $\delta = 4.50$, 7.58, 45.85, 57.20, 66.11, 72.30, 73.55, 75.08, 87.85, 91.47, 103.48. − $C_{21}H_{30}FeINSi$ (507.31): calcd. C 49.72, H 5.96, N 2.76; found C 50.13, H 6.02, N 2.54.

1-(C≡CH),2-(CH$_2$NMe$_2$),3-(I)-ferrocene (**1e**): To a solution of 1-(C≡CSiEt$_3$),2-(CH$_2$NMe$_2$),3-(I)-ferrocene (4.00 g, 7.9 mmol) in CH_3OH (75 ml) was added KOH (4 g) and the mixture was stirred under nitrogen for 3 h. The volatiles were evaporated, water was added and the residue extracted with diethyl ether. The ethereal layer was separated, dried with $MgSO_4$, filtered and concentrated. The remaining oil was purified by flash chromatography (cyclohexane/ethyl acetate, 10:1), yield 2.30 g (75%), red oil. − ^{1}H NMR ($CDCl_3$): $\delta = 2.27$ [s, 6 H, $N(CH_3)_2$], 2.86 (s, 1 H, ≡CH), 3.49 (s, 2 H, CH_2), 4.12 (s, 5 H, C_5H_5), 4.46−4.53 (m, 2 H, CpH). − ^{13}C NMR ($CDCl_3$): $\delta = 45.53$, 57.09, 64.85, 72.44, 75.00, 76.77, 80.80, 87.74. − $C_{15}H_{16}FeIN$ (393.0): calcd. C 45.84, H 4.10, N 3.56; found C 45.55, H 4.00, N 3.67.

[1-(C≡CH),2-(CH$_2$NMe$_3$),3-(I)-ferrocene]$^+$I$^-$ (**1f**): A solution of 1-(C≡CH),2-(CH$_2$NMe$_2$),3-(I)-ferrocene (2.30 g, 5.80 mmol) in diethyl ether (25 ml) was treated with CH_3I (1.65 g, 11.6 mmol) and the mixture stirred for 12 h at room temp. The yellow precipitate was filtered off, washed with diethyl ether and dried in vacuo, to yield a yellow powder, yield 2.85 g (91%), yellow powder. − ^{1}H NMR (CD_3CN): $\delta = 3.10$ [s, 9 H, $N(CH_3)_3$], 3.42 (s, 1 H, ≡CH), 4.27 (s, 5 H, C_5H_5), 4.53−4.76 (m, 4 H, CH_2), 4.84−4.88 (m, 2 H, C_5H_2). − $C_{16}H_{19}FeI_2N$ (535.0): calcd. C 35.92, H 3.58, N 2.62; found C 36.26, H 3.89, N 2.11.

1-(C≡CH),2-[CH$_2$(N-12-c-4)],3-(I)-ferrocene (**1g**): A mixture of [1-(C≡CH),2-(CH$_2$NMe$_3$),3-(I)-ferrocene]$^+$I$^-$ (535 mg, 1.00 mmol), aza-12-crown-4 (210 mg, 1.20 mmol) and K_2CO_3 (0.5 g) in acetonitrile was heated under reflux for 12 h. The cold solution was filtered and the filtrate concentrated to dryness. The residue was dissolved in $CHCl_3$, filtered through an alumina-N plug, concentrated to dryness and chromatographed on alumina-N with cyclohexane/ethylacetate/diethylamine (10:1:1), yield 150 mg (29%), red oil. − ^{1}H NMR ($CDCl_3$): $\delta = 2.79-2.86$ (m, 4 H, NCH_2), 2.89 (s, 1 H, ≡CH), 3.60−3.88 (m, 12 H, CH_2O + $CpCH_2$), 4.14 (s, 5

H, C_5H_5), 4.49−4.54 (m, 2 H, C_5H_2). − ^{13}C NMR ($CDCl_3$): δ = 44.90, 54.13, 54.60, 64.97, 69.88, 70.45, 71.38, 71.86, 72.68, 73.58, 75.37, 81.18, 88.37. − $C_{21}H_{26}FeINO_3$ (523.2): calcd. C 48.21, H 5.01, N 2.68; found C 48.56, H 5.21, N 2.59.

[1-(CH_2NMe_2)-ferrocene-2-yl]-C≡C-[2-(CH_2NMe_2),3(C≡CSiEt$_3$)-ferrocene-1-yl] (**2a**): Typical coupling procedure: 1 mol-% Pd catalyst, 2 mol-% CuI. Scale: 1-(I),2(-CH_2NMe_2),3-(C≡CSiEt$_3$)-ferrocene (**1d**) (2.54 g, 5.00 mmol), 1-(C≡CH),2-(CH_2NMe_2)-ferrocene (**1c**) (1.97 g, 5.00 mmol). Yield 2.68 g (83%), red oil. Chromatography: cyclohexane/ethyl acetate (10:1), R_F = 0.4. − ^{1}H NMR ($CDCl_3$): δ = 0.66 (q, 6 H, $SiCH_2$), 1.07 (t, 9 H, CH_3), 2.17, 2.25, 2.32, 2.34 (s, 12 H, 4 × CH_3), 3.53−3.78 (m, 4 H, CH_2), 4.14 (s, 10 H, C_5H_5), 4.19 ("t", J = 2.5 Hz, 1 H, CpH), 4.32 (br., 1 H, CpH), 4.44 (m, 1 H, CpH), 4.48 (s, 2 H, CpH). − ^{13}C NMR ($CDCl_3$): δ = 4.54, 7.60, 44.87, 45.92, 45.29, 45.38, 55.51, 55.66, 57.20, 57.35, 67.13, 67.18, 67.65, 67.72, 68.07, 68.83, 70.38, 70.43, 71. 04, 71.13, 71.36, 72.47, 72.51, 84.78, 84.89, 85.60, 85.07, 85.07, 85.72, 87.14, 87.40, 93.27, 103.00.

[2-(CH_2NMe_2)-ferrocene-1-yl]-C≡C-[2-(CH_2NMe_2),3(C≡CH)-ferrocene-1-yl] (**2b**): Typical cleavage procedure: 24 h CH_3OH/aq. KOH, [2-(CH_2NMe_2)-ferrocene-1-yl]-C≡C-[2-(CH_2NMe_2),3-(C≡C-SiEt$_3$)-ferrocene-1-yl] (**2a**) (1.29 g, 2.0 mmol). Yield 0.79 g (74%), red oil. Chromatography: cyclohexane/Et_2NH (10:1), R_F = 0.2. − ^{1}H NMR ($CDCl_3$): δ = 2.25 [s, 3 H, $N(CH_3)_2$], 2.28 [s, 3 H, $N(CH_3)_2$], 2.32 [s, 3 H, $N(CH_3)_2$], 2.34 [s, 3 H, $N(CH_3)_2$], 2.85 (s, 1 H, ≡CH), 3.53−3.77 (m, 4 H, CH_2), 4.15−4.32 (m, 11 H, 2 × C_5H_5 + CpH), 4.33 (br., 1 H, CpH), 4.44 (br., 1 H, CpH), 4.48−4.52 (m$_c$, 2 H, CpH). − ^{13}C NMR ($CDCl_3$): δ = 44.85, 44.89, 45.30, 55.58, 55.78, 57.17, 57.31, 66.10, 67.61, 68.06, 68.08, 68.97, 70.36, 70.42, 71.04, 71.07, 71.48, 72.36, 72.41, 75.98, 81.27, 84.76, 85.06, 87.13, 87.40.

[1-(I),2-(CH_2NMe_2)-ferrocene-3-yl]-C≡C-[2-(CH_2NMe_2)-3-(C≡CSiEt$_3$)-ferrocene-1-yl] (**2c**): Typical sequence of lithiation and iodination: [2-(CH_2NMe_2)-ferrocene-1-yl]-C≡C-[2-(CH_2NMe_2),3-(C≡CSiEt$_3$)-ferrocene-1-yl] (**2a**) (1.29 g, 2.0 mmol) *n*BuLi (2.4 mmol), I_2 (0.508 g, 1.95 mmol). Yield 0.97 g (63%), red oil. Chromatography: cyclohexane/ethyl acetate (5:1), $R_{F\,=\,0}$.6. − ^{1}H NMR ($CDCl_3$): δ = 0.66 (q, J = 7.8 Hz, 6 H, $SiCH_2$), 1.06 (t, J = 7.7 Hz, 9 H, CH_3), 2.26−2.38 [m, 12 H, $N(CH_3)_2$], 3.54−3.61 (m, 2 H, CH_2), 3.72−3.80 (m, 2 H, CH_2), 4.08−4.19 (m, 10 H, C_5H_5), 4.46−4.53 (m, 4 H, C_5H_2). − ^{13}C NMR ($CDCl_3$): δ = 4.50, 7.62, 45.16, 45.21, 45.67, 45.76, 55.46, 5.64, 57.38, 57.59, 66.94, 67.06, 67.52, 67.59, 68.20, 68.25, 71.22, 71.52, 71.81, 72.03, 72.49, 72.52, 73.37, 73.40, 73.61, 84.64, 84.74, 85.99, 86.11, 86.70, 87.00, 87.22, 90.70, 103.79.

[1-(CH_2NMe_2)-ferrocene-2-yl]-C≡C-[2-(CH_2NMe_2)-ferrocene-1,3-diyl]-C≡C-[2-(CH_2NMe_2)-ferrocene-1-yl] (**3a**): Typical coupling procedure: [2-(CH_2NMe_2)-ferrocene-1-yl]-C≡C-[2-(CH_2NMe_2),3-(C≡CH)-ferrocene-1-yl] (**2b**) (532 mg, 1.0 mmol), (1-I),(2-CH_2NMe_2)-ferrocene (**1a**) (369 mg, 1.0 mmol). Yield 670 mg (87%), red oil. Chromatography: cyclohexane/ethyl acetate/Et_2NH (10:1:1). − ^{1}H NMR ($CDCl_3$): δ = 2.27 [s, 6 H, $N(CH_3)_2$ in Fc-1 and Fc-3], 2.29 [s, 6 H, $N(CH_3)_2$ in Fc-1 and Fc-3], 2.36−2.42 [m, 6 H, $N(CH_3)_2$ in Fc-2], 3.55 (s, 2 H, CH_2, Fc-1 and Fc-3), 3.59 (s, 2 H, CH_2, Fc-1 and Fc-3), 3.79−3.88 (m, 2 H, CH_2, Fc-2), 4.16 (s, C_5H_5, Fc-1 and Fc-3), 4.19 (s, 2 H, C_5H_5, Fc-2 + CpH at Fc-1 and Fc-3), 4.33 (cm, 2 H, CpH, Fc-1 and Fc-3), 4.45 (cm, 2 H, CpH, Fc1 and Fc-3), 4.52 (s, 2 H, CpH, Fc-2). − ^{13}C NMR ($CDCl_3$): δ = 44.86, 44.91, 45.32, 55.90, 56.03, 57.19, 57.34, 67.68, 67.75, 68.09, 68.50, 68.64, 68.69, 70.40, 70.44, 71.06, 72.20, 72.25, 72.30, 84.74, 85.00, 85.69, 85.78, 85.98, 86.22, 86.47, 86.88.

1,1′-Bis(1″-ethynyl-2″-(CH_2NMe_2)-ferrocene-1-yl)-ferrocene (**3b**): Typical coupling procedure. Scale: **1c** (2.44 g, 9.2 mmol), 1,1′-diiodoferrocene (2.00 g, 4.6 mmol), $(Ph_3P)_2PdCl_2$ (1 mol-%), CuI (2 mol-%), ^{i}Pr$_2$NH (75 ml). Yield 2.70 g (83%), brown-red oil. Chromatography: R_f = 0.5 (cyclohexane/ethyl acetate/Et_2NH, 10:1:1). − ^{1}H NMR ($CDCl_3$): δ = 2.27 (s, 12 H, NCH_3), 3.56 (s, 4 H, NCH_2), 4.17 (s, 10 H, CpH), 4.23 (s, 8 H, CpH), 4.33 (m, 6 H, CpH_3).

[1-(CH_2NMe_2)-ferrocene-2-yl]-C≡C-[2-(CH_2NMe_2)-ferrocene-1,3-diyl]-C≡C-[1-(CH_2NMe_2)-ferrocene-1,3-diyl]-C≡C-[2-(CH_2NMe_2),3-(C≡CSiEt$_3$)-ferrocene-1-yl] (**4a**): To a deoxygenated solution of [1-(I),2-(CH_2NMe_2)-ferrocene-3-yl]-C≡C-[2-(CH_2NMe_2),3-(C≡CSiEt$_3$)-ferrocene-1-yl] (**2c**) (0.772 g, 1 mol) and [2-(CH_2NMe_2)-ferrocene-1-yl]-C≡C-[2-(CH_2NMe_2),3-(C≡CH)-ferrocene-1-yl] (**2b**) (0.532 g, 1.0 mmol) in diisopropylamine (75 ml) were added $(Ph_3P)_2PdCl_2$ (7.0 mg, 1 mol-%) and CuI (7.7 mg, 2 mol-%). The reaction mixture was heated under reflux for 24 h, filtered, the precipitate washed with diethyl ether and the volatiles evaporated to dryness. The remaining solid was purified by chromatography (cyclohexane/ethyl acetate/Et_2NH, 10:1:1), yield 0.86 g (73%), red glassy solid. − ^{1}H NMR ($CDCl_3$): δ = 0.70 (q, J = 7.8 Hz, 6 H, CH_2), 1.08 (t, J = 7.8 Hz, 9 H, CH_3), 2.28−2.43 (m, 24 H, NMe_2), 3.58 (d, J = 9.4 Hz, 2 H, NCH_2), 3.70−3.90 (m, NCH_2, 6 H), 4.17 (s, 10 H, CpH), 4.19 (s, 10 H, CpH), 4.26 (br. s, 1 H), 4.45−4.52 (m, 8 H, CpH). − $C_{66}H_{79}Fe_4N_4Si$ (1179.9): calcd. C, 67.9, H 6.75, N, 4.75; found C 67.78, H 6.89, N 4.76. − ESI-MS; *m/z*: 1178.5.

Polymerisation of **1e**, *Polymer I:* Typical coupling procedure. Scale: **1c** (1.18 g, 3.0 mmol), $(Ph_3P)_2PdCl_2$ (5 mol-%), CuI (10 mol-%), *i*Pr$_2$NH (75 ml), 36 h reflux. The mixture of oligomers and polymers obtained was fractionated by flash chromatography. A low molecular fraction was eluted with cyclohexane/Et_2NH (1:1) while the polymers were eluted by using $CHCl_3$/MeOH (10:1) or cyclohexane/Et_2NH (3:1). The yields of the polymeric (dark-red glassy) material varied between 40 and 60%. − ^{1}H ($CDCl_3$): δ = 2.26−2.38 (br., 6 H, NMe_2), 3.50−3.65 (br. m, 1.8 H, NCH_2), 3.70−3.95 (br. m, 2.2 H, NCH_2), 4.09−4.21 (br. + 2 s at δ = 4.16 and 4.20, 4.3 H, C_5H_5), 4.53−4.60 (br., 2 H, CpH). − In the ^{13}C-NMR spectrum at least 50 different peaks (diastereomers) were observed.

Polymerisation of **1g**, Polymer II: Typical coupling procedure. Scale: **1c** (0.262 g, 0.50 mmol), $(Ph_3P)_2PdCl_2$ (5 mol-%), CuI (10 mol-%), *i*Pr$_2$NH (25 ml), 24 h reflux. The mixture of oligomers and polymers was fractionated by flash chromatography. A low-molecular fraction was eluted with cyclohexane/Et_2NH (10:1) while the polymers were eluted with $CHCl_3$/MeOH (10:1). − ^{1}H NMR ($CDCl_3$): 2.65−2.80 (br.), 3.50−3.8 (br. m), 3.48 (s, C_5H_5), 4.08 (s), 4.35−4.50 (m). − In the ^{13}C-NMR spectrum at least 50 different peaks (diastereomers) were observed.

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