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Main-chain organometallic polymers comprising redox-active iron(II) centers connected by ditopic N-heterocyclic carbenes

Laszlo Mercs, Antonia Neels, Helen Stoeckli-Evans and Martin Albrecht*

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Main-chain organometallic polymers were synthesized from bimetallic iron(II) complexes containing a ditopic N-heterocyclic carbene (NHC) ligand [(cp)(CO)2Fe(NHC–NHC)Fe(cp)(CO)X] (where NHC–NHC represents a bridging dicarbene ligand, X = I or CO). Addition of a diimine ligand such as pyrazine or 4,4’-bipyridine interconnected these bimetallic complexes and gave the corresponding co-polymers containing iron centers that are alternately linked by a dicarbene and a diimine ligand. Diimine coordination was depending on the wingtip groups at the carbene ligands and was accomplished either by photolytic activation of a carbonyl ligand from the cationic [Fe(cp)(NHC)(CO)]2+ precursor (alkyl wingtips) or by AgBF4-mediated halide abstraction from the neutral complex [Fe(cp)(NHC)(CO)] (mesityl wingtips). Remarkably, the polymeric materials were substantially more stable than the related bimetallic model complexes.

Electrochemical analyses indicated metal-metal interactions in the pyrazine-containing polymers, whereas in 4,4’-bipyridine-linked systems the metal centers were electronically decoupled.

Introduction
While the impact of N-heterocyclic carbene (NHC) complexes in catalysis has been widely recognized, the application of organometallic NHC chemistry in other areas of materials science has been much less developed thus far. This is remarkable, especially when considering the relatively robust metal-carbon bond in NHC complexes. In addition, theoretical and experimental results have indicated that the M–C\text{NHC} bond comprises a significant portion of \pi character when bound to electron-rich metal centers. Such bonding may become attractive for designing systems for potential application in molecular electronics, since facile transfer of electron density along \pi networks may also encompass the metal center. Specifically when using redox-active metal centers in the main chain, organometallic polymers have great potential to surpass the versatility of most common organic or inorganic conducting systems, as the oxidation state of the metal center in these organometallic polymers represents an additional function that can be selectively addressed and reversibly switched.

Initial efforts on using organometallic NHC chemistry for polymer synthesis concentrated on metals with low redox activity. Predominantly through the pioneering work of Bielawski and coworkers, a range of ditopic carbene ligands became available for the interconnection of two metal centers. Subsequent exploitation of this approach provided access to redox-active molecular switches and to molecular squares. Stimulated by these achievements, we aimed at expanding the use of ditopic carbene ligands for the fabrication of co-polymers containing redox-active NHC iron(II) units in the main chain.

Our retrosynthetic approach towards such co-polymers was based on the interconnection of a bimetallic synthon with a ditopic, bridging ligand (Figure 1). Since coordination of a second, non-chelating NHC ligand to a Fe–NHC complex proved to be difficult, we focussed our attention on co-polymers that feature two different interconnecting ligands. Hence, the desired co-polymer can be dissected into two bimetallic synthons A and B (Figure 1), comprising each a different ditopic ligand. Here we report on the synthesis and electrochemical properties of iron NHC polymers and their bimetallic synthons A and B. Metal-metal interactions in these systems are strongly dependent on the type of diimine ligand employed.

Fig. 1 Retrosynthetic approach towards organometallic polymers comprising NHC metal complexes in the main chain.
Experimental Section

General Comments

All manipulations were performed using standard Schlenk techniques under an argon atmosphere unless stated otherwise.

Toluene, THF and CH₂Cl₂ were dried by passage through Celite and evaporated to dryness. The purity of all reagents was confirmed by thin layer chromatography.

Microanalytical Laboratory of the ETH Zürich (Switzerland) performed microanalysis of the compounds. Elemental analyses were performed by the Analytical Laboratories of the ETH Zürich (Switzerland).

Chemical shifts (δ) are given in ppm, coupling constants (J) in Hz. Assignments are based either on distortionless enhancement of polarization transfer (DEPT) experiments or on homo- and heteronuclear shift correlation spectroscopy.

Syntheses

**Synthesis of 3.** To a suspension of the diimidazolium salt 1 (0.32 g, 0.5 mmol) in dry THF (10 mL) was added nBuLi (1.6 M in hexanes, 0.63 mL, 1.0 mmol) at −78 °C. After stirring for 30 min at RT, the mixture was frozen and overlaid with a solution of [FeL(cpx)(CO)]₂ (0.76 g, 2.5 mmol) in dry toluene (30 mL). The reaction mixture was gradually warmed to RT and stirred for 16 h. The formed precipitate was separated by centrifugation, washed with dry toluene (30 mL) and then extracted with dry CH₂Cl₂ (2 x 20 mL). The combined CH₂Cl₂ fractions were reduced to ca. 20 mL and subsequently irradiated for 16 h. All volatiles were removed in vacuo, and the residue was purified by gradient column chromatography (SiO₂, CH₂Cl₂/acetone) and by subsequent precipitation from CH₂Cl₂/pentane. The product was obtained as a green powder (0.32 g, 68%) as a mixture of diastereoisomers. X-ray quality crystals were grown by slow diffusion of pentane into a CH₂Cl₂ solution of 3 at −20 °C. Analytically pure material was obtained by recrystallisation from toluene/pentane. **1H NMR** of major isomer (CDCl₃, 400 MHz): δ 8.49 (s, 2H, NCH₃-N), 7.34 (d, 1H, H₂, H₃,N,N), 7.05, 7.03 (2 x s, 4H, H₅,Me₃), 6.79 (d, 1H, H₂, H₃,N,N), 4.56 (s, 10H, H₂, 2.41 (s, 6H, p-CH₃), 1.90, 1.88 (2 x s, 12H, o-CH₃). **13C NMR** of minor isomer (CDCl₃, 400 MHz): δ 8.42, 8.20 (2 x d), 7.12, 7.11 (2 x s, 4H, H₅,Me₃). 7.01 (d, 1H, H₂, H₃,N,N), 6.92 (d, 1H, H₂, H₃,N,N), 2.12 (2 x s, 12H, o-CH₃). The purity of the obtained 1H NMR (CDCl₃, 400 MHz) was confirmed by IR spectroscopy (KBr, 1000-500 cm⁻¹).

**Synthesis of 4.** To a suspension of the diimidazolium salt 2 (1.16 g, 2.0 mmol) in dry THF (20 mL) was added LiN(SiMe₃)₂ (1 M in THF, 4.0 mL, 4.0 mmol) at RT. After 16 h, the mixture was filtered and washed with Et₂O. The filtered precipitate was separated by centrifugation, washed with dry toluene (30 mL) and then with dry CH₂Cl₂ (2 x 20 mL). The product was obtained as a yellow powder (0.31 g, 67%). Single crystals suitable for X-ray diffraction analysis were grown in the dark by slow Et₂O diffusion into a MeNO₂ solution. **1H NMR** (CDCl₃, 400 MHz): δ 7.99 (s, 2H, H₃,N,N), 7.78 (s, 6H, H₃,N,N), 5.45 (s, 10H, H₂, 4.23 (s, 4H, NCH₂), 1.89 (s, 1H, NCH₂), 1.50 (s, 1H, NCH₂), 1.01 (t, 2H, NCH₂). The purity of the obtained 1H NMR (CDCl₃, 400 MHz) was confirmed by IR spectroscopy (KBr, 1000-500 cm⁻¹).

**Synthesis of 5.** Complex 4 (0.28 g, 0.3 mmol) and AgBF₄ (0.12 g, 0.6 mmol) were stirred in MeNO₂ and CH₂Cl₂ (20 mL, 1:1 V/V) in the dark for 3 h. The suspension was filtered through Celite and evaporated to dryness, affording the crude product as a yellow powder (0.24 g, 96%). An analytically pure sample was obtained by recrystallisation of 5 from MeNO₂/Et₂O. **1H NMR** (CDCl₃, 400 MHz): δ 7.99 (s, 2H, H₃,N,N), 7.78 (s, 6H, H₃,N,N), 5.44 (s, 10H, H₂, 4.22 (s, 4H, NCH₂), 1.88 (s, 1H, NCH₂), 1.50 (s, 1H, NCH₂), 1.01 (t, 2H, NCH₂). The purity of the obtained 1H NMR (CDCl₃, 400 MHz) was confirmed by IR spectroscopy (KBr, 1000-500 cm⁻¹).

**Synthesis of 6.** A solution of 4 (0.186 g, 0.2 mmol) in dry CH₂Cl₂ (10 mL) was irradiated for 16 h, upon which the yellow solution became green. Evaporation of the solvent gave the crude product as a green powder, which was purified by precipitation from CH₂Cl₂/pentane (0.14 g, 80%). Recrystallisation from CH₂Cl₂/toluene/Et₂O at 44 °C gave an analytically pure sample. **1H NMR** (CDCl₃, 400 MHz): δ 7.33 (d, 1H, H₂, H₃,N,N), 7.31 (d, 1H, H₂, H₃,N,N), 7.30–7.13 (br, 4H, H₃,N,N), 7.21 (d, 1H, H₂, H₃,N,N), 7.09 (d, 1H, H₂, H₃,N,N), 5.10–4.95, 4.91–4.79 (2 x m, 4H, NCH₂), 4.44, 4.43 (2 x s, 10H, H₂, 2.13–1.87 (2 x s, 4H, NCH₂), 1.73–1.56 (m, 4H, CH₂,CH₂). The purity of the obtained 1H NMR (CDCl₃, 100 MHz) was confirmed by IR spectroscopy (KBr, 1000-500 cm⁻¹).
irradiated for 16 h. During this time the initially yellow solution turned purple and a precipitate formed. Separation of the precipitate by filtration and washing with dry CH\textsubscript{2}Cl\textsubscript{2} gave 9a as a purple solid (0.116 g, 54\%), which was precipitated from MeNO\textsubscript{2}/acetone/Et\textsubscript{2}O at 0 °C to give an analytically pure sample. \textsuperscript{1}H NMR (MeNO\textsubscript{2}-d\textsubscript{4}, 400 MHz, 258 K): \(\delta 8.12-7.63\) (br, 4H, \(\text{H}_\text{Bu}\)), 7.63-7.40 (m, 4H, \(\text{H}_\text{Me}\)), 5.1-4.9 (br, 2H, CH\textsubscript{Me}), 4.98 (s, 10H, \(\text{H}_\text{p}\)), 4.78-4.60 (br, 2H, CH\textsubscript{Me}), 1.71-1.57, 1.57-1.43, 1.43-1.27, 0.85-0.66 (4 x m, 24H, \(\text{CH}(\text{CH}_2)_3\)). The resonances of the second isomer are strongly overlapping, additional signals were detected at \(\delta_c\): 221.7 (CO), 174.3 (C\textsubscript{pyrazine}), 153.9 (C\textsubscript{Bu-H}), 123.2, 122.7 (2 x C\textsubscript{NHC-H}), 85.4 (C\textsubscript{p}), 54.2, 53.5 (2 x C\textsubscript{CHMe}), 24.4, 23.9, 23.5, 22.3 (4 x CH(CH\textsubscript{2})\textsubscript{3}). IR (neat, cm\textsuperscript{-1}): 1947 v(CO). Anal. Calc'd for C\textsubscript{4}H\textsubscript{6}B\textsubscript{2}F\textsubscript{2}Cl\textsubscript{2}O\textsubscript{2} (1236.55): 3/4 CH\textsubscript{2}Cl\textsubscript{2}; C 59.81, H 5.23, N 6.46. Found: C 59.79, H 5.28, N 6.69.

**Synthesis of 11.** Irradiation of a solution of 7 (0.17 g, 0.4 mmol) in dry MeCN (10 mL) for 16 h and subsequent solvent evaporation gave 11 as an orange solid in quantitative yield (0.18 g). Analytically pure material was obtained by recrystallisation from MeCN to CH\textsubscript{2}Cl\textsubscript{2}/Et\textsubscript{2}O at -4 °C. \textsuperscript{1}H NMR (acetone-d\textsubscript{6}, 400 MHz): \(\delta 7.74\) (s, 2H, H\textsubscript{3}), 5.35-5.05 (br, 2H, CH\textsubscript{Me}), 4.96 (s, 5H, \(\text{H}_\text{Bu}\)), 2.46 (s, 3H, CH\textsubscript{3}CN), 1.59, 1.41 (2 x d, \(J_{\text{HH}} = 6.7\) Hz, 12H, CH\textsubscript{2}(CH\textsubscript{3})\textsubscript{3}). \textsuperscript{13}C\textsuperscript{1}H NMR (acetone-d\textsubscript{6}, 100 MHz): \(\delta 221.0\) (CO), 173.7 (C\textsubscript{pyrazine}), 136.1 (CH\textsubscript{CN}), 122.4 (C\textsubscript{NHC-H}), 83.2 (C\textsubscript{p}), 53.1 (CH\textsubscript{3}Me), 23.8, 23.7 (2 x CH\textsubscript{2}(CH\textsubscript{3})\textsubscript{2}), 4.8 (CH\textsubscript{3}CN). IR (neat, cm\textsuperscript{-1}): 1964 v(CO). Anal. Calc'd for C\textsubscript{4}H\textsubscript{6}B\textsubscript{2}F\textsubscript{2}Cl\textsubscript{2}O\textsubscript{2} (429.04): C 47.59, H 5.64, N 9.79. Found: C 47.72, H 5.46, N 9.68.

**Synthesis of 12.** In analogy to the preparation of 5, irradiation of a solution of 7 (0.11 g, 0.3 mmol) and pyridine (0.11 g, 1.3 mmol) in dry CH\textsubscript{2}Cl\textsubscript{2} (10 mL) for 16 h and subsequent solvent evaporation of the volatiles yielded the crude product as a dark brown solid in quantitative yield (0.13 g). Recrystallisation from acetone/acetone at -4 °C gave an analytically pure sample. \textsuperscript{1}H NMR (acetone-d\textsubscript{6}, 400 MHz): \(\delta 8.26\) (d, \(J_{\text{HH}} = 5.3\) Hz, 2H, \(\text{H}_\text{Bu}\)), 7.74 (s, 1H, \(\text{H}_\text{Bu}\)), 7.27 (m, 2H, \(\text{H}_\text{Bu}\)), 5.20 (m, 2H, CH\textsubscript{Me}), 5.10 (s, 5H, \(\text{H}_\text{Bu}\)), 1.63 (d, \(J_{\text{HH}} = 6.5\) Hz, 6H, \(\text{CH}(\text{CH}_2)_3\)). \textsuperscript{13}C\textsuperscript{1}H NMR (acetone-d\textsubscript{6}, 100 MHz): \(\delta 223.4\) (CO), 177.3 (C\textsubscript{pyrazine}), 159.1 (\(\text{C}_{\text{py}-}\)), 138.6 (\(\text{C}_{\text{py}-}\)), 126.8 (\(\text{C}_{\text{NHC}-}\)), 122.7 (C\textsubscript{NHC-H}), 83.8 (C\textsubscript{p}), 53.3 (CH\textsubscript{3}Me), 24.2, 22.7 (2 x CH\textsubscript{2}(CH\textsubscript{3})\textsubscript{2}). IR (neat, cm\textsuperscript{-1}): 1927 v(CO). Anal. Calc'd for C\textsubscript{4}H\textsubscript{6}B\textsubscript{2}F\textsubscript{2}Cl\textsubscript{2}O\textsubscript{2} (467.09): C 51.43, H 5.61, N 9.00. Found: C 51.65, H 5.55, N 9.12.

**General procedure for the preparation of polymers 13a and 14a.** An acetone solution (10 mL) containing complex 5 (0.15 mmol) and diimine (0.15 mmol) was irradiated for 16 h. The product precipitated from the reaction mixture and was collected by filtration and washed with CH\textsubscript{2}Cl\textsubscript{2} (2 x 2 mL). Analytical data are collected in Table 6.

**General procedure for the preparation of polymers 13b and 14b.** Complex 3 (0.15 mmol), diimine (0.15 mmol) and AgBF\textsubscript{4} (0.33 mmol) were stirred in dry CH\textsubscript{2}Cl\textsubscript{2} (10 mL) for 16 h. The reaction mixture was filtered through Celite, evaporated to dryness and then precipitated twice from CH\textsubscript{2}Cl\textsubscript{2}/MeNO\textsubscript{2}/Et\textsubscript{2}O to give the desired polymers. Analytical data are collected in Table 6.

**Electrochemical Measurements.**

Electrochemical studies were carried out using an EG&G Princeton Applied Research Potentiostat Model 273A employing a gastight three-electrode cell under an argon atmosphere. For compounds 3, 6, 11 and 12 a Pt disk with a
3.80 mm² surface area or a glassy-carbon disk with a 3.14 mm² surface area was used as the working electrode and was polished before each measurement. The reference was a Ag/AgCl electrode; the counter electrode was a Pt wire.

Bu₄NF (0.1 M) in dry CH₂Cl₂ was used as a base electrolyte with analyte concentrations of approximately 1 × 10⁻² M. Measurements were carried out at RT and at a 100 mV s⁻¹ sweep rates unless stated otherwise. The redox potentials were measured against ferrocenium/ferrocene (Fc⁺/Fc; E₁/₂ = 0.46 V vs. SCE)¹⁰ or against [Ru(bpy)₃]³⁺/²⁺ (E₁/₂ = 1.39 V vs. SCE),¹⁶ which were used as internal standards. For compounds 9, 10, 13 and 14 a similar setup was used except that measurements were carried out in MeNO₂ at –20 °C and referenced to Fc⁺/Fc as internal standard (E₁/₂ = 0.35 V vs. SCE) in MeNO₂.

Crystal structure determination

Suitable single crystals were mounted on a Stoe Mark II Imaging Plate Diffractometer System (Stoe & Cie, 2002; for 3, 4, 9b and 12) and on a Nonius KappaCCD area-detector diffractometer (for 11) equipped with a graphite-monochromator. Data collections were performed at −100 °C (for 3, 4, 9b and 12) and at −113 °C (for 11) using Mo-Kα radiation (λ = 0.71073 Å). All structures were solved by direct methods using SHELXS-97¹⁷ (for 3, 4, 9b and 12) or SIR92²⁰ for (11) and refined by full-matrix least-squares on F² with SHELXL-97.³¹ Hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL-97 default parameters. All non-hydrogen atoms were refined anisotropically. A semi-empirical absorption correction was applied for 4, 9b, 11 and 12 using Sortav²² or MULscanABS as implemented in PLATON.²² An empirical absorption correction was applied for 3 using DELrefABS as implemented in PLATON.

For complex 3, a region of electron density related to a disordered molecule of CH₂Cl₂ was squeezed out using the SQUEEZE routine in PLATON03 (82 electrons for 305.7 Å³ per unit cell). In complex 12, the BF₄⁻ anion is disordered. Further details on data collection and refinement parameters are collected in Table 1. Crystallographic data (excluding structure factors) for the structures 3, 4, 9b, 11, and 12 have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 726484-726552. Copies of the data can be obtained free of charge on request to CCDS, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (int) +44-1223-336-033; E-mail: deposit@ccds.cam.ac.uk].

Table 1 Crystallographic data for complexes 3, 4, 9b, 11, and 12

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<th>unique reflns, R(int)</th>
<th>obsd. reflections [1 &gt; 2σ(I)]</th>
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Results and Discussion

Carbene-connected dinuclear iron(II) complexes (Synthon A)

Formation of synthon A required a ditopic carbene ligand precursor. For this purpose, we investigated the diimidazolium salts 1 and 2 comprising a flexible methylene and a rigid phenylene linker, respectively. The bimetallic iron(II) complexes 3–6 containing these bridging NHC ligands were synthesized via the free carbene route (Scheme 1). In order to prevent chelation of the flexible dicarbene ligand derived from 1, metal coordination was performed at low ligand concentrations. After deprotonation of 1 by BuLi in THF, the reaction mixture was thus frozen and overlaid with an excess of the metal precursor [Fe₂(cp)(CO)₅] dissolved in toluene. Upon gradual melting and warming of the resulting
suspension to RT, the bimetallic tetracarbonyl complex formed as a precipitate. Subsequent solvent exchange and irradiation of this intermediate in CH$_2$Cl$_2$ yielded the bimetallic neutral complex 3. Compounds 4–6 featuring a rigid phenylene spacer between the carbene units were synthesized similarly, though freezing of the free carbene solution was redundant, as the ligand cannot adopt a chelating coordination mode. The tetracarbonyl complex 4 was isolated and fully characterized. AgBF$_4$-mediated exchange of the non-coordinating anion from I$^-$ to BF$_4^-$ afforded complex 5, and photochemically induced CO dissociation from 4 gave the neutral diiron complex 6.

The bridging coordination mode of the dicarbenic ligands in complexes 3–6 was confirmed by the pertinent 1:1 cp/imidazole molecular ratio in the $^1$H NMR spectra. The $^1$H NMR spectrum of complex 3 revealed two partially overlapping sets of signals in approximate 4:1 ratio. The presence of diastereomers was rationalized by the fact that the iron centers in 3 are stereogenic and should therefore result in mixtures of rac and meso forms. Most diagnostic are the resonances due to the methylene protons, which appeared as a pair of overlapping singlets for the rac isomer (Figure 2a), thus corroborating the results deduced from solution measurements. The Fe–C$_\text{carbene}$ distances are 1.956(8) and 1.978(7) Å, respectively (Table 2), and hence similar to those in related Fe–NHC complexes. The metal-metal separation is 6.8089(17) Å. In addition, short intermolecular contacts were found between a cp-bound hydrogen and the iodide, which leads to a dimeric structure in the solid state.

Table 2 Selected bond lengths (Å) of complexes 3 and 4

![Fig. 2 ORTEP representation and labelling scheme of complex 3 (30% probability ellipsoids; H atoms omitted for clarity).](image)

In the molecular structure of 4, the two iron-carbene units are symmetry-related also in the solid state (Figure 3). The Fe–C$_\text{carbene}$ bond length is 1.983(6) Å and similar to those observed in complex 3. The metal centers are separated by 8.657(2) Å. Notably, the phenylene ring is arranged nearly orthogonal to the carbene heterocycles, which may be relevant for intramolecular electronic interactions. The large torsion angle (average 78.7(16)°) suggests no overlap between the two $\pi$-systems in the ground state.
Electrochemical analysis allowed for probing the electronic coupling of the two metal centers in these bimetallic complexes. Cyclic voltammetry (CV) measurements showed a single reversible oxidation for complexes 3 and 6 ($E_{1/2} = 0.58$ V and 0.47 V vs. SCE, respectively; Table 3). These values compare well with other mono- and bimetallic Fe–NHC complexes and indicate little or no metal-metal communication. Deconvolution of the differential pulse voltammogram of 6 using the oxidation curve of the related monometallic monocarbene complex suggests two sequential oxidations that are separated by $\Delta E_{1/2} = 60 $ mV. This separation corresponds to a comproportionation constant $K_c = 10^{14}$, and hence to a valence-localized, electronically coupled class II system according to the Robin and Day classification. Earlier studies on the monometallic [Fe(cp)(NHC)(CO)]$^+$ cation indicated very high oxidation potentials (1.84 V vs. SCE) for dicarbonyl derivatives, hence the tetracarbonyl complexes 4 and 5 were not analyzed.

**Table 3** Spectroscopic and electrochemical data for complexes 3, 5 and 6

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<th>$\nu_{\text{sym}}$</th>
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<th>$E_{1/2}(\Delta E_p)$</th>
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<td>1939</td>
<td>0.58 (143)</td>
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<tr>
<td>5</td>
<td>2051, 1984</td>
<td>0.47 (201)</td>
</tr>
<tr>
<td>6</td>
<td>1941</td>
<td>n.d.</td>
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</table>

$\nu_{\text{sym}}$ in cm$^{-1}$, measured neat
$\Delta \nu_{\text{as}}$ in cm$^{-1}$, measured neat
$E_{1/2}(\Delta E_p)$ in mV

Characteristically, complexes 9 and 10 rapidly change color from purple in the solid state to yellow upon dissolution at RT. This color change is independent of the presence of O$_2$ or moisture and occurred in coordinating (DMSO, MeCN) as well as in non-coordinating solvents like MeNO$_2$. However, the color change was markedly slower at low temperatures and at high concentrations. UV-Vis spectroscopic analysis of a freshly prepared MeNO$_2$ solution of 9 featured two absorption maxima located at 434 nm and 578 nm (for 9a) and 424 nm and 563 nm (for 9b; Figure 4a and Table 4). Complexes 10a and 10b displayed a single maximum at 463 nm and 452 nm, respectively. The absorptions were attributed to charge transfer bands and provided a useful probe for the stability of the complexes. Time-dependent monitoring of the absorption at room temperature indicated that the pyrazine-bridged complex 9a is considerably less stable than the corresponding bipyridine analogue 10a. The low energy band of solutions of 9a completely disappeared in less than 5 min (Figure 4b), while the decrease was much less pronounced for 10a (Figures 4b, c).
Concomitant $^1$H NMR spectroscopy indicated the gradual formation of free pyrazine from solutions of complex 9a in MeNO$_2$-$d_4$. Pyrazine dissociation was evidenced by the decrease of the signal at δ 7.82, assigned to bridging pyrazine coordination. Transient appearance of two signals (δ 8.23 and 8.26) suggested the formation of an intermediate complex comprising probably and end-on bound rather than a bridging pyrazine iron complex. Eventual complex decomposition was noted by the growth of the signal at δ 8.56, diagnostic for unbound pyrazine, and by the formation of an imidazolium salt. This result correlates well with the observed color change upon increasing the temperature to RT and which was associated to fluxional behavior of the bridging ligand. Notably, no line broadening was observed for 9b presumably because the mesityl substituents lock the conformation of the pyrazine. Similarly, the resonances due to the bipyridine ligand in complexes 10 were well resolved. At low temperature, rotation about the N–C$_{mesityl}$ bond appeared to be hindered and each CH$_3$ group of the iPr and mesityl substituents gave rise to a distinct resonance. The C$_{3}$-centered chemical shifts of 9 and 10 appeared between δc 174.3 and 180.8, a typical range for iron(II)-bound NHC carbons. While no diastereoisomers due to the chirality at iron were detected by $^1$H NMR spectroscopy, the $^{13}$C NMR spectrum of complex 9a revealed a second set of signals. The chemical shift differences were generally small (< 0.2 ppm) and some signals were overlapping. The largest differences were observed for the chemical shifts of C$_{tip}$, C$_{CO}$ and C$_{ortho}$, i.e. the nuclei directly attached to and hence most affected by the stereoatomic center.

The structure of the pyrazine-bridged dimetallic complex 9b was analyzed by single crystal X-ray diffraction. Suitable crystals were grown at 4 °C from MeNO$_2$/Et$_2$O solution. Perhaps the most remarkable feature of the molecular structure of 9b consists of the π interactions between the pyrazine heterocycle and two mesityl wingtip groups, one from each NHC ligand (Figure 5). The interplanar separation

![Image](55x169 to 291x599)

**Fig. 5** ORTEP representation of 9b (50% probability ellipsoids; H atoms, solvent molecules and BF$_4$ anions omitted for clarity); a denotes symmetry operation $x$+2, $y$, $z$+1. Selected bond lengths (Å): Fe1–Fe1a 1.741(4), Fe1–C7 1.977(5), Fe1–C$_{mesityl}$ 1.735(3), Fe1–C6 1.741(6), Fe1–N3 1.994(4), C7–N1 1.381(6), C7–N2 1.363(6), N1–C8 1.386(6), N2–C9 1.390(6), C8–C9 1.324(7); selected bond angles (°): C7–Fe1–N3 95.4(2), C7–Fe1–C6 96.5(2), C6–Fe1–N3 94.9(2), N1–C7–N2 102.3(4).

**Table 4** Spectroscopic and electrochemical data of complexes 9 and 10

<table>
<thead>
<tr>
<th></th>
<th>$\nu$ (cm$^{-1}$)</th>
<th>$\Delta E_{pc}$ (mV)</th>
<th>$\Delta E_{c}$ (mV)</th>
<th>log $K$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9a</td>
<td>1952</td>
<td>434, 578</td>
<td>1.06 (107), 1.28 (122)</td>
<td>216</td>
</tr>
<tr>
<td>9b</td>
<td>1946</td>
<td>424, 563</td>
<td>1.18 (97), 1.53 (117)</td>
<td>352</td>
</tr>
<tr>
<td>10a</td>
<td>1937</td>
<td>463</td>
<td>0.94 (136)</td>
<td>---</td>
</tr>
<tr>
<td>10b</td>
<td>1947</td>
<td>452</td>
<td>0.98 (111)</td>
<td>---</td>
</tr>
</tbody>
</table>

Table 4 calculated according to log $K$ = $\Delta E_{pc}$/95 mV

pyrazine bridge appeared as a broad signal, which sharpened upon increasing the temperature to RT and which was associated to fluxional behavior of the bridging ligand.
MeCN and a pyridine ligand, respectively, were synthesized. The mononuclear Fe–NHC complexes 11 and 12 containing a MeCN and a pyridine ligand, respectively, were synthesized. These complexes were obtained by irradiation of the dicarbonyl precursor 7 in dry MeCN as solvent, or in dry CH₂Cl₂ in the presence of excess pyridine (Scheme 3).  

Fig. 6 Cyclic voltammetry diagram of complexes 9a and 10a in MeNO₂ at –20 °C (100 mV s⁻¹ scan rate, Bu₄NPF₆ as supporting electrolyte, Pt rotating disk working electrode).

The CV of 9a in MeNO₂ at –20 °C revealed two reversible waves centered at E₁/₂ = 1.06 V and 1.28 V, indicating electronic coupling between the metal centers (Figure 6). The separation of the two oxidation processes is 216 mV. The CV of 10a and 11a showed a single reversible oxidation only (E₁/₂ = 0.94 V and 1.53 V. The larger separation between the redox processes (ΔE = 352 mV) translates to Kₚ = 10⁷.9, thus identifying complex 9b as a class III compound in which the metal centers are coupled and valences delocalized. Interestingly, the CV of complexes comprising bridging bipyridine showed a single reversible oxidation only (E₁/₂ = 0.94 V for 10a and E₁/₂ = 0.98 V for 10b), suggesting electronically decoupled metal centers. The electron delocalization observed for the pyrazine-bridged complexes 9 may be a consequence of the favorable overlap between the metal d orbitals and the π-system of the pyrazine ligand. Such overlap seems to be more pronounced in 9b than in 9a, probably due to the locked conformation of the pyrazine ligand (cf. NMR X-ray analyses). Apparently, such overlap is absent in the bipyridine complexes 10.

In order to investigate the binding properties of imine donors to the [Fe(CO)cp(carbene)]⁺ fragment, the mononuclear Fe–NHC complexes 11 and 12 containing a MeCN and a pyridine ligand, respectively, were synthesized. These complexes were obtained by irradiation of the dicarbonyl precursor 7 in dry MeCN as solvent, or in dry CH₂Cl₂ in the presence of excess pyridine (Scheme 3).

Table 5 Selected bond lengths (Å) and angles (°) for 11 and 12

Table 5

<table>
<thead>
<tr>
<th>Bond/Length</th>
<th>11</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe1–C7</td>
<td>1.969(3)</td>
<td>1.972(2)</td>
</tr>
<tr>
<td>Fe1–C₅₋₋₋₋</td>
<td>1.716(2)</td>
<td>1.736(1)</td>
</tr>
<tr>
<td>Fe1–C6</td>
<td>1.770(3)</td>
<td>1.750(2)</td>
</tr>
<tr>
<td>Fe1–N3</td>
<td>1.913(2)</td>
<td>2.017(1)</td>
</tr>
<tr>
<td>C7–N1</td>
<td>1.362(3)</td>
<td>1.363(2)</td>
</tr>
<tr>
<td>C7–N2</td>
<td>1.360(3)</td>
<td>1.365(2)</td>
</tr>
<tr>
<td>N1–C8</td>
<td>1.381(4)</td>
<td>1.383(2)</td>
</tr>
<tr>
<td>N2–C9</td>
<td>1.390(4)</td>
<td>1.389(2)</td>
</tr>
<tr>
<td>C8–C9</td>
<td>1.340(4)</td>
<td>1.338(2)</td>
</tr>
<tr>
<td>C7–Fe1–N3</td>
<td>93.5(1)</td>
<td>88.69(5)</td>
</tr>
<tr>
<td>C7–Fe1–C6</td>
<td>94.3(1)</td>
<td>98.79(7)</td>
</tr>
<tr>
<td>C6–Fe1–N3</td>
<td>92.0(1)</td>
<td>90.22(6)</td>
</tr>
<tr>
<td>N1–C7–N2</td>
<td>104.2(2)</td>
<td>104.09(12)</td>
</tr>
</tbody>
</table>

* estimated standard deviations in parentheses

An X-ray diffraction analysis of complexes 11 and 12 did not uncover any unexceptional features (Figure 7, Table 5). It is worth noting, however, that crystals of 11 were obtained by recrystallization of the diimine complex 9a from MeCN/Et₂O.

Further investigation on the stability of the pyridine ligand in 12 supported the lability of the imine donor. Thus, addition of minute amounts of MeCN to an acetone-d₆ solution of the pyridine complex 12 induced the instantaneous appearance of signals identical to those of 11 along with those of free pyridine. These results suggest that MeCN binds significantly stronger to the [Fe(CO)cp(carbene)]⁺ fragment than pyridine, emphasizing the labile coordination of the imine.

Scheme 3 Synthesis of monodentate Fe(II)–NHC model complexes

Fig. 7 ORTEP representation of 11 (a; 50% probability ellipsoids, H atoms and BF₄⁻ anion omitted for clarity) and 12 (b; 50% probability ellipsoids, H atoms and BF₄⁻ anion omitted for clarity).
ligands. Weak imine binding corroborates the low stability of the bimetallic complexes 9 and 10.

**Redox-Active Organometallic Polymers**

Combination of the two synthons, i.e. the dicarbene bridged bimetallic complexes and the diimine linked systems, allowed for synthesizing main-chain organometallic co-polymers. Due to the mild conditions required for imine coordination as opposed to carbene bonding, the polymers were prepared starting from synthon A, that is, complexes containing the dicarbene ligand already installed at the metal center. Based on the reactivity protocols established for imine coordination to the monometallic precursor 7 and 8 (viz. the synthesis of the bimetallic complexes 9 and 10) the bimetallic complex 5 containing butyl wingtip groups and a rigid phenylene spacer between the carbene units was irradiated in the presence of pyrazine or bipyridine as interlinking diimine ligand.

Photochemically induced CO dissociation thus yielded the corresponding polymers 13a and 14a, which readily precipitated from the reaction mixture (Scheme 4). The bimetallic complex 3 comprising mesityl wingtip groups required treatment with 1 molequiv of diimine in the presence of 2 molequiv of AgBF₄ to afford the analogous polymers 13b and 14b.

Formation of oligo- or polymeric products was indicated by spectroscopy and electrochemistry. While ¹H NMR spectroscopy showed considerably broadened resonances, the UV-vis absorption spectra of 13 and 14 are reminiscent to those of complexes 9 and 10 and suggest binding of the diimine ligand to the iron centers. The pyrazine-containing polymers showed two absorption maxima located at around 420 nm and 540 nm (Table 6), which is in excellent agreement with the bimetallic synthon 9 (cf. Table 4). The polymers with bipyridine exhibit a single absorption maximum with ƛₘₐₓ around 460 nm. Similarly, the single ν₃(t) absorption provided a diagnostic probe, specifically when starting from the dicarbonyl precursor 5. For 14a, the strongest absorption was located at ν₃(t) = 1937 cm⁻¹, which corroborates the data for 10a. When pyrazine was used, however, the presence of the two bands at higher energy (ν = 2043 and 1991 cm⁻¹) along

![Scheme 4](image)

**Scheme 4** Synthesis of organometallic co-polymers; reagents and conditions: i) pyrazine or 4,4'-bipyridine, hv, acetone; ii) pyrazine or 4,4'-bipyridyl, AgBF₄, CH₂Cl₂.

---

**Fig. 8** a) CV of the pyrazine-containing polymer 13b and its bipyridine analog 14b in MeNO₂ (100 mV s⁻¹ scan rate, Bu₄NPF₆ as supporting electrolyte, Pt rotating disk working electrode); b) spectral change of 13a in MeNO₂, at 5 min time intervals; inset shows the time-dependent absorption at 568 nm.

**Table 6** Spectroscopic and electrochemical data for polymers 13 and 14

<table>
<thead>
<tr>
<th></th>
<th>ν₃(t) (cm⁻¹)</th>
<th>ƛₘₐₓ (nm)</th>
<th>E½ (mV) (ΔE)</th>
<th>Elem. anal</th>
</tr>
</thead>
<tbody>
<tr>
<td>13a</td>
<td>1969</td>
<td>420 (sh), 568</td>
<td>1.23 (broad)</td>
<td>C 46.76, H 4.53, N 7.69</td>
</tr>
<tr>
<td>13b</td>
<td>1961</td>
<td>419, 537</td>
<td>1.26 (broad)</td>
<td>C 49.94, H 4.80, N 8.26</td>
</tr>
<tr>
<td>14a</td>
<td>1937 (b)</td>
<td>470</td>
<td>0.97 (177)</td>
<td>C 51.93, H 4.53, N 8.59</td>
</tr>
<tr>
<td>14c</td>
<td>1960</td>
<td>444</td>
<td>1.09 (163)</td>
<td>C 52.86, H 4.73, N 7.98</td>
</tr>
</tbody>
</table>

a) in cm⁻¹, measured neat
b) in nm, measured in MeNO₂
c) in V, measured in MeNO₂ and calibrated to Fe⁺/Fe⁺ (E½ = 0.35 V vs. SCE) as internal standard, ΔE = E½-E½ in mV
d) additional shoulders at 1975 and 1963 cm⁻¹.
with a band at \( v_{\text{CO}} = 1699 \text{ cm}^{-1} \) suggested that, while the desired polymer was formed, some starting material was not consumed.

Electrochemical analysis using CV also supported polymer formation. The half-wave potentials were similar to those of the bimetallic model complexes and hence indicate the anticipated substitution of a carbonyl or iodide ligand at iron with the corresponding diimine ligand (Table 6). Notably, the quasi-reversible redox wave of the pyrazine-containing polymers 13 were unusually broad, and the maximum current \( I_{\text{max}} \) was relatively low (Figure 6a). Such behavior may be explained either by multiple metal-metal interactions, similar to those observed in the corresponding bimetallic system 9b, or more likely, by the fact that the electron transfer is not only diffusion-controlled. The latter is expected in polymers because of their limited rotational flexibility as compared to molecular species in solution. The redox process of the bimetallic analog 14b was considerably sharper, perhaps as a consequence of a low polymerization degree and formation of oligomers only. Indeed, microanalysis of complexes 14 were in line with the presence of tri- and tetramers.\( ^{\S} \)

Unexpectedly, time-dependent monitoring of the UV-vis absorption at \( \lambda_{\text{max}} \) revealed a substantially better stability of the polymeric systems as opposed to the bimetallic complexes. This effect was particularly pronounced in the pyrazine-containing polymer 13a. While the half-life time of the bimetallic analog 9a in MeNO\(_2\) was on the order of 30 s, polymer 13a had \( t_{1/2} \approx 10 \text{ min} \) (Figure 8b). Such increased stability may be useful for processing these polymers, e.g. by spin coating. After solvent evaporation, the stability increases significantly and in the solid state, no decomposition has been observed thus far.

Conclusions

Organometallic polymers comprising redox-active metal centers in the polymer main chain have been synthesized by co-polymerization of bimetallic iron(II) NHCTMC complexes with pyrazine and 4,4'-bipyridine as ditopic diimine ligands. The polymers are redox active and cyclic voltammetry experiments indicate that the metal centers are electronically coupled when pyrazine was used as interconnecting ligand. The polymers formed are reasonably stable towards air and moisture in the solid state, but they decompose gradually in solution. Comparative studies on analogous bimetallic complexes revealed that the decomposition is due to the dissociation of the weakly coordinating N-donor ligands. In order to use such types of polymers in molecular electronic applications, therefore, it will be necessary to increase the stability of the imine bonding, perhaps via chelation. Studies in this direction and also towards the full exploitation of the electrochemical properties of the polymers are in progress.

Acknowledgments

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Notes and references

\( ^{*} \) Department of Chemistry, University of Fribourg, Chemin du Musée 9, CH-1700 Fribourg, Switzerland. Fax: +41 2630 09738; Tel: +41 26 30 087 86; E-mail: martin.albrecht@unifr.ch

\( ^{1} \) XRD Application Lab, CSEM, Rue Jaquet Droz 1, CH-2000 Neuchâtel, Switzerland

\( ^{2} \) Institute of Physics, University of Neuchâtel, rue Emile Argand 11, CH-2009 Neuchâtel, Switzerland

\( ^{3} \) School of Chemistry and Chemical Biology, University College Dublin

\( ^{4} \) Belfield, Dublin 4, Ireland.

\( ^{\dagger} \) Electronic Supplementary Information (ESI) available: CIF-files for complexes 3, 4, 9b, 11 and 12. See DOI: 10.1039/b000000s/

\( ^{\ddagger} \) From CV measurements, a 1:1 electron oxidation process is not evident for 9a. However, the DPV signals, albeit weak, show nearly identical peak currents for the oxidations at 1.06 and 1.28 V, consistent with two sequential one-electron processes.

\( ^{\S} \) A characteristic feature of the \( ^{1}H \) NMR spectrum of 12 is the magnetic inequivalence of the CH protons of the \( \beta \)-wingtip groups giving rise to two signals at RT (\( \delta_{i} = 1.63 \) and 0.99 in acetone-\( d_{6} \)). On cooling to \( -35 \) °C the signals decoalesce into four magnetically inequivalent resonances. The two signals at lower field coalesce at \( T_{c} = 251(\pm 2) \text{ K} \), corresponding to an approximate free energy of activation \( \Delta G^{\ddagger} \approx 51.7(\pm 0.5) \text{ kJ mol}^{-1} \), while the two signals at higher field show coalescence at \( T_{c} = 278(\pm 2) \text{ K} \) (\( \Delta G^{\ddagger} \approx 52(\pm 0.4) \text{ kJ mol}^{-1} \)). Such dynamic behavior may be rationalized by hindered rotation about the N–C=N bond. This rotation is expected to be slightly different for the two \( \beta \)-wingtip because of the unequal steric demand of the CO and pyridine ligands. In addition, line broadening was observed for the ortho \( \text{H}_{2} \) resonances at low temperature, suggesting that rotation about the Fe–N\(_{6}\) bond is slow on the NMR time scale. This result is in good agreement with the broad pyrazine resonances observed for 9a.

\( ^{\S} \) The weak imine coordination prevented further analyses such as mass spectrometry or gel permeation chromatography. Only (polycationic fragments of the type [(cp)Fe(dicarbene)Fe(cp)] were detectable.


Ditopic N-heterocyclic carbenes have been employed in combination with diimines such as pyrazine and 4,4'-bipyridine to ligate redox-active iron(II) centres, thus providing access to electronically active polymeric architectures.