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Diferrocenylbispyrylium Salts and Electron-Rich Diferrocenylbispyran from Oxidative Coupling of Ferrocenylpyran. Induced Electron Transfer C−C Bond Making/Breaking Involving a Metallocenyl Radical Intermediate

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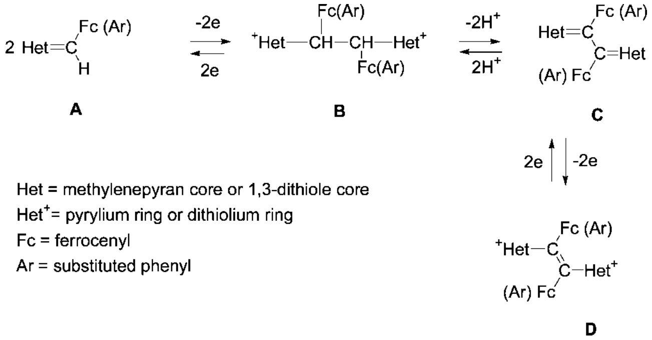
Summary: Electrochemical or chemical dimerization of electron-rich ferrocenylmethylenepyran **1** *gave the first dimetallocenyl-bispyrylium salt* **2** *known today, through a reverse process that implies reductive C−C bond breaking. Deprotonation of the bispyrylium salt* **2** *afforded extended electron-rich diferrocenyl bispyran* **3**, *which was subsequently reversibly oxidized to diferrocenyl bispyrylium salt* **4**. *This study constitutes a new system in which two ox/red sequences of different nature were separated by proton/deprotonation steps.*

Scheme 1. Possible Reversible Steps in Aryl and Ferrocenyl Heterocyclic Series



In comparison to the numerous studies devoted to dithiafulvene, tetrathiafulvene (TTF), and extended TTF-bearing electroactive ferrocenyl group(s)[1] with related applications in material science,[1a,2] the chemistry of the isoelectronic electron-rich metallocenyl methylenechalcogenopyrans, bischalcogenopyrans, and extended bischalcogenopyrans remains unexplored.[3] With the aim to develop the molecular solid state chemistry of metallocenylbispyran charge transfer (CT) complexes[4] and to explore their electrical and magnetic properties, we decided to investigate, in a first approach, the oxidative coupling of ferrocenylmethylenepyran of type **A** (Scheme 1, Het = pyran core) by a procedure widely used for the dithiafulvene series (Scheme 1, Het = 1,3 dithiole core) to prepare TTF vinylogues **C** via a radical cation intermediate (Scheme 1, Het = 1,3 dithiole core).[1a,5]

In sharp contrast with the thiaheterocyclic series, we disclose in this communication that a fine control of the reactivity allowed the observation of a new multistep process (Scheme

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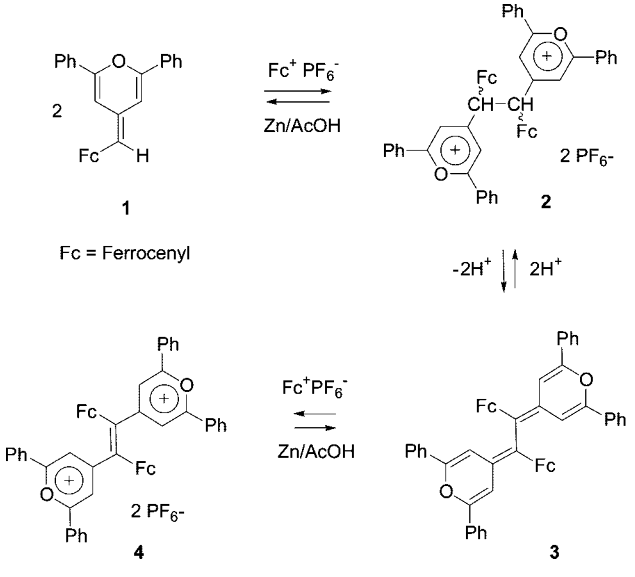
1), consisting in a reversible C−C bond making/breaking followed successively by deprotonation/protonation and ox/red steps (Scheme 1). Recently, much attention has been focused on molecular devices based on C−C bond making/breaking under electron stimuli[6] and by an ox/red process for which molecular motion accompanies the electron transfer (ET).[1b,5a,7] The key step is the isolation of the first dimetallocenyl bispyrylium salt of type **B** (Scheme 1, Het = pyrylium ring) known today,[8] whereas, due to its easy deprotonation, the analogous aryl or ferrocenyl bisdithiolium salt **B** (Scheme 1, Het = dithiolium ring) has never been isolated or detected by spectroscopic or electrochemical methods.[1,5] In addition, the unknown diferrocenylbismethylenepyran was also described. Therefore, we shall report in this communication that association of heterocyclic pyrylium units with ferrocenyl groups should be a good substitute for highly aryl-stabilized dicarbocation in molecular devices, for which, as in our case, two redox pairs of different nature can be switched by proton transfer.[9]

Previous studies have shown the propensity of the α-aryl-γ-methylbenzopyrylium salt to dimerize upon brief heating in pyridine.[10] The formation of the isolated extended bispyran proceeds by proton removal and a one-electron transfer from the deprotonated species to the benzopyrylium salt, followed by dimerization of the resulting radical cation with further loss of proton.

To tentatively control oxidative coupling of the easily available ferrocenylmethylenepyran **1** (red-orange solid) (Scheme 2),[11] the electron acceptor ferricinium salt ($FcH^+PF_6^-$) was used as the oxidant. Mixing **1** and $FcH^+PF_6^-$ in CH_2Cl_2 at − 70 °C gave a green precipitate **2** (76% yield, Scheme 2). As expected formation of ferrocene was also detected (TLC observation and comparison with an authentic sample).

Scheme 2. Interconversions in Ferrocenylpyran Chemistry



Due to the presence of two asymmetric carbon atoms, the ^1H NMR spectrum recorded in acetone-d_6 showed two sets of signals with different intensities, reflecting the presence of two diastereoisomers. A careful integration, taking into account the well-separated peaks, gave a 64/36 ratio of isomers (±2%). The structure of **2** was confirmed by the presence of two singlets at 9.11 ppm (major isomer) and 8.86 ppm (minor isomer) attributable to the β-hydrogen atoms of the pyrylium rings.[12] Two singlets observed at 5.23 ppm (minor isomer) and 5.15 ppm (major isomer), corresponding to the acidic hydrogen atoms of the ethane part of the molecule, were also present. In addition, the protons of the substituted Cp ring, which exhibit diastereotopic character, give four signals for each isomer. The ^{13}C NMR spectrum showed all the expected pyrylium signals.[13] For example the C_α atom resonates at 172.8 ppm (major isomer) and 171.9 ppm (minor isomer). On the other hand the asymmetric carbon was observed at 54.8 ppm (minor isomer) and 54.6 ppm (major isomer).

The X-ray analysis confirmed the proposed structure.[14] Compound **2** is built from two crystallographically independent centrosymetric half-molecules labeled **A** and **B**, yielding two independent erythro conformers (*R*, *S*) with slight differences of the torsion angles between the Cp rings and the pyrylium rings, respectively (Figure 1). In the asymmetric units, the pyrylium and the Cp rings bound to C2 atoms form an angle of 52.94(22)° and 61.97(23)° for molecule **2A** and **2B**, respectively. Furthermore, the two Cp rings of one of the ferrocene group form an angle of 5.51(68)° and 4.54(35)° for **2A** and **2B**, respectively. Due to the center of symmetry of the molecules, the two pyrylium cycles as well as the Cp rings lie in parallel planes. The central centrosymetric $C2-C2^i$ bond lengths are equal to 1.532(11) Å for **2A** and 1.535(11) Å for **2B**, as expected for a Csp^3-Csp^3 bond. This value is in accordance with the lack of a high degree of strain in **2**.

It is likely that the formation of **2** proceeded via the radical pyrylium cation $1^{+\bullet}$, which may also involve contribution of

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(14) Empirical formula: $C_{56}H_{44}F_{12}Fe_2O_2P_2$, $M = 1150.55$, triclinic, $P\bar{1}$, dark green block, $a = 13.2117(9)$ Å, $b = 14.6163(12)$ Å, $c = 15.5367(14)$ Å, $\alpha = 92.319(4)°$, $\beta = 109.009(4)°$, $\gamma = 89.863(3)°$, $V = 2834.1(4)$ Å^3, $Z = 2$, $T = 293(2)$ K, 15 902 total reflections, 9765 independent (R_{int}) 0.0581, 4092 with $I > 2\sigma(I)$, R_1 ($I > 2\sigma(I)$) = 0.0824, wR_2 (all data) 0.2198.

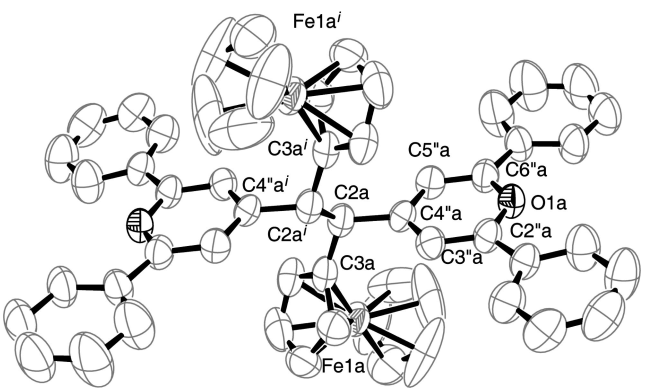
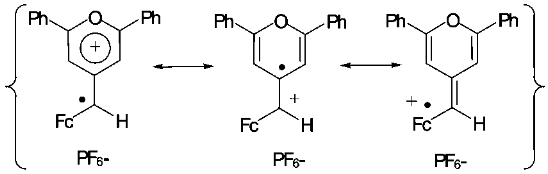


Figure 1. ORTEP drawing of molecule **A** in compound **2** with thermal ellipsoids at the 50% probability level. Labeling scheme, given here for molecule **A** with symmetries *i*: $-x$, $2-y$, $1-z$, is similar for molecule **B** with symmetries *ii*: $1-x$, $1-y$, $-z$.

Chart 1



$1^{+\bullet}$

the α-ferrocenylcarbenium and ferricinium forms (Chart 1), resulting from single electron transfer between **1** and ferricinium salt. Electrochemical studies of compounds **1** and **2** confirmed this view. The voltammogram of **1** (Figure 2a) shows an irreversible anodic peak at −0.15 V (vs FcH) followed by two reversible systems ($E^{1/2\prime}$ = 0.12 V and $E^{1/2\prime}$ = 0.28 V) attributable to the ferrocenyl groups.[15a,b] Interestingly, on the reverse scan, an irreversible cathodic peak is observed at −0.76 V. This reduction peak appears only if the potential is raised above −0.15 V before scanning cathodically. Maintaining the potential at −0.15 V for a few seconds leads to an increase of the cathodic peak, suggesting an ECE mechanism. A quantitative electrolysis performed at −0.10 V showed the complete disappearance of **1** through a one-electron redox process, with formation of a compound that can be reduced at −0.76 V. Counterelectrolysis at − 0.80 V yielded back compound **1**.

The voltammetric study of the bispyrylium salt **2** has also been performed. When scanning cathodically, an irreversible cathodic two-electron peak is detected at −0.76 V, with appearance of an oxidation irreversible peak at −0.15 V on the back scan. This oxidation peak is not present when scanning anodically (Figure 2b), thus confirming the hypothesis that the electrochemical oxidation of **1** to the radical cation $1^{+\bullet}$ is followed by a coupling reaction leading to **2**.

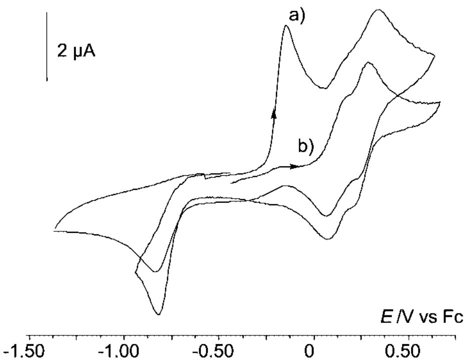


Figure 2. Cyclic voltammogram at a Pt electrode of **1** (a) and **2** (b) in CH_2Cl_2/NBu_4PF_6 0.2 M. Concentration in electroactive species: 7×10^{-4} M, $v = 0.1$ V s^{-1}, *E*/V vs FcH, temperature 298 K.

From these electrochemical results, a chemical reduction of compound **2** was performed by using Zn powder in a AcOH/CH_2Cl_2 mixture. This reaction gave compound **1** in 66% yield. These results unambiguously show the electrochemical and chemical interconversion between **2** and **4** via a C−C bond making/breaking process. To the best of our knowledge, this reverse process has been rarely observed in the ligand-centered reaction of organometallic radicals.[16] However, C−C bond making/breaking upon electron transfer is well documented in particular for molecular systems for which a ring opening is involved.[6] This has recently been observed for triaryl-substituted ethenes, which are reversibly dimerized to stable 1,4-dicarbocations via a radical process.[9] As pointed out in the introduction, our results differ from those found for the isoelectronic aryl- and ferrocenyl-substituted dithiafulvene **A** (Scheme 1, Het = 1,3-dithiole core).[1,5] Whatever the chemical or electrochemical oxidation method used, only the unsaturated dithiolium salt of type **D** (Scheme 1, Het = dithiolium ring) or the extended TTF of type **C** was isolated. Indeed, it appears that the bispyrylium salt **2** is more resistant to deprotonation than its dithiolium counterpart. High steric strain in the extended bispyran **3** formed by deprotonation and/or lower pK_a values for the dithiolium salt **2** could be responsible for this different behavior.

However, deprotonation of **2** was successfully obtained by using a (pH 9) buffer in a biphasic medium (H_2O/CH_2Cl_2). Under these experimental conditions, formation of a pseudobase by ring opening of the pyrylium nucleus upon OH^- action[8a] is precluded and the red-orange diferrocenyl bispyran **3** is isolated in 47% yield (Scheme 2).

The ^1H and ^{13}C NMR spectra confirmed the proposed structure. A comparison of the pyran atom chemical shift values of **1** and **3** showed the great similarity between the two heterocyclic molecules (**1**, C_α, C_β, C_γ pyran atoms; δ(ppm): 151.0 (and 149.0), 108.4 (and 103.0), 134.2, respectively; **3**, C_α, C_β, C_γ pyran atoms; δ(ppm): 150.1 (and 149.9), 106.6 (or 105.2), 125.1, respectively). However, one of the H_β signals of **3** is deshielded (**3**, δ (ppm): H_β: 7.81 and 6.54), as anticipated from the sensitivity of the β-pyran hydrogen to the susbstituent group of the exocyclic double bond.[7a]

The similarity between NMR data of **1** and **3** suggests that the presence of the ferrocenyl and pyran groups in **3** precludes,

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[15] (a) Voltammetric studies of the phenyl-substituted pyran analogous to **1** show one single reversible system at $E^{0\prime}$ =−0.32 V vs Fc, corresponding to the one-electron oxidation/reduction of the pyran moiety. Ba, F., unpublished results. (b) The sharp-like shape of the oxidation one-electron peak at *E* =−0.15 V vs Fc may be due to a weak adsorption of compound **1** onto the Pt working electrode. Wopschall, R.-H.; Shain, I. *Anal. Chem.* **1967**, *39*, 1514.

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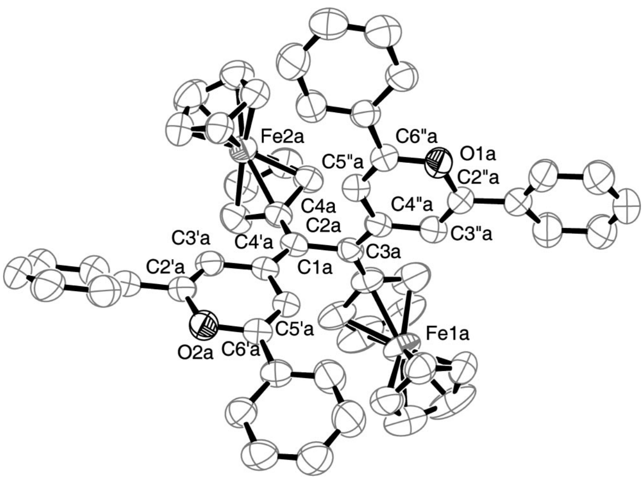

Figure 3. ORTEP drawing with thermal ellipsoids at the 50% probability level of molecule **A** with labeling scheme in compound **3**. Labeling scheme is similar for molecule **B**. Selected bond distances (Å): C2a−C4″a = 1.367(6), C1a−C4′a = 1.352(6), C1a−C2a = 1.506(7).

for steric reasons, effective π conjugation between the two symmetric parts of the molecule. Interestingly, on the ferrocene side, hydrogen and carbon atoms of the substituted Cp rings gave four signals (two for **1**). This is probably a consequence of a restricted rotation around the Cipso−C bond due to steric strain between the ferrocene and the pyran group.[17]

This is confirmed by the X-ray analysis of **3** (Figure 3).[18] Compound **3** crystallizes in the $P\bar{1}$ space group, with two independent complexes, **A** and **B**, in the asymmetric unit. The two conformers **3A** and **3B** differ in the torsion angles between rings; for example, the angle observed between the pyran group and the phenyl ring connected to C6′a is 20.60(19)° for molecule **3A**. The corresponding angle is 49.45(16)° for **3B**. The two pyran rings form an angle of 85.04(14)° in molecule **3A** and 79.43(15)° in molecule **3B**. These values confirm the lack of conjugation. This is also exemplified by the length of the central bond of 1.506(7) Å for **3A** and 1.513(6) Å for **3B**. In addition the exocyclic C═C bonds are shorter (C1a−C4′a = 1.352(6) and C2a−C4″a = 1.367(6) Å for **3A**, C1b−C4′b = 1.365(6) and C2b−C4″b = 1.364(6) Å for **3B**) than those found for push−pull methylenepyran Fischer-type carbene complexes for which a pyrylium character exists.[7a,19] It can be noted that an extended bispyran synthesized by Doney et al., in which a cyclobutane ring forces a planar conformation on the pyran rings, showed a central C−C bond distance of 1.457(5) Å.[20] Such a staggered conformation around the central C−C bond has been previously found in diferrocenyl extended dithiafulvene synthesized by Bryce et al. (Scheme 1, molecule **C**, Het = 1,3-dithiole core).[1b] In that case a distance of 1.50(1) Å for the C−C central bond length and a torsion angle of 101.7° between the two 1,4-dithiafulvene rings were reported. The similarity observed between the two heterocyclic series indicates that the lack of conjugation in **3** is not the main reason for the different behavior toward the deprotonation of the related dications.

Finally, a solution of bispyran **3** in CH_2Cl_2 was treated with ferricinium salt (PF_6^-) to yield a green precipitate upon addition of ether (63% yield). The ^1H NMR spectrum, recorded in acetone-d_6, is in accordance with the unsaturated bispyrylium structure **4**, as exemplified in Scheme 1. In particular the spectrum shows the characteristic signal of the pyrylium atom H_β at 8.90 ppm (one detectable isomer).[12] The unsaturated bispyrylium salt **4** likely results from electron transfer between bispyran **3** and ferricinium salt. As expected, we observed the formation of ferrocene (TLC observation). In addition, a solution of **4** in CH_2Cl_2/AcOH gave back compound **3** upon Zn powder addition (50% yield). Small quantities of **1** (yield <5%) were also isolated. This observation exemplified the total chemical reversibility of the multistep process.

In conclusion, we have described a reversible multistep process that includes a C−C bond making/breaking, based on the use of heterocyclic molecules containing ferrocenyl group(s). Because electrochemical control of C−C bond making/breaking processes and geometric molecular motions play an important role in the construction of molecular devices (switches, clips, etc.), we will consider in the future an intramolecular version of this work, using two ferrocenyl pyran units linked by an alkyl chain through the Cp rings.

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Supporting Information Available: Complete experimental section, ^1H NMR spectra of **2**, and crystallographic data of **2** and **3** are given as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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[18] Empirical formula: $C_{56}H_{42}Fe_2O_2$, $M = 858.60$, triclinic, $P\bar{1}$, $a = 12.9686(3)$ Å, $b = 16.0334(3)$ Å, $c = 21.8690(5)$ Å, $\alpha = 109.837(1)$, $\beta = 99.327(1)$, $\gamma = 90.918(1)°$, $V = 4208.49(16)$ Å^3, $Z = 4$, $T = 293(2)$ K, 31 133 total reflections, 17 721 independent ($R_{int} = 0.0671$), 8149 with $I > 2\sigma(I)$, R_1 $(I > 2\sigma(I)) = 0.0711$, w$R_2$ (all data) 0.1709.

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