2-Arylimino(diferrocenyl)- and (di-*p*-anisyl)dihydropyrimidines: Novel Synthesis, Structures, and Electrochemistry

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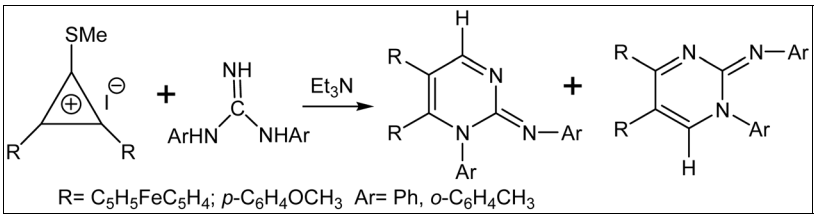

2,3-Differocenyl- and 2,3-dianisyl-1-methylsulfanylcyclopropenilium iodides react with 1,3-diphenyl- and 1,3-di-*o*-tolylguanidine to give 1-aryl-2-arylimino-5,6- (**5a**,**5b**) and -4,5-diferrocenyl-1,2-dihydropyrimidines (**6a**,**6b**) (~ 2:1) and, respectively, 5,6- and 4,5-dianisyl-3-phenyl-2-phenylimino-1,2-dihydropyrimidines (~ 2:1). Their structures were established based on the spectroscopic data and X-ray diffraction analysis of 5,6-diferrocenyl-1-(*o*-tolyl)-2-(*o*-tolyl)imino- and 4,5-diferrocenyl-1-phenyl-2-phenylimino-1,2-dihydropyrimidines (**5b** and **6a**, respectively). Electrochemical behavior of compounds **5b, 6b,** and **5a+6a** were investigated using experiments of cyclic voltammetry and chronoamperometry. For all the compounds, two electrochemical processes (**I**, **II**), attributed to the oxidations of the ferrocenes moieties were observed. The values of $\Delta E^{0'}$ (**II-I**) and comproportionation constant K_{com} are also reported. Additionally, an electrochemical oxidation with a fast coupled chemical reaction related to the pyrimide ring was also detected.

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INTRODUCTION

Pyrimidine and its derivatives pertain to important heterocyclic compounds, which is determined by the presence of pyrimidines in nucleic acids vital for every organism as their essential components (thymine, cytosine, and uracil) [1,2], in many other compounds with practically valuable properties, for example, barbituric and orotic acids [2–4]. Vitamin B_1 is a pyrimidine derivative, it is a constituent of carboxylase, the enzyme which catalyses carbohydrate metabolism. Several antibiotics, antitumor, antiepileptic, and other therapeutics, photographical materials, and so on, comprise pyrimidine structural elements.

The most general approach to the synthesis of pyrimidine derivatives is coupling of 1,3-dicarbonyl compounds with *gem*-diamino (or *gem*-amino-imino) compounds such as urea, guanidines or amidines [5–8]. First monoferrocenyl-substituted pyrimidines have been prepared by coupling of ferrocenyl-α, β-enones with urea [9,10]. However, ferrocenylpyrimidines still pertain to little-studied compounds.

The presence of one or several ferrocenyl substituents in heterocycles, especially in those containing conjugated multiple bonds, is known to confer them, in addition to biological activity, certain useful properties. These compounds are characterized by magnetic behavior, electrical conductivity (even superconductivity), nonlinear optical effects, and so on [11]. This fact increased interest in introduction of ferrocene fragments in diverse organic compounds aimed at preparing long-chained conjugated systems (linear, carbocyclic, and heterocyclic) as important category of materials.

The development of novel methods for an access to ferrocenyl-substituted polynitrogen six-membered heterocycles with a system of conjugated double bonds is of considerable importance. The use of diferrocenylcyclopropenylium salts for the synthesis of heterocycles allows introduction of two ferrocenyl substituents at a time. This served as the basis for the preparation of diferrocenyl-1,2,3-triazines [12], -pyridazines [13], -1,2,4-triazines [14], and –oxazines [15]. So far, diferrocenylcyclopropenylium salts have not been used for the synthesis of diferrocenylpyrimidines.

In this work, we studied reactions of 2,3-differocenyl- and 2,3-dianisyl-1-methylsulfanylcyclopropenylium iodides (**1a** and **1b**) with 1,3-diphenyl- and 1,3-di-*o*-tolylguanidine.

RESULTS AND DISCUSSION

The starting cyclopropenylium salts **1a** and **1b** were prepared according to a well-proven procedure developed earlier [16,17]: 2,3-diferrocenyl- and 2,3-di(*p*-anisyl)-cyclopropenones were converted into morpholino derivatives **2a,b** (Scheme 1), which were elaborated to 2,3-differocenyl- and 2,3-di(*p*-anisyl)-1-methylsulfanylcyclopropenylium iodides (**1a** and **1b**) *via* thiones **3a,b**.

We found that diferrocenyl(morpholino)cyclopropenylium tetrafluoroborate **1a** reacts with 1,3-diphenyl- and 1,3-di-*o*-tolylguanidine (**4a** and **4b**) in the presence of triethylamine in boiling benzene to afford regioselectively two reaction products, *viz*., **5a,b** and **6a,b,** in the ratio ~ 2:1 separated by column chromatography on alumina (Scheme 2).

The structures of compounds obtained were established based on the data from ^{1}H and ^{13}C NMR spectroscopies, mass spectrometry, and elemental analysis. 1,2-Dihydropyrimidines **5a** and **5b** were isolated as dark red crystalline substances stable on storage. 1,2-Dihydropyrimidines **6a** and **6b** represented dark violet crystalline substances. The ^{1}H NMR spectra of the former pair contain each one singlet for the olefinic proton (δ 8.76 and 8.78, respectively) and the appropriate amount of signals for the protons of two ferrocenyl and two aryl substituents. The olefinic protons in the ^{1}H NMR spectra of pyrimidines **6a** and **6b** resonate at higher field (δ 8.07 and 7.85, respectively). The ^{13}C NMR spectra of compounds **5a**,**5b** and **6a**,**6b** corroborate completely their pyrimidine structures.

X-Ray diffraction analysis of single crystals of compounds **5b** and **6a** obtained by crystallization from dichloromethane was undertaken to determine the spatial structures of the compounds obtained. The general views of the molecules **5b** and **6a** are given in Figure 1(a,b) and their principal geometric parameters are listed in Table 1.

The data from X-ray diffraction showed that compound **5b** is 5,6-diferrocenyl-1-(*o*-tolyl)-2-(o-tolyl)imino-1,2-dihydropyrimidine and compound **6a** is 4,5-diferrocenyl-1-phenyl-2-phenylimino-1,2-dihydropyrimidine.

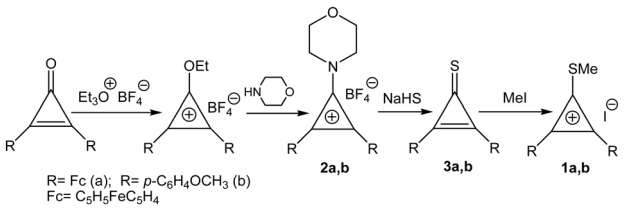
We found further that 2,3-di(*p*-anisyl)-1-methylsulfanylcyclopropenylium iodide (**1b**) reacted analogously with 1,3-diphenylguanidine (**4a**) to afford a mixture of two heterocycles **7** and **8** (*ca*. 1:1, ^{1}H NMR data) (Scheme 3):

The structures of compounds **7** and **8** were established based on the data from ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis. The olefinic signal in the ^{1}H NMR spectrum of compound **7** resonated in a lower field (δ 7.78) as compared with the position of the corresponding resonance in the ^{1}H NMR spectrum of compound **8** (δ 7.42), therefore, by analogy with diferrocenyl-1,2-dihydropyrimidines **5a**,**5b** and **6a**,**6b** the structure of 5,6-di(*p*-anisyl)-1-phenyl-2-phenylimino-1,2-dihydropyrimidine was ascribed to the former and 4,5-di(*p*-anisyl)-1-phenyl-2-phenylimino-1,2-dihydropyrimidine was ascribed to the latter.

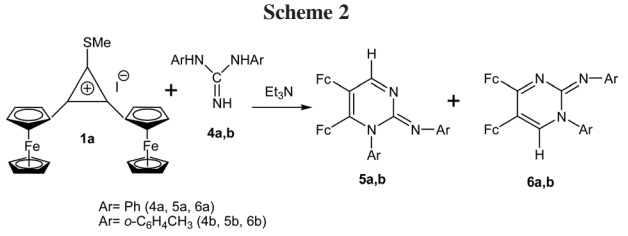
Putative mechanisms of formation of 1,2-dihydropyrimidines **5a**, **5b**, **7** and **6a**, **6b**, **8** are depicted in Schemes 4–6. The two nucleophilic sites of 1,3-diarylguanidines attack sequentially (Schemes 4 and 5) or simultaneously (Scheme 6) the carbon atoms in positions 1 and 2 of the starting compounds **1a**,**1b** to afford bicyclic intermediates **9** and **10**. Their intramolecular transformations *via* divinylcarbenes **11** and **12** result ultimately in 1,2-dihydropyrimidines **5 - 8**.

The following features of the reactions studied are noteworthy: (1) in all cases, mixtures of structurally similar diferrocenyl- or di(*p*-anisyl)-1,2-dihydropyrimidines formed; (2) the ratios of the isomeric 5,6- and 4,5-disubstituted 1,2-dihydropyrimidines was always about 2:1; (3) the presence of ferrocenyl or *p*-anisyl (aryl) substituents in the starting cyclopropenylium salts exerted no effect on the ratios of the final products; (4) unambiguous identification of each compound is possible based on the position of the characteristic signal for the olefinic proton in its ^{1}H NMR spectrum.

Scheme 1



Scheme 2



ELECTROCHEMISTRY

Figure 2 shows a typical voltammetric response of compound **6b** in acetonitrile solution containing 0.1*M* tetra-*N*-butylammonium tetrafluoroborate ($TBABF_4$). When the potential scan was initiated in positive direction, three oxidation signals ($\mathbf{I}_a$ and $\mathbf{II}_a$ $\mathbf{III}_a$) were detected. It can be noticed a slightly overlap between signals $\mathbf{I}_a$ and $\mathbf{II}_a$. Then when the cycle was completed two reduction

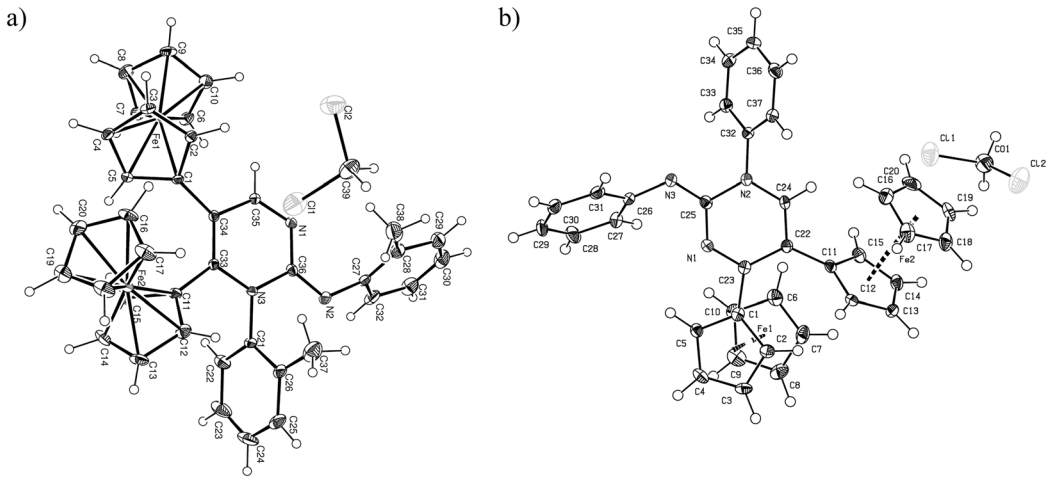


Figure 1. (a) Crystal structure of **5b**; (b) crystal structure of **6a**.

signals ($\mathbf{I}_c$ and $\mathbf{II}_c$) were observed. In this case, there is also an overlap between the reduction signals $\mathbf{I}_c$ and $\mathbf{II}_c$.

The estimated anodic peak potentials values $E_{pa}(\mathbf{II}_a)$ and $E_{pa}(\mathbf{III}_a)$ are 0.174 and 0.654 V/Fc-Fc$^+$, respectively. On the other hand, the cathodic peak potential value for signals $\mathbf{I}_c$ was –0.0150 V/Fc-Fc$^+$. This electrochemical behavior is typical for a two consecutive electron transfer mechanism (EE), with slightly electronic communication between redox moieties. Therefore, for compound **6b**, the processes **I** and **II** correspond to the consecutive oxidations of ferrocene moieties. According to literature, for the obtained value of ΔE_p ($\mathbf{II}_a$-$\mathbf{I}_c$) of 0.189, it was calculated a value of $\Delta E^{0'}$(**II-I**) = 0.140 V with a comproportionation constant K_{com} of 236 [18,19].

To obtain the number of exchanged electrons in process **IIIa**, one-step chronoamperometry experiments were performed at two potential step conditions; first at E_2 = 0.3 V V/Fc-Fc$^+$, related to processes **Ia** and **IIa** and then at E_2 = 0.8 V V/Fc-Fc$^+$, where all the oxidation processes are presented (Fig. 3).

For two consecutive electron transfer reactions controlled by diffusion, the currents are established by the Cottrell eqs. (1) and (2) [18]. These relationships indicate that when a potential is held at the electrode surface with a constant value that promotes either the first (eq. 1) or the second electrochemical reaction [eq. 2], the current depends on the diffusion of the electroactive species from a solution to the electrode surface and the number of exchanged electrons. Under these conditions, the current $I(t)$ is a function of $t^{-1/2}$, due to the growth of a diffusion layer caused by the electrolysis near the electrode.

$$I(t) = n_1 \mathrm{FAD}_0^{1/2} \pi^{-1/2} \mathrm{Co} * t^{-1/2} \quad (1)$$

$$I(t) = (n_1 + n_2) \mathrm{FAD}_0^{1/2} \pi^{-1/2} \mathrm{Co} * t^{-1/2} \quad (2)$$

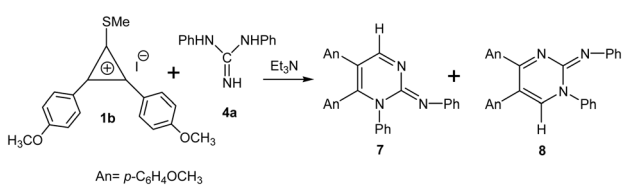
For the first condition, where the oxidation on both ferrocene moieties is presented, a linear relationships of

Table 1

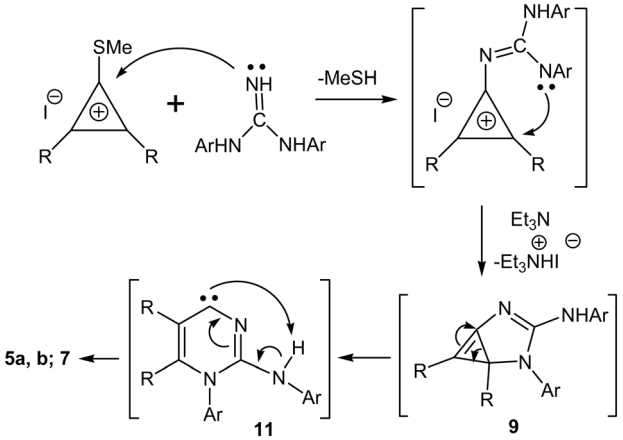
Selected bond lengths and angles for compounds **5b** and **6a**.

Bond lengths [Å]		Bond angles [°]	
5b			
N(1)–C(35)	1.294(4)	C(34)–C(33)–N(3)	118.2(3)
N(1)–C(36)	1.366(4)	C(33)–C(34)–C(35)	115.8 (3)
N(2)–C(36)	1.281(4)	N(1)–C(35)–C(34)	126.8(3)
N(3)–C(36)	1.418(4)	C(35)–N(1)–C(36)	118.5(3)
N(3)–C(33)	1.384(4)	N(1)–C(36)–N(3)	117.9(3)
C(33)–C(34)	1.375(4)	C(36)–N(3)–C(33)	122.6(2)
C(34)–C(35)	1.420(4)	C(36)–N(2)–C(27)	120.6(3)
N(2)–C(27)	1.403(4)	N(2)–C(36)–N(3)	116.8(3)
N(3)–C(21)	1.448(4)	N(2)–C(36)–N(1)	125.4(3)
6a			
N(1)–C(23)	1.319(3)	N(3)–C(25)–N(2)	117.0(2)
N(2)–C(25)	1.412(3)	C(25)–N(2)–C(24)	119.2 (2)
N(2)–C(24)	1.362(3)	N(2)–C(24)–C(22)	124.1(2)
C(23)–C(22)	1.450(3)	C(24)–C(22)–C(23)	114.7(2)
C(22)–C(24)	1.356(3)	C(22)–C(23)–N(1)	121.5(2)
N(1)–C(25)	1.363(3)	C(23)–N(1)–C(25)	122.7(2)
N(3)–C(25)	1.291(3)	N(1)–C(25)–N(3)	125.4(2)
N(3)–C(26)	1.409(3)	C(25)–N(2)–C(32)	121.2(2)
C(23)–N(1)	1.319(3)	N(1)–C(25)–N(2)	117.5(2)
N(2)–C(32)	1.434(3)	C(11)–C(22)–C(23)	126.2(2)

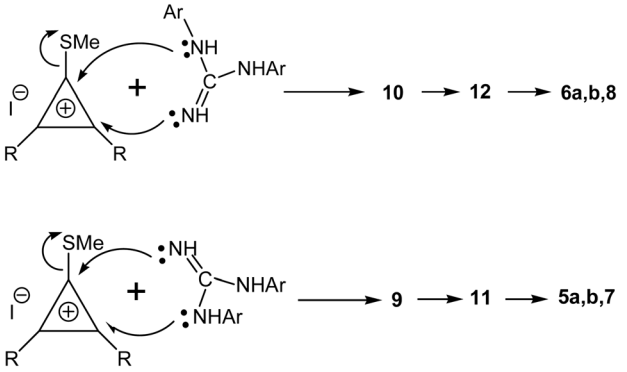
Scheme 3



Scheme 4



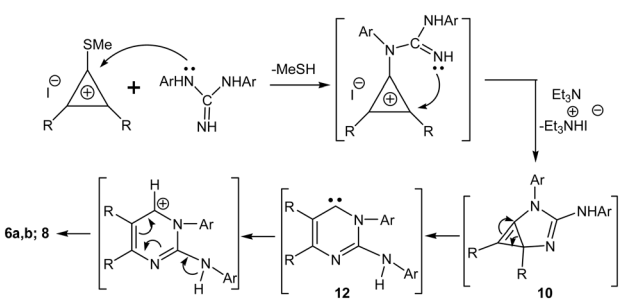
Scheme 6



current $I(t)$ and $t^{-1/2}$ was obtained, with the equation $I(t) = 9.77\ t^{-1/2} + 0.28$ ($r = 0.998$). For the second condition a similar relationship was estimated $I(t) = 14\ t^{-1/2} + 0.8$ ($r = 0.999$). Considering the same values of diffusion coefficient, and that for the first relationship two electrons are exchanged ($n_1 = 2$), the ratio of the slopes from the obtained relationships allows us to estimate that one electron is exchanged in the oxidation process **IIIa** ($n_2 = 1$). Despite the different pulse time width in chronoamperometric experiments and that a scan rate of 2 V s^{-1} was used in cyclic voltammetry, the product of the oxidation in the process **IIIa** was not detected. An inspection of molecular structure suggests that this signal is related to the pyrimide ring oxidation with an electrochemical reaction (EC) mechanism.

Figure 4 shows the voltammetry of compounds **5a**+**6a**, which allows to observe the presence of three oxidation signals ($\mathbf{I}_a$, $\mathbf{II}_a$, and $\mathbf{III}_a$) and two reduction signals ($\mathbf{I}_c$ and $\mathbf{II}_c$). The obtained values of anodic and cathodic peak potentials E_{pa}(**I**) and E_{pc}(**I**) for signal $\mathbf{I}_a$ and $\mathbf{I}_c$ were 0.056 V/Fc-Fc^+ and −0.020 V/Fc-Fc^+, respectively. For signals $\mathbf{II}_a$ and $\mathbf{II}_c$, the peak potential values E_{pa}(**II**) and E_{pc}(**II**) are 0.240 and 0.089 V/Fc-Fc^+.

Scheme 5



The processes **I** and **II** correspond to the reversible oxidation of ferrocene moieties. The formal electrode potential for processes **I** and **II** was calculated as $E^{0'} = (E_{pa} + E_{pc})$. The calculated values were $E^{0'}$ (**I**) = 0.018 V/Fc-Fc^+ and $E^{0'}$(**II**) = 0.165 V/Fc-Fc^+. The value of $\Delta E^{0'}$(**II-I**) for processes **I** and **II** was 0.147 V with its corresponding value of comproportionation constant K_{com} of 310. The anodic peak potential for signal $\mathbf{III}_a$ E_{pa} ($\mathbf{III}_a$) was 0.680 V/Fc-Fc^+, which is also related to pyrimide ring as it was observed in compound **6b**.

The electrochemical response of compounds **5b** is very similar than that presented in compound **6b**. A summary of the electrochemical responses for all the compounds studied is presented in Table 2.

The calculated values of K_{com} for all compounds suggests that the electronic charge is slightly delocalized in the mixed valence state generated electrochemically, according to the Robin-Day classification (class II) [19,20]. The similar value of K_{com} for all compounds suggests no effect of the substituent in the mixed valence state.

EXPERIMENTAL

All the solvents were dried according to the standard procedures and were freshly distilled before use [20]. Column chromatography was carried out on alumina (Brockmann activity III). The ^{1}H and ^{13}C NMR spectra were recorded on a Unity Inova Varian spectrometer (300 and 75 MHz) for solutions in $CDCl_3$ and CD_2Cl_2, with Me_4Si as the internal standard. The IR spectra were measured with an FTIR spectrophotometer (Spectrum RXI PerkinElmer instruments) using KBr pellets. The mass spectra were obtained on a Varian MAT CH-6 instrument (electron impact mass spectrometry (EI MS), 70 eV). Elementar Analysensysteme LECO CHNS-900 was used for elemental analyses. The following reagents were purchased from Aldrich: tetrachlorocyclopropene, 98%; ferrocene, 98%; anisole anhydrous, 99.7%; aluminum chloride, 99.99%; triethyloxonium tetrafluoroborate, 1.0*M* solution in dichloromethane; morpholine, 99+%; sodium hydrosulfide hydrate NaHS·xH_2O; iodomethane, 99.5%; 1,3-di-*o*-tolylguanidine, 99%; 1,3-diphenylguanidine, 97%.

All electrochemical measurements were performed in acetonitrile solution containing 0.1*M* $TBABF_4$. A potentiostat/galvanostat

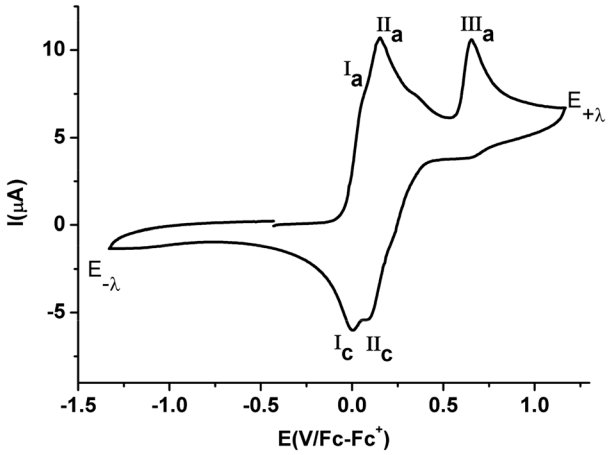


Figure 2. Cyclic voltammograms for a solution 1.0×10^{-3} mol dm^{-3} of compound **6b** in the presence of 0.1*M* $TBABF_4$ in acetonitrile. Working electrode platinum, scan rate 0.1 V s^{-1}.

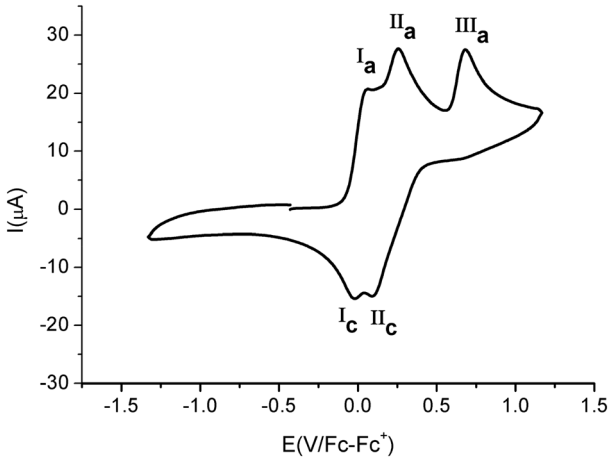


Figure 4. Cyclic voltammograms for a solution 1.0×10^{-3} mol dm^{-3} of compound **5a+6a** in the presence of 0.1 M $TBABF_4$ in acetonitrile. Working electrode platinum, scan rate 0.10 V s^{-1}.

EG&G PAR model 263A was used. A typical three-electrode array was used for all electrochemical measurements: platinum disk as working electrode, platinum wire as counter-electrode, and a silver wire as pseudo reference electrode. The silver electrode was immersed in a acetonitrile (MeCN) solution with 0.1*M* tetra-*N*-butylammonium chloride in a separate compartment that was connected to the working cell through a bioanalytical system (BAS) vycor™ tip. All potentials were reported versus the couple Fc/Fc$^+$ according to International Union of Pure and Applied Chemistry (IUPAC) [21]. Cyclic voltammetry were initiated from open circuit potential (E_{ocp}). One-step chronoamperometry experiments were performed, initiating at $E_1 = E_{ocp}$ to different potential values, E_2, using a pulse width of 1 s.

2,3-Diferrocenyl- and 2,3-di(*p*-anisyl)cyclopropenones were obtained from ferrocene and anisole and tetrachlorocyclopropene in the presence of $AlCl_3$ according to a standard procedure [16] and converted to ethoxy(diferrocenyl)- and -di(*p*-anisyl)cyclopropenylium tetrafluoroborates by treatment

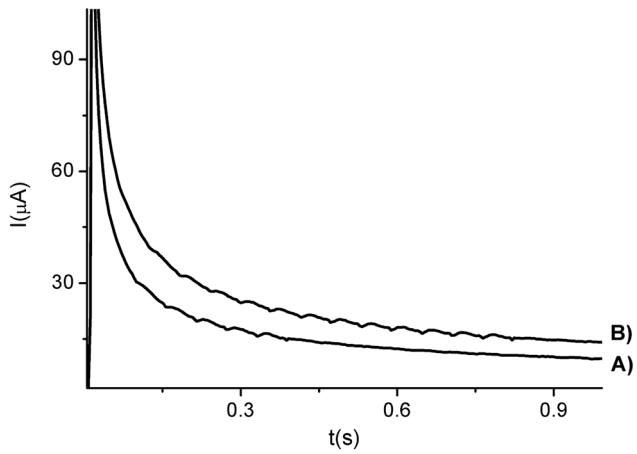


Figure 3. One-step potential chronoamperometric experiments for **6b** in the presence 0.1*M* $TBABF_4$ in CH_3CN. The initial potential was the open potential circuit value E_{ocp}. The potential step values (E_1) were (a) 0.3 V/Fc-Fc$^+$ and (b) 0.8 V/Fc-Fc$^+$.

with triethyloxonium tetrafluoroborate (1.0*M* solution in dichloromethane) [17]. Their reactions with morpholine in dichloromethane [17,22] afforded morpholino(differocenyl)- and -di(*p*-anisyl)cyclopropenylium tetrafluoroborates (**2a** and **2b**). The latter gave 2,3-diferrocenyl- and 2,3-di(*p*-anisyl) cyclopropenethiones (**3a** and **3b**) when treated with an aqueous solution of NaSH [22].

2,3-Diferrocenyl- and 2,3-di(*p*-anisyl)(methylthio)cyclopropenylium iodides (**1a** and **1b**) were obtained from the cyclopropenethiones **3a,b** and iodomethane [22].

Freshly prepared and thoroughly dried iodides **1a** and **1b** were used in the reactions with 1,3-diarylguanidines (**4a** and **4b**). The physical and ^{1}H-NMR spectroscopic characteristics of compounds **1a**, **2a**, and **3a** were in accord with the literature data [16,17,22].

2,3-Di(*p*-anisyl)cyclopropenone. Yield 78%, white power, m.p. 142–143°C; IR: 1455, 1512, 1551, 1599 (C=C, C_6H_4), 1832 (C=O), 1070, 1175, 1255, 2844 (OCH_3), 3101 (C—H) cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 3.79 (s, 6H, $2CH_3$), 7.11 (d, 4H, *J* = 8.7 Hz, C_6H_4), 7.99 (d, 4H, *J* = 8.7 Hz, C_6H_4) ppm; ms: *m/z* 266 (M)$^+$. Anal. Calcd. for $C_{17}H_{14}O_3$: C, 76.67; H, 5.30. Found: C, 76.49; H, 5.45.

1-Mopholino-2,3-di(*p*-anisyl)cyclopropenilium tetrafluoroborate (2b). Yield 72%, white crystals, m.p. 167–169°C; ^{1}H-NMR (CD_2Cl_2): δ 3.96 (s, 6H, $2CH_3$), 4.02 (m, 4H, $2CH_2$), 4.10 (m, 4H, $2CH_2$), 7.19 (d, 4H, *J* = 9.0 Hz, C_6H_4), 8.03 (d, 4H, *J* = 9.0 Hz, C_6H_4) ppm; ms: *m/z* 423 (M)$^+$. Anal. Calcd. for $C_{21}H_{22}$ BF_4NO_3: C, 59.58; H, 5.24; N, 3.31. Found: C, 59.63; H, 5.18; N, 3.39.

2,3-Di(*p*-anisyl)cyclopropenethione (3b). Yield 81%, yellow powder, m.p. 155–156°C; IR: 1461, 1503, 1598 (C_6H_4), 1653 (C=S), 1789 (C=C), 1173, 1248, 2835 (OCH_3), 2993, 3199 (C—H) cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 3.90 (s, 6H, $2CH_3$), 7.04 (d, 4H, *J* = 8.7 Hz, C_6H_4), 7.91 (d, 4H, *J* = 8.7 Hz, C_6H_4) ppm; ms: *m/z* 282 (M)$^+$. Anal. Calcd. for $C_{17}H_{14}SO_2$: C, 72.33; H, 5.00; S, 11.33. Found: C, 72.21; H, 4.87; S, 11.42.

2,3-Di(*p*-anisyl)-1-methylsulfanylcyclopropenilium iodide (1b). Yield 66%, yellow powder, m.p. 177–178°C; ^{1}H-NMR (CD_2Cl_2): δ 3.52 (s, 3H, CH_3), 5.97 (s, 6H, $2CH_3$), 9.25 (d, 4H,

Table 2

Electrochemical behavior, $E_{pa}(II_a)$, $E_{pc}(I_c)$, $E_{pa}(III_a)$, ΔE^0 (II-I), and constant K_{com} for compounds **6b, 5b,** and **5a+6a**.

Compounds	$E_{pa}(\mathbf{II_a})$[a]	$E_{pa}(\mathbf{I_c})$[a]	$E_{pa}(\mathbf{III_a})$[b]	$\Delta E_p(\mathbf{II_a}\text{-}\mathbf{I_c})$[a]	$\Delta E^\circ(\mathbf{II}-\mathbf{I})$[a]	K_{com}[a]
6b	0.174	−0.015	0.654	0.189	0.140	236
5b	0.250	0.116	0.653	0.134	0.095	40.75
5a+6a	0.240	−0.02	0.680	0.260	0.147[£]	310

Reported potentials versus ferrocene in 0.1 M $TBABF_4$-acetonitrile.
[a]Scan rate 0.10 V s^{-1} related to ferrocene.
[b]Scan rate 0.10 V s^{-1} related to Pyrimidine moieties.[c]Calculated directly from two waves.

J = 8.7 Hz, C_6H_4), 10.15 (d, 4H, J = 8.7 Hz, C_6H_4) ppm; ms: *m/z* 424 $(M)^+$. Anal. Calcd. for $C_{18}H_{17}IO_2S$: C, 50.95; H, 4.04; S, 7.54. Found: C, 50.83; H, 4.11; S, 7.62.

2-Arylimino-1,2-dihydropyrimidines 5a,b; 6a,b; 7 and 8. A mixture of the 1-methylsulfanylcyclopropenilium iodides (**1a** or **1b**, 5.0 mmol), 1,3-diarylguanidines (**4a** or **4b**, 7.0 mmol), and 1.0 mL triethylamine in bezene (60 mL) was stirred in a dry inert atmosphere under reflux (4 h). The solvents were removed *in vacuo*, the residues were dissolved in dichloromethane (50 mL). The solution was mixed with Al_2O_3 (activity III) (20 g), and the solvent was evaporated in air. This sorbent was applied onto a column with Al_2O_3 (the height of alumina is *ca*. 30 cm) and the reaction products were eluted from the column first with petroleum ether and then with a 1:2 dichloromethane–petroleum ether solvent system. The elution order is as follows: (i) 2,3-diferrocenyl- or 2,3-di(*p*-anisyl)cyclopropenethione (**3a** or **3b**; ∼ 5–8%); (ii) 5,6-diferrocenyl-2-phenylimino-, 5,6-diferrocenyl-2-(*o*-tolyl) imino- or 5,6-di(*p*-anisyl)-2-phenylimino-1,2-dihydropyrimidines **5a, 5b**, or **7**; (iii) compounds **6a**, **6b**, or **8**.

5,6-Diferrocenyl-1-phenyl-2-phenylimino-1,2-dihydropyrimidine 5a. Yield 1.66 g (54%), red powder, m.p. 206–207°C; IR: 809, 820, 1003, 1027, 1104, 1381, 1442, 1471, 1594, 1613, 1675 (C=C, C=N, Fc, C_6H_4), 1176, 1298 (C—N), 2929, 3012, 3069, 3179 (C—H) cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 3.84 (s, 5H, C_5H_5), 4.18 (s, 5H, C_5H_5), 3.69 (m, 2H, C_5H_4), 4.02 (m, 2H, C_5H_4), 4.24 (m, 2H, C_5H_4), 4.30 (m, 2H, C_5H_4), 6.91 (m, 3H, C_6H_5), 7.23 (m, 3H, C_6H_5), 7.34–7.45 (m, 4H, C_6H_5), 8.76 (s, 1H, CH=) ppm; ^{13}C-NMR ($CDCl_3$): δ 69.47, 70.07 ($2C_5H_5$), 67.98, 68.86, 70.51, 72.97 ($2C_5H_4$), 86.16, 99.84 (2 C_{ipso}Fc), 148.94 (CH=), 122.58, 127.95 (2C), 128.62 (2C), 128.66 (3C), 130.27 (2C) ($2C_6H_5$), 138.87, 149.93, 152.18, 161.20, 165.60 (5C) ppm; ms: *m/z* 615 $(M)^+$. Anal. Calcd. for $C_{36}H_{29}Fe_2N_3$: C, 70.27; H, 4.75; Fe, 18.16; N, 6.82. Found: C, 70.15; H, 4.83; Fe, 18.21; N, 7.01.

4,5-Diferrocenyl-1-phenyl-2-phenylimino-1,2-dihydropyrimidine 6a. Yield 0.83 g (27%), violet crystals, m.p. 214–216°C; IR: 811, 820, 1000, 1033, 1106, 1384, 1440, 1469, 1601, 1617, 1681 (C=C, C=N, Fc, C_6H_4), 1178, 1293 (C—N), 2929, 3017, 3068, 3193 (C—H) cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 4.04 (s, 5H, C_5H_5), 4.19 (s, 5H, C_5H_5), 4.23 (m, 2H, C_5H_4), 4.27 (m, 2H, C_5H_4), 4.29 (m, 2H, C_5H_4), 4.34 (m, 2H, C_5H_4), 7.17 - 7.30 (m, 2H, C_6H_5), 7.42 (m, 3H, C_6H_5), 7.55 (m, 3H, C_6H_5), 7.66 (m, 2H, C_6H_5), 8.07 (s, 1H, CH=) ppm; ^{13}C-NMR ($CDCl_3$): δ 68.87, 69.98 ($2C_5H_5$), 67.96, 70.88, 71.45, 72.08 ($2C_5H_4$), 80.17, 85.12 ($2C_{ipso}$Fc), 148.11 (CH =), 121.28, 123.72 (2C), 126.26 (2C), 127.93 (3C), 129.5 (2C) ($2C_6H_5$), 142.21, 149.71, 149.90, 166.50, 170.63 (5C) ppm; ms: *m/z* 615 $(M)^+$. Anal. Calcd. for $C_{36}H_{29}Fe_2N_3$: C, 70.27; H, 4.75; Fe, 18.16; N, 6.82. Found: C, 70.49; H, 4.64; Fe, 18.17; N, 6.76.

5,6-Diferrocenyl-1-(*o*-tolyl)-2-(*o*-tolyl)imino-1,2-dihydropyrimidine 5b. Yield 1.81 g (56%), red crystals, m.p. 223–224°C; IR: 815, 825, 1002, 1036, 1106, 1382, 1434, 1468, 1592, 1615, 1677 (C = C, C = N, Fc, C_6H_4), 1172, 1290 (C—N), 2921, 3014, 3076, 3177 (C—H) cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 2.01 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 3.92 (s, 5H, C_5H_5), 4.17 (s, 5H, C_5H_5), 3.39 (m, 1H, C_5H_4), 3.90 (m, 1H, C_5H_4), 4.04 (m, 1H, C_5H_4), 4.07 (m, 1H, C_5H_4), 4.13 (m, 1H, C_5H_4), 4.25 (m, 1H, C_5H_4), 4.36 (m, 1H, C_5H_4), 4.42 (m, 1H, C_5H_4), 6.81–6.88 (m, 2H, C_6H_4), 7.10 (m, 2H, C_6H_4), 7.31 (m, 4H, C_6H_4), 8.78 (s, 1H, CH =) ppm; ^{13}C-NMR ($CDCl_3$): δ 18.18, 18.42 ($2CH_3$), 69.57, 70.26 ($2C_5H_5$), 67.94, 68.23, 68.58, 69.92, 70.04,71.06, 7.13, 73.09 ($2C_5H_4$), 86.63, 111.88 ($2C_{ipso}$Fc), 147.12 (CH=), 122.08, 126.12, 126.45, 128.64, 130.04 (2C), 130.89, 131.14 ($2C_6H_4$), 140.89, 141.50, 148.70, 150.64, 154.57, 162.89, 165.67 (7C) ppm; ms: *m/z* 643 $(M)^+$. Anal. Calcd. for $C_{38}H_{33}Fe_2N_3$: C, 70.94; H, 5.17; Fe, 17.36; N, 6.53. Found: C, 70.79; H, 5.23; Fe, 17.42; N, 6.35.

4,5-Diferrocenyl-1-(*o*-tolyl)-2-(*o*-tolyl)imino-1,2-dihydropyrimidine 6b. Yield 0.9 g (27%), red crystals, m.p. 241–243°C; IR: 816, 823, 1005, 1037, 1104, 1385, 1439, 1472, 1590, 1615, 1686 (C=C, C=N, Fc, C_6H_4), 1181, 1289 (C—N), 2932, 3028, 3079, 3163 (C—H) cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 2.13 (s, 3H, CH_3), 2.48 (s, 3H, CH_3), 3.98 (s, 5H, C_5H_5), 4.14 (s, 5H, C_5H_5), 4.20 (m, 2H, C_5H_4), 4.22 (m, 2H, C_5H_4), 4.28 (m, 2H, C_5H_4), 4.31 (m, 2H, C_5H_4), 7.11–7.14 (m, 4H, C_6H_4), 7.39–7.45 (m, 4H, C_6H_4), 7.85 (s, 1H, CH=) ppm; ^{13}C-NMR ($CDCl_3$): δ 18.24, 18.57 ($2CH_3$), 69.43, 70.32 ($2C_5H_5$), 69.35, 69.78, 70.41, 71.08 ($2C_5H_4$), 81.21, 84.46 ($2C_{ipso}$Fc), 149.41 (CH=), 126.24, 126.45, 126.64, 127.13, 128.72, 130.37, 130.89, 131.14 ($2C_6H_4$), 139.20, 143.11, 150.44, 151.19, 154.38, 163.22, 166.18 (7C) ppm; ms: *m/z* 643 $(M)^+$. Anal. Calcd. for $C_{38}H_{33}Fe_2N_3$: C, 70.94; H, 5.17; Fe, 17.36; N, 6.53. Found: C, 70.81; H, 5.05; Fe, 17.39; N, 6.68.

5,6-Di(*p*-anisyl)-1-phenyl-2-phenylimino-1,2-dihydropyrimidine 7. Yield 1.2 g (52%), red powder, m.p. 138–139°C; IR: 1467, 1492, 1513, 1572, 1590, 1602, 1627, 1643 (C=C, C=N, C_6H_5, C_6H_4), 1072, 1245, 2835 (OCH_3), 1180,1350 (C—N), 2932, 2956, 3006 (C—H) cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 3.77 (s, 3H, CH_3), 3.81 (s, 3H, CH_3), 6.80 (d, 2H, J = 8.7 Hz, C_6H_4), 7.12 (d, 2H, J = 8.7 Hz, C_6H_4), 7.45 (d, 2H, J = 9.0 Hz, C_6H_4), 7.57 (d, 2H, J = 9.0 Hz, C_6H_4), 6.99 (m, 3H, C_6H_5), 7.22 (m, 2H, C_6H_5), 7.33 (m, 3H, C_6H_5), 7.70 (m, 2H,

C_6H_5), 7.78 (s, 1H, CH=) ppm; ^{13}C-NMR ($CDCl_3$): δ 54,87, 55.34 ($2CH_3$), 147.23 (CH=), 113.25, 114.15, 123.68, 123.74, 126.77, 128.23, 128.32, 129.91, 130.08, 131.87 ($2C_6H_5$, $2C_6H_4$), 142.11, 146.70, 146.76, 147.06, 149.28, 149.61, 158.91, 161.29, 167.49 (9C) ppm; ms: *m/z* 459 $(M)^+$. Anal. Calcd. for $C_{30}H_{25}N_3O_2$: C, 78.41; H, 5.49; N, 9.14. Found: C, 78.57; H, 5.38; N, 9.22.

4,5-Di(*p*-anisyl)-1-phenyl-2-phenylimino-1,2-dihydropyrimidine 8. Yield 0.6 g (26%), red powder, m.p. 151–152°C; IR: 1468, 1510, 1574, 1590, 1600, 1627, 1648 (C=C, C=N, C_6H_5, C_6H_4), 1100, 1245, 2835 (OCH_3), 1174,1351 (C—N), 2931, 2956, 3001 (C=H) cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 3.75 (s, 3H, CH_3), 3.84 (s, 3H, CH_3), 6.68 (d, 2H, J = 8.7 Hz, C_6H_4), 6.82 (d, 2H, J = 8.7 Hz, C_6H_4), 7.03 (d, 2H, J = 8.4 Hz, C_6H_4), 7.24 (d, 2H, J = 8.4 Hz, C_6H_4), 6.93 (m, 2H, C_6H_5), 7.18 (m, 3H, C_6H_5), 7.35 (m, 3H, C_6H_5), 7.47 (m, 2H, C_6H_5), 7.42 (s, 1H, CH–) ppm; ^{13}C-NMR ($CDCl_3$): δ 55,36, 55.41 ($2CH_3$), 147.03 (CH–), 118.52, 117.13, 123.65, 123.98, 125.42, 127.39, 128.51, 129.07, 130.43, 131.95 ($2C_6H_5$, $2C_6H_4$), 138.23, 140.79, 145.34, 147.77, 148.53, 149.79, 157.84, 161.63, 168.04 (9C) ppm; ms: *m/z* 459 $(M)^+$. Anal. Calcd. for $C_{30}H_{25}N_3O_2$: C, 78.41; H, 5.49; N, 9.14. Found: C, 78.36; H, 5.53; N, 9.07.

Determining the crystal structures. The unit cell parameters and the X-ray diffraction intensities were recorded on a Siemens P4 diffractometer. The structures of compounds **5b** and **6a** were solved by the direct method (SHELXS -97 [23]) and refined using full-matrix least-squares on F^2.

Crystal data for $C_{38}H_{33}Fe_2N_3 \cdot CH_2Cl_2$ (5b). M = 728.30 $gmol^{-1}$, monoclinic Cc, a = 21.9397(5), b = 19.8766(4), c = 7.5004(2) Å, α = 90, β = 98.509(2), γ = 90°, V = 3234.82 (13) $Å^3$, T = 103(2) K, Z = 4, ρ = 1.495 Mg/m^3, λ (Mo – $K\alpha$) = 0.71073 Å, F(000) = 1504, absorption coefficient 1.096 mm^{-1}, index ranges $-2 \le h \le 27$, $-24 \le k \le 24$, $-9 \le l \le 8$, scan range $3.43 \le \theta \le 26.05°$, 5376 independent reflections, R_{int} = 0.0280, 11664 total reflections, 417 refinable parameters, final R indices $[I > 2\sigma(I)]$ R_1 = 0.0311, wR_2 = 0.0689, R indices (all data) R_1 = 0.0376, wR_2= 0.0705, goodness-of-fit on F^2 0.986, largest difference peak and hole 0.710/−0.303 $eÅ^{-3}$.

Crystal data for $C_{36}H_{29}Fe_2N_3CH_2Cl_2$ (6a). M = 700.25 $gmol^{-1}$, monoclinic P-1, a = 10.5679(5), b = 12.0009(8), c = 12.1763(8) Å, α = 76.602(5), β = 84.849(4), γ = 84.793 (5)°, V = 1492.25(16) $Å^3$, T = 424(2) K, Z = 2, ρ = 1.558 Mg/m^3, λ (Mo − $K\alpha$) = 0.71073 Å, F(000) = 720, absorption coefficient 9.696 mm^{-1}, index ranges $-12 \le h \le 8$, $-14 \le k \le 13$, $-14 \le l \le 14$, scan range $3.74 \le \theta \le 68.20°$, 5428 independent reflections, R_{int} = 0.0280, 10388 total reflections, 397 refinable parameters, final R indices $[I > 2\sigma(I)]$ R_1 = 0.0344, wR_2 = 0.0829, R indices (all data) R_1 = 0.0477, wR_2= 0.0868, goodness-of-fit on F^2 1.011, largest difference peak and hole 0.737/−0.710 $eÅ^{-3}$.

CCDC-813003 (for **5b**) and CCDC-813004 (for **6a**) contain the supplementary crystallographic data for this article. These data can be obtained free of charge at www.ccdc.cam.ac.uk/const/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road,Cambridge DB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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