ORGANOMETALLICS

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1,1′-Homodisubstituted Ferrocenes Containing Adenine and Thymine Nucleobases: Synthesis, Electrochemistry, and Formation of H-Bonded Arrays

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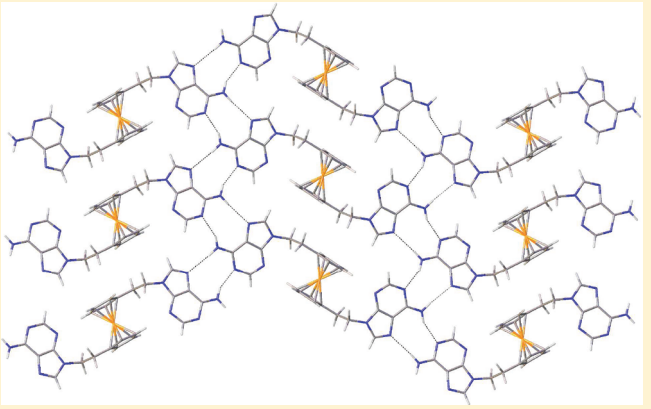
Supporting Information

ABSTRACT: Four organometallic nucleobases have been prepared and characterized, each consisting of a disubstituted ferrocene unit connected through either a conjugated or saturated linker group to adenine or thymine nucleobases. Their assembly behavior has been studied in the solid state via X-ray crystallography, revealing intermolecular H-bonded arrays. The electrode potentials in DCM are strongly dependent upon the nature of the linker group between the ferrocene unit and the nucleobase.



INTRODUCTION

Bioorganometallic chemistry is a growing research area in which classical organometallic chemistry is combined with biology to achieve materials with unique and novel properties.[1] Within this area, the tagging of ferrocene to nucleic acids[2] is a topical theme, mainly due to continued interest in the electrochemical sensing of various biomolecules and biological units. Ferrocenes are commonly connected to nucleosides (i.e., base plus sugar) via derivatization at a carbon atom on the base,[3] which if required would allow incorporation into a nucleic acid strand by standard automated chemical synthesis. Alternatively, the idea of using metallocene-containing nucleobases[4] (i.e., base minus sugar) as bioorganometallic H-bonding motifs can be conveniently explored by attaching groups at the nitrogen atom where normally the sugar would be connected (i.e., *N*1 in thymine and *N*9 in adenine). The *N*1 position of thymine has received some attention in this respect, and recently bis-functionalized ferrocene derivatives with alkyl linker lengths $n = 1$[4a] and 4[4b] (Figure 1) have been reported. Adenine-containing derivatives are generally less common than their thymine/uracil counterparts, although a monofunctionalized ferrocene attached at the *N*9 position with a linker length $n = 1$ is known.[4c]

Herein we report the synthesis, via a novel route, of bis-functionalized ferrocenylalkyl conjugates to thymine **1** and adenine **2**, each with an ethyl linker, as well as their unsaturated analogues **3** and **4** (Figure 2). Their solid-state and electrochemical behavior are also examined and compared through X-ray crystallographic analysis and voltammetric analysis, respectively.

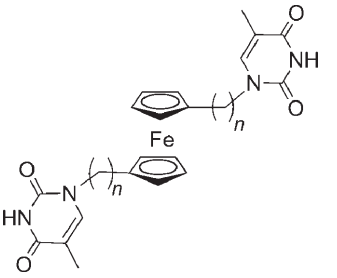


Figure 1. Known examples of thymine nucleobases bridged by a ferrocene unit attached at the *N*1 position, where $n = 1$ and $n = 4$. The $n = 2$ linker (compound **1**) is reported in this study.

RESULTS AND DISCUSSION

Synthesis. The four target compounds were made starting from readily accessible ferrocene-1,1′-dicarboxaldehye **5**,[5] which was reacted via a Horner−Wadsworth−Emmons procedure with the corresponding phosphonates **6**[6] and **7** (Scheme 1), the latter which was made by reacting 9-(diphenylphosphorylmethyl)adenine[6] with benzoyl chloride in pyridine.

Although trial reactions with the monocarboxaldehyde indicated no significant difference in the yield of the coupling reaction whether the *N*3 of thymine was protected or not, the

Received: July 23, 2011
Published: September 08, 2011

dx.doi.org/10.1021/om200671b | *Organometallics* 2011, 30, 5284–5290

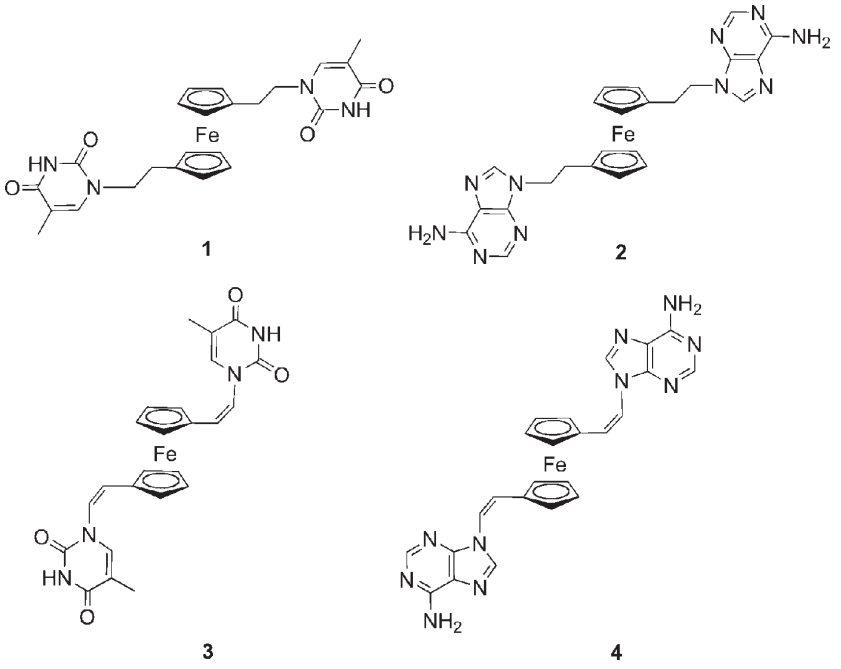
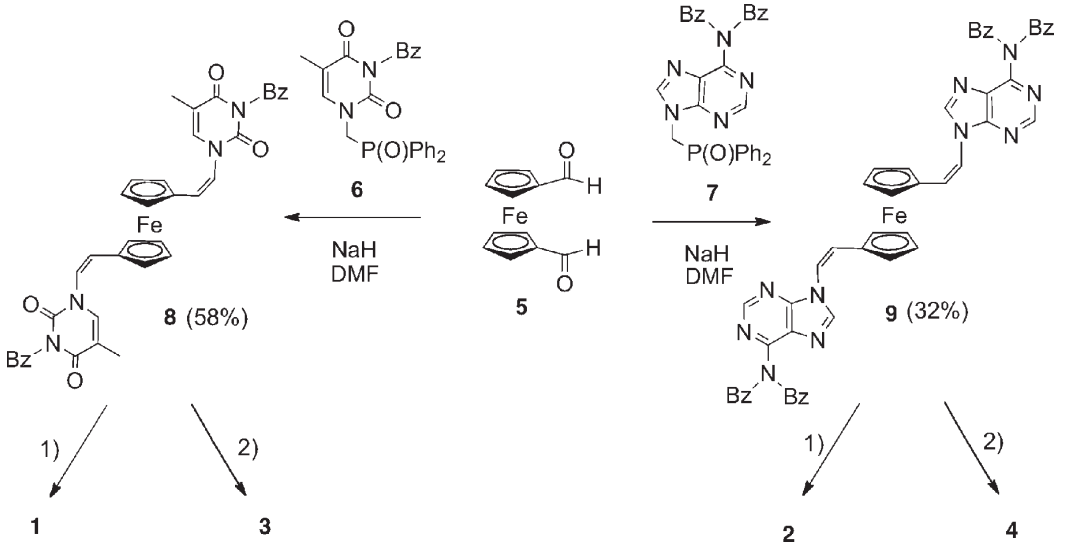


Figure 2. The four target compounds synthesized in this study.

Scheme 1. Synthetic Scheme for the Formation of the Four Target Compounds[a]



[a] Reagents: (1) (a) $Pd(OH)_2/C$, H_2 balloon, (b) $MeNH_2$; (2) $MeNH_2$. Compounds **8** and **9** formed as a mixture of isomers (only the major *Z* isomer is drawn).

yields of the bis-coupling reaction were greatly improved if this atom was benzoylated first. Therefore the adenine system was bis-benzoylated to preclude the occurrence of similar problems. The products gave approximately a 4:1 ratio of *Z* (shown as compounds **8** and **9** in Scheme 1) to (*E* + *E*/*Z*) isomers in both the thymine and adenine systems, as determined by vicinal CH═CH coupling constant values on the ^{1}H NMR spectra. This was further verified when the major fractions in each case were debenzoylated with methylamine solution to afford the target compounds **3** and **4**, with the X-ray crystal structure of **3** clearly indicating a *Z* geometry for both alkenes (Figure 3).

Hydrogenation of the protected **8** and **9** with $Pd(OH)_2/C$ (20%) and H_2 (gas at 1 atm), followed by debenzoylation with methylamine solution afforded the saturated targets **1** and **2** in good yields.[7] It is worth noting that hydrogenation of the unprotected bis-thymine **3** via the above method was not successful, even using an alternative hydrogenation method[8] ($Pd(OH)_2/C$ (20%), cyclohexene in ethanol). As with compound **3**, compound **1** was recrystallized by slow evaporation from a DCM/MeOH mixture to afford crystals suitable for X-ray diffraction (Figure 4). The X-ray structure of the adenine analogue, crystals of which were also grown from a DCM/MeOH mixture, is presented in Figure 5.

dx.doi.org/10.1021/om200671b |*Organometallics* 2011, 30, 5284–5290

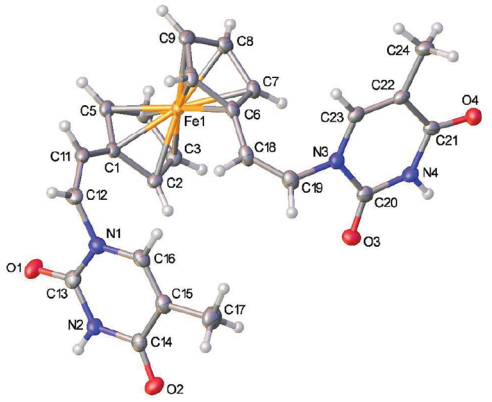


Figure 3. Molecular structure of compound **3** showing the atom-numbering scheme with the ellipsoids drawn at the 50% probability level. The structure of **3** contains two crystallographically independent molecules (see Figure 7 and also Supporting Information), with only one shown here for clarity.

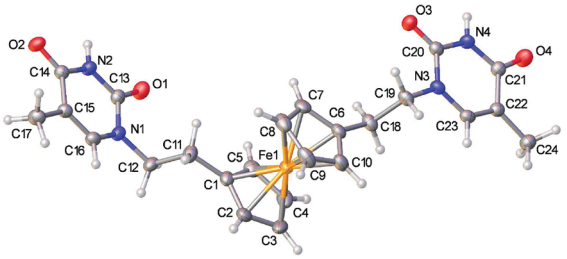


Figure 4. Molecular structure of compound **1** showing the atom-numbering scheme with the ellipsoids drawn at the 50% probability level.

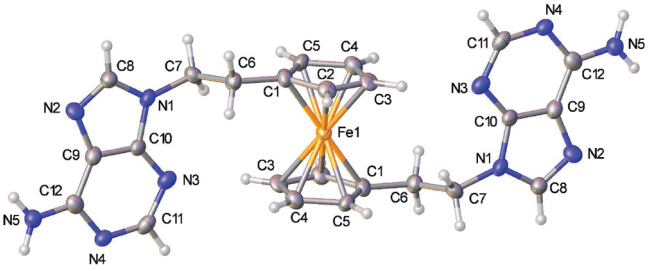


Figure 5. Molecular structure of compound **2** showing the atom-numbering scheme with the ellipsoids drawn at the 50% probability level. The iron atom is located on an inversion center such that only half of the molecule is crystallographically unique. Selected bond lengths (Å) and angles (deg): C6−C7 = 1.536(9), N2−C8 = 1.31(1), N2−C9 = 1.415(9), N5−C12 = 1.321(9), C1−C6−C7 = 115.1(6), C6−C7−N1 = 110.3(6), C8−N2−C9 = 103.6(6), N4−C12−N5 = 117.9(7), C9−C12−N5 = 126.0(7).

X-ray Crystallography. Selected bond lengths and angles for the thymine derivatives **1** and **3** are presented in Table 1 to allow a comparison between the two structures. The major difference is the larger C11−C12 and C18−C19 bond lengths in **1** for the saturated linkage, which are similar to the analogous bonds in **2**. However the particular arrangement of the arms and the Cp twist angles in each system derive from their packing, which is mediated by intermolecular H-bonding interactions, a common

Table 1. Selected Bond Lengths (Å), Angles (deg), and Torsion Angles (deg) for 1 and 3[a]

	1	3[a]
C11−C12	1.519(2)	1.317(4)
C18−C19	1.520(2)	1.325(3)
O1−C13	1.217(2)	1.224(3)
O2−C14	1.230(2)	1.217(3)
O3−C20	1.224(2)	1.207(3)
O4−C21	1.220(2)	1.227(3)
N2−C13	1.371(2)	1.362(3)
N2−C14	1.373(2)	1.390(3)
N4−C20	1.361(2)	1.368(3)
N4−C21	1.382(2)	1.377(3)
C1−C11−C12	112.8(1)	129.7(2)
C11−C12−N1	110.1(1)	124.1(2)
C6−C18−C19	109.0(1)	129.5(2)
C18−C19−N3	112.7(1)	124.0(2)
O1−C13−N2	122.2(1)	122.4(2)
O2−C14−N2	120.3(1)	119.7(2)
C13−N2−C14	126.9(1)	127.4(2)
O3−C20−N4	122.7(1)	122.7(2)
O4−C21−N4	119.9(1)	119.9(2)
C20−N4−C21	127.5(1)	127.1(2)
C1−C11−C12−N1	−168.5(1)	0.8(4)
C6−C18−C19−N3	−178.3(1)	7.0(4)

[a] The structure of **3** includes two crystallographically independent molecules. Parameters for one molecule only are given, with the equivalents from the other molecule being virtually identical. Parameters for both molecules are given in the Supporting Information.

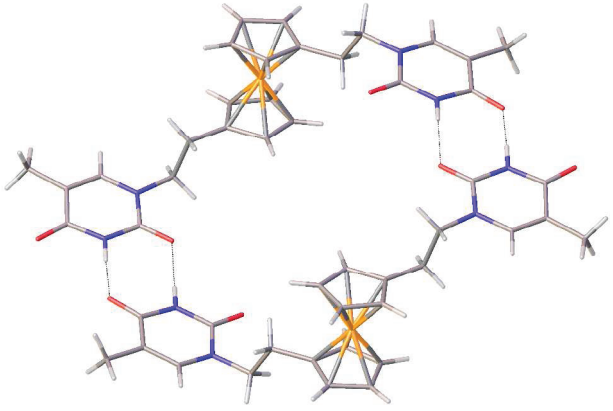


Figure 6. Molecular structure of the H-bonded dimer formed by **1** in the solid state.

feature of ferrocene-containing nucleobases in the solid state.[4a,b] It is interesting to note that the three structures show remarkably different packing arrangements as outlined below.

First, compound **1** forms an intermolecular H-bonded dimer in the solid state, with each imide NH H-bonded to a carbonyl oxygen (Figure 6). In each molecule, a carbonyl *para* to the alkyl-substituted nitrogen on one thymine and a carbonyl *ortho* to the substituent on the other partakes in H-bonding. Hydrogen bond lengths and angles are presented in Table 2. The Cp rings are virtually eclipsed (twist angle = 10.8(2)°), and to allow the

Table 2. Hydrogen Bonds (Å and deg) in 1, 2, and 3

$D-H\cdots A$	$d(D-H)$	$d(H\cdots A)$	$d(D\cdots A)$	$\angle(DHA)$
1: N2−H2A···O3[a]	0.88	1.97	2.839(2)	171.8
1: N4−H4A···O2[a]	0.88	1.89	2.768(2)	172.0
2: N5−H5A···N2[b]	0.88	2.28	3.159(8)	175.3
2: N5−H5B···N4[c]	0.88	2.02	2.850(8)	156.8
3: N2−H2A···O102[d]	0.88	1.96	2.830(2)	170.3
3: N4−H4A···O103	0.88	1.90	2.768(2)	170.5
3: N102−H10A···O1[e]	0.88	1.92	2.797(3)	175.0
3: N104−H10B···O4	0.88	1.99	2.857(3)	166.9

[a] Symmetry transformations used to generate equivalent atoms: $-x+2$, $-y+1$, $-z+2$. [b] $-x-2$, $y-0.5$, $-z+0.5$. [c] $-x-2$, $y+0.5$, $-z+0.5$. [d] $x+1$, y, z. [e] $x-1$,y, z.

formation of the dimer, the structure adopts a rather open position, with the torsion angle between the two substituents (C11−C1−C6−C18) being −122.3(2)°. The use of polar solvents to render compound **1** sufficiently soluble at NMR concentrations prevented the observation of any similar intermolecular interactions in solution (as was also the case for compounds **2**, **3**, and **4**).

In contrast compound **3**, the unsaturated analogue of **1**, forms an H-bonded chain (Figure 7) involving oligomers of the two crystallographically independent molecules. In this ribbon-like structure, the torsion angles between the subsitutuents on the ferrocenes (C11−C1−C6−C18 and C111−C101−C106−C118) are 67.4(2)° and 55.9(2)°, respectively, with Cp twist angles of 3.5(3)° and 17.0(4)°. However the arrangement of H-bonding atoms within each molecule is in fact the same as in **1**, with each thymine forming a pair mediated by two H-bonds and the methyl groups on each thymine being *cisoid* to one another across the T:T pair. The H-bond lengths and angles in **1** and **3** are generally similar (see Table 2).

There are some notable differences with previous examples of ferrocenes disubstituted with linker units to thymine (Figure 1, n = 1[4a] and n = 4[4b]). First these previous examples form H-bonded arrays, whereas the direct analogue here (compound **1**, n = 2) forms an intermolecular dimer. Second, in contrast to the array formed by **3**, these arrays exibit more secondary supramolecular interactions (e.g., C−H···O interactions) in their packing and in fact adopt a *transoid* orientation of methyl groups in T:T base pairings, with only the carbonyl *ortho* to the alkyl substituent forming H-bonds.

Finally compound **2**, the adenine analogue of **1**, forms an array best described as a sheet of H-bonded ribbons (Figure 8). Each adenine forms four H-bonds, two involving separate nitrogen heteroatoms on the purine ring as H-bond acceptors and two involving the amine group as an H-bond donor. However the symmetry of the molecule is such that there are only two different H-bonds in the structure, as summarized in Table 2.

The iron atom in **2** is located on an inversion center such that only half of the molecule is crystallographically unique and the two Cp rings are identical. Thus the torsion angle between the ferrocene substituents (C6−C1−C1−C6) is exactly 180° by symmetry with the Cp twist angle being exactly 36°.

Electrochemistry. The redox properties of all four compounds were examined by cyclic voltammetry in DCM. The general poor solubility of the compounds necessitated filtration of the electrolyte solution before each experiment. Cyclic voltammograms for the adenine compounds **2** and **4** are shown in Figure 9, and the electrode potentials for all four compounds are presented in Table 3. The compounds gave satisfactory electrochemical reversibility (see Supporting Information for further details).

It is clear that the nature of the linker between the nucleobase and the ferrocene unit has a significant effect on the electrode potential values, with the double bonds in **3** and **4** making oxidation more difficult with respect to compounds **1** and **2**. Similar trends have been observed previously in studies on related compounds containing either an ethyl spacer or a conjugated double bond between the ferrocene unit and aromatic moieties.[9] However in this case the difference in potentials (greater than +0.2 V) is larger and in fact is similar in magnitude to studies on adenine-based derivatives[4d] containing either a triple bond or an ethyl group between the ferrocene unit and the nucleobase. In all these studies, the saturated linker lowers the ferrocene-centered redox couple, which is consistent with the ferrocenium center being stabilized through a positive inductive effect.

In conclusion four bis-substituted ferrocenes, containing either thymine or adenine units, have been synthesized, which has widened our understanding of the electrochemical behavior and the solid-state aggregation behavior of organometallic nucleobases. Further studies are now planned to examine connectivities to other nucleobases and improve the solubility of this class of compound to facilitate studies of aggregation behavior in solution.

EXPERIMENTAL SECTION

General Comments. Reagent grade reactants and solvents were used as received from chemical suppliers. Anhydrous solvents were dried by the usual procedures and were stored over 4 Å molecular sieves. All reactions were carried out under an inert atmosphere of nitrogen or argon. Column chromatography was performed on silica gel (Merck, grade 60).

*N-Benzoyl-N-(9-((diphenylphosphoryl)methyl)-9H-purin-6-yl)benzamide, **7**.* To a solution of 9-(diphenylphosphorylmethyl)adenine[6] (100 mg; 0.286 mmol) in pyridine (4 mL) at 0 °C was added 132 μL of benzoyl chloride. The solution was stirred for 5 min. The mixture was then warmed to room temperature overnight. The pyridine was removed using high vacuum, and the residue was then dissolved in dichloromethane, washed with 5% sodium bicarbonate, dried on sodium sulfate, and evaporated. The crude product was purified on silica gel using an initial 70/30 ethyl acetate/hexane mixture. A gradient of ethyl acetate in hexane was then used from 70% to 100% followed by a gradient of methanol in ethyl acetate from 2% to 10%. A white foam was obtained (124 mg; 78%). ^{1}H NMR δ_H (400 MHz, $CDCl_3$): 8.51 (1 H, s), 8.48 (1 H, s), 7.85−7.74 (9 H, m), 7.56 (2 H, td, J 7.4, 1.3), 7.52−7.43 (7 H, m), 7.34 (5 H, t, J 7.8), 5.10 (2 H, d, J 6.2). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.14, 153.04, 151.88, 151.74, 145.06, 134.06, 133.02, 132.90, 131.14, 131.05, 129.41, 129.09, 128.97, 128.64, 128.21, 126.54, 43.80, 43.09. MS (ES) (m/z): calcd for $C_{32}H_{24}N_5O_3P$ 580.1514, found 580.1511 (M^+ + Na). IR (cm^{-1}): 3059, 2975, 2924, 1696, 1597, 1577, 1234. Mp: 108−110 °C.

*1,1′-Bis[(Z)-2-(N^3-benzoylthymin-1-yl)ethenyl]ferrocene, **8**.* In a 200 mL Schlenk tube compound **6** (1.39 g; 3.13 mmol) was dissolved in dry pyridine (10 mL) with gentle heating. The pyridine was evaporated, and the mixture was redissolved with dry DMF (15 mL). NaH (119 mg, 4.69 mmol, 95%) was added, and the mixture was stirred under an inert atmosphere at room temperature for 1 h before 1,1′-dicarboxylaldehyde ferrocene[5] (**5**, 215 mg, 0.89 mmol) dissolved in DMF (20 mL) was added. After 16 h the reaction mixture was quenched with water (100 mL) and extracted with EtOAc (30 mL × 3). The combined organic fractions were dried over $MgSO_4$, the solvent was removed, and the crude material was purified on silica gel to give the product as an orange foam (358 mg, 58%, mixture of

dx.doi.org/10.1021/om200671b |*Organometallics* 2011, 30, 5284–5290

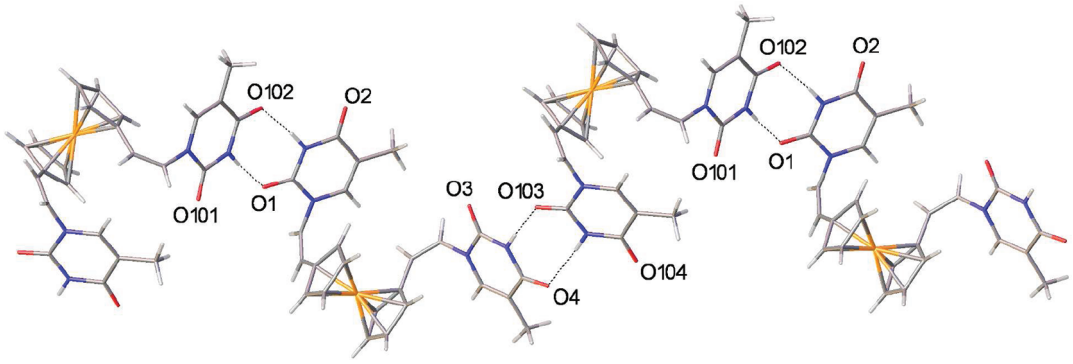


Figure 7. Molecular chain formed by T:T base pairs between pairs of crystallographically independent molecules of **3**.

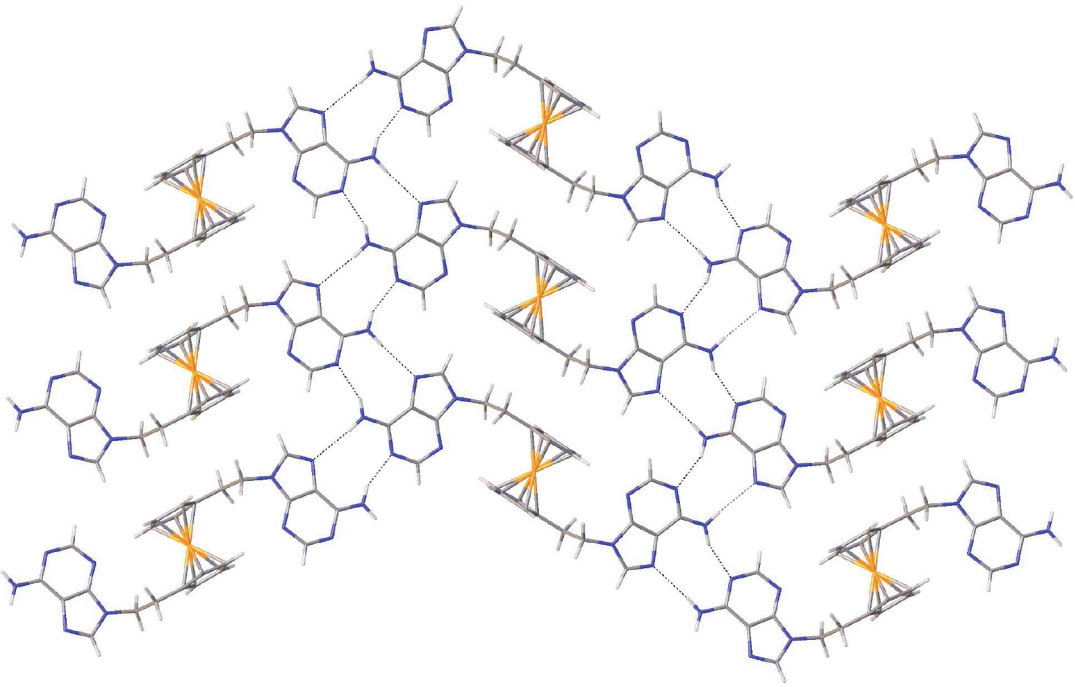


Figure 8. Molecular packing diagram of **2** showing the H-bonded sheet.

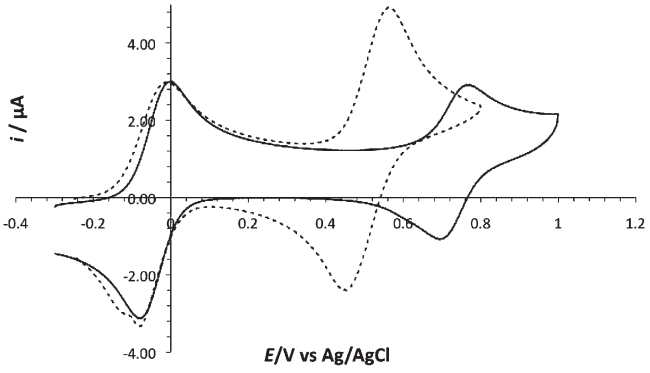


Figure 9. Cyclic voltammograms of **2** (dotted line) and **4** in the presence of decamethylferrocene (dmfc, shown at ca. −0.04 V vs Ag/AgCl) in DCM. Scan rate = 500 mV/s. For other experimental conditions, see Table 3 and the Supporting Information.

Table 3. Electrochemical Data at 500 mV/s in DCM[a]

	1	2	3	4
$E^{0\prime}$	0.524	0.552	0.765	0.770

[a] Electrode potentials, $E^{0\prime}$, where $E^{0\prime} = (E_{pa} + E_{pc})/2$, are referenced to decamethylferrocene (ca. 1 mM), which was used as an internal reference. The confidence limit is ±5 mV. Pt working, Pt counter, and Ag/AgCl reference electrodes were used with tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte.

ca. 4:1 ratio of *Z* to (*E* + *E*/*Z*)). Z isomer data: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (4 H, dd, *J* 8.4, 1.3), 7.73−7.65 (2 H, m), 7.60−7.49 (4 H, m), 7.02 (2 H, d, *J* 1.2), 6.47 (2 H, d, *J* 8.4), 6.25 (2 H, d, *J* 8.5), 4.39 − 4.33 (4 H, m), 4.29−4.22 (4 H, m), 1.90 (6 H, d, *J* 1.2); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.81, 163.10, 148.98, 140.40, 135.10, 131.71, 130.54, 129.17, 125.60, 121.61, 110.77, 77.46, 71.31, 70.94, 12.26; IR (cm^{-1}) 1646, 1743, 2926; MS (ES) (*m*/*z*) calcd for $C_{38}H_{30}FeN_4O_6Na$ 717.1412, found 717.1422 (M^+ + Na).

1,1′-Bis[(Z)-2-(N^6-dibenzoyladenin-9-yl)ethenyl]ferrocene, ***9***. Compound **7** (800 mg; 1.43 mmol) was dissolved in 6 mL of pyridine. The solution was evaporated using high vacuum. The residue was then redissolved in 6 mL of DMF under argon. After 5 min of stirring, 36 mg of sodium hydride 95%

dx.doi.org/10.1021/om200671b |*Organometallics* 2011, 30, 5284–5290

Table 4. Crystal Data and Structure Refinement for 1, 2, and 3

	1	2	3
formula	$C_{24}H_{26}FeN_4O_4$	$C_{24}H_{24}FeN_{10}$	$C_{24}H_{22}FeN_4O_4$
fw	490.34	508.38	486.31
space group (no.)	$P2_1/c$ (14)	$P2_1/c$ (14)	$P2_1/c$ (14)
a; b; c (Å)	16.7580(8); 10.9624(6); 11.9973(6)	6.3611(6); 8.0936(11); 20.680(3)	20.6631(9); 11.7587(5); 19.2280(8)
β (deg)	98.978(3)	90.135(8)	112.103(3)
V (Å^3)	2177.0(2)	1064.7(2)	4328.5(3)
Z	4	2	8
temperature (°C)	−123(2)	−153(2)	−153(2)
λ (Å)	1.54184	0.71073	1.54184
D_{calcd} (g cm^{-3})	1.496	1.586	1.492
μ (cm^{-1})	5.895	0.747	5.929
final R indices ($I > 2\sigma(I)$)	R1 = 0.0278, wR2 = 0.0757	R1 = 0.0674, wR2 = 0.1285	R1 = 0.0368, wR2 = 0.0902
final R indices (all data)	R1 = 0.0298, wR2 = 0.0770	R1 = 0.0932, wR2 = 0.1461	R1 = 0.0476, wR2 = 0.950

(1.505 mmol) was added in one portion at room temperature. The mixture was stirred at room temperature for 2 h. Then the bis-carboxaldehyde[5] **5** (116 mg; 0.478 mmol), previously dissolved in 5 mL of DMF, was added at room temperature. After stirring overnight, the reaction was quenched with water/ethyl acetate (1:1) (20 mL) at 0 °C and extracted with ether. The organic layers were combined, dried over sodium sulfate, and concentrated. The crude material was purified on silica gel using an initial 6:4 ethyl acetate/hexane mixture and then a gradient from 60% to 100% of ethyl acetate. An orange foam was obtained (84 mg; 32%; mixture of ca. 4:1 ratio of Z to (E + E/Z)). Z isomer data: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (2 H, s), 8.09 (2 H, s), 7.89 (9 H, d, J 7.1), 7.50 (4 H, t, J 7.5), 7.37 (9 H, t, J 7.7), 6.84 (2 H, d, J 8.7), 6.39 (2 H, d, J 8.7), 4.20 − 4.17 (4 H, m), 3.85 (4 H, t, J 1.8); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.25, 152.99, 152.81, 152.00, 144.29, 134.16, 132.97, 129.46, 128.68, 127.06, 126.29, 116.15, 77.67, 71.44, 70.43; MS (ES) (m/z) calcd for $C_{52}H_{36}FeN_{10}O_4Na$ 943.2168, found 943.2198 (M^++ Na); IR (cm^{-1}) 3063, 2961, 2923, 2853, 1697, 1596, 1572, 1229; Mp 106−108 °C (dec).

1,1′-Bis[(Z)-2-(thymin-1-yl)ethenyl]ferrocene, ***3***. In a 100 mL round-bottom flask compound **8** (200 mg; 0.29 mmol) was stirred with $MeNH_2$ (5 mL) for 10 min before being evaporated under high vacuum (0.1 mmHg). Purification on silica gel gave the product as an orange solid (134 mg, 96%), which was recrystallized by slow evaporation from a DCM/MeOH mixture to yield single orange crystals: ^{1}H NMR (300 MHz, DMSO) δ 11.45 (2 H, s), 7.20 (2 H, s), 6.37 (2 H, d, J 8.4), 6.24 (2 H, d, J 8.5), 4.27 (8 H, dd, J 20.8, 19.1), 1.74 (6 H, s); ^{13}C NMR (101 MHz, DMSO) δ 164.17, 149.84, 140.78, 124.70, 122.42, 109.01, 77.77, 70.75, 70.47, 11.79; IR (cm^{-1}) 1651, 2965, 3172; MS (ES) (m/z) calcd for $C_{24}H_{22}FeN_4O_4Na$ 509.0888, found 509.0894 (M^+ + Na); Mp 285−286 °C (dec). Anal. Calcd for $C_{24}H_{22}FeN_4O_4$: C, 59.28; H, 4.56; N, 11.52. Found: C, 59.26; H, 4.43; N, 11.33.

1,1′-Bis[(Z)-2-(adenin-9-yl)ethenyl]ferrocene, ***4***. Compound **9** (31mg; 0.034 mmol) was dissolved in 1 mL of methylamine. The mixture was stirred at room temperature for half an hour under argon, and the methylamine then evaporated. The crude material was purified on silica gel with a 45:5 DCM/methanol mixture. An orange solid was obtained (13 mg; 77%): ^{1}H NMR (300 MHz, DMSO) δ 8.16 (1 H, s), 8.00 (1 H, s), 7.33 (2 H, s), 6.78 (1 H, d, J 8.5), 6.50 (1 H, d, J 8.6), 4.21−4.09 (2 H, m), 3.86−3.69 (2 H, m); ^{13}C NMR (75 MHz, DMSO) δ 156.51, 153.50, 150.00, 140.27, 127.74, 118.82, 117.63, 78.43, 71.16, 70.46; MS (ES) (m/z) calcd for $C_{24}H_{20}FeN_{10}$ 527.1119, found 527.1138 (M^+ + Na); IR (cm^{-1}) 3303, 3122, 1670, 1645, 1595, 1572, 1302; Mp 256−258 °C (dec).

1,1′-Bis[2-(thymin-1-yl)ethyl]ferrocene, ***1***. To a 100 mL round-bottom flask containing compound **8** (200 mg; 0.29 mmol), dissolved in EtOAc (10 mL) was added $Pd(OH)_2$ (20% wt on carbon, 465 mg, 1.05 mmol). The reaction was stirred under a H_2 (ballon pressure) atmosphere at room temperature for 16 h, after which time the mixture was filtered through a short pad of Celite to yield a pale yellow solution. The solvent was then removed, and the residue was stirred with $MeNH_2$ (5 mL) for 10 min before being evaporated under high vacuum (0.1 mmHg). Purification on silica gel gave the product as a pale yellow solid (165 mg, 78%), which was recrystallized by slow evaporation from a DCM/MeOH mixture to yield single pale yellow crystals: ^{1}H NMR (300 MHz, DMSO) δ 11.23 (2 H, s), 7.43 (2 H, s), 4.07 (8 H, d, J 6.4), 3.83−3.66 (4 H, m), 2.66−2.53 (4 H, m), 1.72 (6 H, s); ^{13}C NMR (101 MHz, DMSO) δ 164.26, 150.71, 141.50, 108.10, 84.33, 68.57, 68.04, 48.12, 28.15, 11.84; IR (cm^{-1}) 1648, 2998, 3155; MS (ES) (m/z) calcd for $C_{24}H_{26}FeN_4O_4Na$ 513.1201, found 513.1206 (M^+ + Na); Mp 204−205 °C (dec). Anal. Calcd for $C_{24}H_{26}FeN_4O_4 \cdot {}^1/_3H_2O$: C, 58.08; H, 5.42; N, 11.29. Found: C, 57.89; H, 5.51; N, 11.66.

1,1′-Bis[2-(adenin-9-yl)ethyl]ferrocene, ***2***. The same procedure as described above for the preparation of compound **1** was applied using compound **9** (92mg; 0.099 mmol). The crude was purified on silica gel using a 45:5 DCM/methanol solvent mixture. A yellow solid was obtained (33 mg, 66%): ^{1}H NMR ^{1}H NMR (300 MHz, DMSO) δ 8.15 (1 H, s), 8.02 (1 H, s), 7.17 (1 H, s), 4.28 (1 H, t, J 7.4), 4.05 (1 H, d, J 1.7), 4.01 (1 H, d, J 1.6), 2.84 (1 H, t, J 7.4); ^{13}C NMR (75 MHz, DMSO) δ 156.38, 152.81, 149.92, 141.22, 119.25, 84.99, 69.00, 68.55, 44.40, 29.67; MS (ES) (m/z) calcd for $C_{24}H_{25}N_{10}Fe$ 508.1613, found 509.1638 (M^+ + H); IR (cm^{-1}) 3273, 3109, 2924, 2852, 1659, 1598, 1571, 1305; Mp 284−286 °C (dec).

X-ray Crystallography. Suitable crystals were selected, and data sets were measured on a Bruker SMART 6000 diffractometer for **1** and **3** and on a Bruker APEXII CCD diffractometer at the window of a Bruker FR591 rotating anode for **2**. The data collections were driven by SMART[10] and processed by SAINTPLUS[11] for **1** and **3** and were driven by COLLECT[12] and processed by DENZO[13] for **2**. Absorption corrections for all three structures were applied using SADABS.[14] The structures were all solved and refined by a full-matrix least-squares procedure on F^2 in SHELXTL.[15] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were added at calculated positions and refined by use of a riding model with isotropic displacement parameters based on the equivalent isotropic displacement parameter (U_{eq}) of the parent atom. Figures were produced using OLEX2,[16] and structural analysis was carried out in Mercury 2.4.[17] The crystal of sample **2** was a merohedral twin with the two domains related by the twin law (1 0 0 0 −1 0 0 0 −1). The refined percentage ratio of the twin domains was 52:48. Crystal data and structure refinement details are given in Table 4.

■ ASSOCIATED CONTENT

Supporting Information. NMR spectra of selected compounds, electrochemical data showing variable scan rate dependence,

dx.doi.org/10.1021/om200671b |*Organometallics* 2011, 30, 5284–5290

X-ray data including CIF file (CCDC deposition numbers **1**: 831176, **2**: 831177, and **3**: 831178), and tables of bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENT

Advantage West Midlands (AWM) is acknowledged for equipment funding, and the EPSRC is thanked for the award of a Leadership Fellowship to J.H.R.T. The UK National Crystallography Service is also acknowledged for data collection on compound **2**.

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