The redox properties of ferrocenyl-substituted aryl azines

Vittorio A. Sauro and Mark S. Workentin

Abstract: A series of ferrocenyl substituted azines (1-Fc/Ar, where Ar = $4-NO_2C_6H_4$, $4-CNC_6H_4$, $4-OCH_3C_6H_4$, C_5H_4N , ferrocene, anthracene, and pyrene) were investigated by electrochemical and photochemical techniques. All the 1-Fc/Ar exhibited oxidation waves within 60 mV of each other, consistent with the expected oxidation of the ferrocene moiety. The reduction properties of 1-Fc/Ar is governed by the nature of the Ar substituent. The standard reduction potentials suggest that ferrocene has comparable electron donating abilities as a 4-methoxyphenyl and 4-dimethyl-aminophenyl group. The anthracenyl azines exhibit one-electron reversible reduction followed by dimerization of the radical anion resulting in dimerization rate constants (k_d) between 5.1×10^4 and 1.5×10^5 M⁻¹ s⁻¹. 1-Fc/Anth and related azines undergo photochemical E/Z isomerization of the C=N bonds to produce E/Z and Z/Z isomers from the thermodynamically most stable E/E form. Fluorescence at 77 K, was observed for these compounds only after long-wavelength irradiation to produce a mixture of E/E, E/Z, and Z/Z isomers. Fluorescence quantum yields of 0.042, 0.090, and 0.176 were determined for 2-Anth/H, 2-Anth/Anth, and 1-Fc/Anth, respectively. The electrochemical, photochemical, and X-ray data suggest that the azine unit is a conjugation "limiter" and may be a general characteristic of azine molecules.

Key words: azines, electrochemistry, cyclic voltammetry, reduction, electron transfer.

Résumé : Faisant appel à des techniques électrochimiques ainsi que photochimiques, on a étudié une série d'azines de ferrocényles substitués (1-Fc/Ar dans lesquels Ar = $4-NO_2C_6H_4$, $4-CNC_6H_4$, $4-OCH_3C_6H_4$, C_5H_4N , ferrocène, anthracène et pyrène). Tous les 1-Fc/Ar présentent des vagues d'oxydation à moins de 60 mV les uns des autres, ce à quoi on peut s'attendre pour l'oxydation de la partie ferrocène. Les propriétés de réduction des 1-Fc/Ar sont définies par la nature du substituant Ar. Les potentiels de réduction standards suggèrent que les propriétés du ferrocène en ce qui a trait à ses possibilités de donner des électrons sont semblables à celles des groupes 4-méthoxyphényle et 4diméthylaminophényle. Les azines dérivés de l'anthracène donnent lieu à une réduction réversible à un électron suivie d'une dimérisation de l'anion radical avec des constantes de vitesse de dimérisation (k_d) qui vont de 5,1 × 10⁴ à 1,5 × 10^5 M⁻¹ s⁻¹. La 1-Fc/Anth et les azines apparentées subissent des isomérisations photochimiques E/Z des liaisons C=N qui conduisent à des mélanges d'isomères E/Z et Z/Z à partir de la forme E/E, thermodynamiquement la plus stable. Ces composés ne donnent lieu à de la fluorescence à 77 K qu'après avoir été soumis à une irradiation à grande longueur d'onde qui permet de produire un mélange des isomères E/E, E/Z et Z/Z. On a déterminé des rendements quantiques de fluorescence de 0,042, 0,090 et 0,176 respectivement pour les 2-Anth/H, 2-Anth/Anth et 1-Fc/Anth. Les données électrochimiques, photochimiques ainsi que celles relatives à la diffraction des rayons X suggèrent que l'unité azine « limite » la conjugaison et que cette propriété est peut-être une caractéristique générale pour les molécules d'azine.

Mots clés : azines, électrochimie, voltampérométrie cyclique, réduction, transfert d'électron.

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Introduction

Ferrocene and its derivatives have been investigated for their use in a variety of applications, including in organic synthesis (1), in applications tied to their electrochemical properties (1-5), in biological systems (6), as molecular wires and in other nanoelectronic devices (7), and in anion recognition applications (8). Due to the special chemical,

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stereochemical, and electrochemical properties (1) of ferrocene, there is great interest in ferrocene based ligands for the production of multi-metal containing organometallic complexes that can be used for a variety of applications (9, 10). Ferrocene-containing compounds have also been investigated for their second-order non-linear optical (NLO) properties (3, 11–13).

Ferrocene and its derivatives have been studied extensively using electrochemical techniques (1) and generally show a single one-electron reversible oxidation whose potential varies depending on the substituent attached to the cyclopentadienyl ring (3, 5, 10, 13, 14). The redox properties of the ferrocene group have been exploited to produce molecules that may have potential applications as molecular switches and molecular sensors (15, 16).

Azines (>C=N-N=C<) appear to have the structural elements necessary to allow for complete conjugation between the substituents used to make up its structure, although there is now general agreement that the azine unit stops, or at the very least limits, conjugation. The question of conjugation through the azine unit has been investigated both theoretically and experimentally (17-29). Glaser and co-workers (20-29) examined the solid-state structures of a large number of structurally related aryl azines, paying particular attention to the structural consequences of conjugative interactions that manifest themselves in the solid-state structures. As a result of their extensive X-ray analyses, including the conformational properties about the N-N and Ar-C bonds, bond length analysis, and theoretical studies, Glaser and co-workers (25, 27) conclude that the azine unit is a "conjugation stopper," at least in the solid state.

Early and recent electrochemical investigations (2, 30–38) of azines have suggested that they do not exhibit extensive electronic communication through the azine unit. In a more recent study, we reported (39) the redox behavior of an extensive series of substituted acetophenone azines with emphasis on their extent of conjugation. The standard reduction potentials (E°) were found to vary as a function of substituent, with electron donating substituents causing the molecules to reduce at more negative potentials than those containing electron withdrawing groups. The azines were found to preferentially reduce at the C=N bond closest to the aryl group substituted with the most electron withdrawing substituent. Based on our extensive substituent-effect study, in this investigation (39) the azine unit was found to impede conjugation, and the limited electronic effects measured could have been purley inductive, supporting the notion of Glaser (20-29).

The electrochemical behavior of ferrocenyl azines has been previously investigated in a few cases (2, 4). Xu-Bing et al. (4) report the redox behavior of ferrocene coupled to bipyridine by an azine linkage, and the cyclic voltammetry (CV) plot shows the expected one-electron reversible oxidation typical of ferrocene-containing molecules. In addition, two-reduction processes were reported by the authors and attributed to the reduction of the -CHNNC(C₁₀H₆N₂) group, which is consistent with the reduction of other types of azines (30, 35-39). Osborne et al. (2) report the electrochemistry of several azines and related compounds that contain one or two ferrocene groups. The single ferrocene compounds exhibit the expected one-electron reversible oxidation with standard oxidation potentials in the range of +0.38 to +0.67 V vs. SCE in 0.2 M tetrabutylammonium perchlorate – CH₂Cl₂. For compounds containing two ferrocenyl groups, including the azine 1-Fc/Fc in Scheme 1, the CV show two almost overlapping reversible one-electron oxidations. This indicates that the electronic communication between the two ferrocene subunits through the azine moiety is small. No reduction processes were observed up to -0.5 V vs. SCE in 0.2 M tetrabutylammonium perchlorate - CH₂Cl₂ solution.

To extend our study into the electronic nature of azines, a series of azines containing a ferrocene group were investigated by cyclic voltammetry (CV). Ferrocene was chosen as a substituent because it is an excellent electron donor (1) and when coupled to a substituted aryl azine containing an electron acceptor, the resultant compound could potentially exScheme 1.



hibit the NLO response seen in other azines (24, 25) and ferrocene-containing molecules (11-13). Each ferrocene containing molecule investigated for the various applications listed above took advantage of the same general strategy, mainly, to produce molecules where electronic communication between ferrocene and a second group was realized usually by the use of a conjugated bridge. For this reason, the azine unit is synthetically simple to incorporate and could serve as an ideal linkage to allow for the electronic communication between ferrocene and an aryl group; results with other azines, however, show that the azine unit will not allow for conjugative interaction. In the absence of any conjugative effects, the versatility of the azine unit as a linker and the ease in which azines can be synthesized makes them ideal synthons for coupling electron donating and acceptor groups for many applications. An important aspect of any application is an understanding of their electronic properties and that is what we describe here. The various compounds examined are illustrated in Scheme 1, along with a shorter notation used within the text to quickly identify each molecule. The terms Fc, Ar, Anth, Py, and Pyrd refer to ferrocene, aryl, anthracene, pyrene, and pyridine, respectively. In addition, nitro, cyano, and methoxy substituted phenyl rings will be denoted by 4-NO₂, 4-CN, and 4-OCH₃, respectively, where the number four refers to para substitution of the phenyl rings. An unsubstituted phenyl ring will be denoted by H (e.g., 2-Anth/H).

Results and discussion

The electrochemical behavior of the series of ferrocenyl azines (1-Fc/Ar) was studied in *N*,*N*-dimethylformamide (DMF), using cyclic voltammetry (CV). The electrochemical characteristics depend on the structure of the aryl

Scheme 2.

Scheme 3.



substituent. Ferrocenyl azines that contain a para-substituted aryl group exhibit electrochemical behavior similar to that observed for the acetophenone azines (39). Figures 1a-eshows a series of cyclic voltammograms for acetylferrocene-4-cyanoacetophenone azine (1-Fc/4-CN) in 0.1 M TEAP-DMF using various scan directions and switching potentials. A characteristic voltammetric feature is a single electron anodic wave at positive potentials that is reversible at all scan rates investigated (the wave labeled A in Fig. 1e) and is common to all of the 1-Fc/Ar investigated. The anodic waves are due to formation of the azine radical cation (1- Fc^{+}/Ar) and the position of the oxidation is typical for ferrocene-containing molecules, representing the oxidation of the iron core from the Fe^{II} to the Fe^{III} state and vice versa (2). Other voltammetric features include a cathodic wave at negative potentials that is reversible at all scan rates investigated (wave B in Fig. 1e), followed at more negative potentials by a second single electron cathodic wave (wave C in Fig. 1e). The two reduction waves represent the successive reduction of the corresponding azine to its radical anion (1- Fc/Ar^{-}) and then its dianion (1- Fc/Ar^{2-}), respectively. This series of events is shown schematically in Scheme 2.

When the CV is scanned in the negative potential direction and goes through the formation of dianion, minor oxidation waves are observed on the reverse scan. These processes are evident only when the scan goes through the formation of 1-Fc/Ar²⁻ and result from the protonation or some other reaction of 1-Fc/Ar²⁻. The dianion is sufficiently basic to be protonated by solvent molecules or, more likely, residual H₂O. Reduction and protonation most likely occur at the C=N moiety adjacent to the substituted aryl group to give a hydrazone (Scheme 3) similar to that observed in the reactions of acetophenone azine radical anions and dianions with trifluoroethanol (TFE) (39). Reduction of the azomethine bond adjacent to the ferrocenyl group occurs at much more negative potential as evidenced by the irreversible reduction at -2.303 V vs. SCE for 1-Fc/Fc (see below). The identity of the minor products were not determined.

Azines 1-Fc/Pyrd, 1-Fc/4-OCH₃, and 1-Fc/4-NO₂ showed similar voltammetric features as 1-Fc/4-CN described above. In the cases of 1-Fc/4-CN, 1-Fc/Pyrd, 1-Fc/4-OCH₃, and 1-Fc/4-NO₂ (Figs. 1*e*-*h*) the formation of 1-Fc/Ar⁻⁻ is completely chemically reversible (dashed line). For this series, standard reduction potentials $(E_{0/--})^{\circ}$ vary as a function of the electronic properties of the substituent and are summarized in Table 1. The reduction potentials of 1-Fc/Ar exhibit a significant substituent effect with values differing by more than 1.2 V between 1-Fc/4-NO₂ and 1-Fc/4-OCH₃. The more electron withdrawing the substituent the easier the azine is to reduce and the more positive the E° value. The $E_{0/\bullet-}^{\circ}$ are comparable to the E° of the similarly substituted acetophenone azines but with a 4-methoxyphenyl or 4-dimethylaminophenyl group in place of the ferrocene unit (39). This illustrates that ferrocene has similar electron donating characteristics as the two aryl groups, as has been previously suggested by other researchers (10, 12). The reductions of 1-Fc/Ar are single electron based on the i_p/\sqrt{v} values in comparison with the Fe^{II}/Fe^{III} couple.

The dianions of 1-Fc/4-CN, 1-Fc/Pyrd, 1-Fc/4-OCH₃, and 1-Fc/4-NO₂ are not reversible on the CV timescale up to 50 V s⁻¹ in DMF. Typical CVs at low scan rates are also illustrated in Figs. 1*e*-*h*. The potentials $(E_{p\bullet-/2-})$ for the second reduction follow the same trend with substituent donating and withdrawing ability (see Table 1) and become easier to reduce when electron withdrawing substituents act to reduce the electron density from the radical anion. The substituent effect is slightly smaller for the second wave with potentials differing by 0.8 V through the series 1-Fc/4-NO₂ to 1-Fc/4-OCH₃. Once again, the $E_{p\bullet-/2-}$ values indicate that ferrocene has comparable electron donor capabilities as 4-methoxyphenyl and (or) 4-dimethylaminophenyl in comparison to the appropriate acetophenone azines (39). The second reduction wave observed for 1-Fc/4-OCH₃, however, may not be due to dianion formation but may result from reduction of the azomethine bond adjacent to the ferrocenyl group since the $E_{p \bullet -/2-}$ is comparable to that observed for the first reduction of 1-Fc/Fc to 1-Fc/Fc*-. The exact nature of this reduction process could not be investigated because it occurs at very negative potentials and into the solvent discharge.

The reduction of the nitro containing ferrocenyl azine warrants further discussion. We previously reported (39) that the reduction of all the nitro containing acetophenone azines occurs at almost identical potentials (~ -1 V vs. SCE). This was attributed to the fact that the reduction appears to be that of azine substituted nitrobenzene molecules and not an aryl-nitro substituted azine. Similarly, reduction of 1-Fc/4-NO₂ occurs at -0.956 V vs. SCE and supports our earlier suggestion that reduction is occurring at the Ar-NO₂ group and not at one of the azine C=N imine bonds. The reduction

Fig. 1. Cyclic voltammograms of selected azines measured in 0.1 M TEAP-DMF at 0.2 V s⁻¹. Arrows indicate the scan direction. Parts a-e are of 1-Fc/4-CN: (a) CV starting at 0 potential and switching after the appearance of wave B. (b) CV starting at 0 potential and switching after the appearance of wave C. (c) CV starting at 0 potential and switching after the appearance of wave A. (d) CV starting at 0 potential and switching after the appearance of wave B and continuing into the positive potential region and switching again after the appearance of wave A. (e) CV starting at 0 potential and switching after the appearance of wave C and continuing into the positive potential region and switching again after the appearance of wave A. Parts f-h are the CVs of 1-Fc/Pyrd, 1-Fc/4-OCH₃, and 1-Fc/4-NO₂, respectively. Solid lines are the CV going through radical anion and dianion formation and continuing into positive potentials where the radical cation is formed. Dashed lines are the CV when the potential is reversed after formation of the radical anion and continuing into positive potentials where the radical cation is formed.



potentials of the nitro containing azines all occur within 44 mV of each other and their values are all approximately equal to -1 V vs. SCE, roughly the same potential as nitrobenzene in the same solvent (-1.1 V vs. SCE). **1**-Fc/4-NO₂ also shows a second less well-defined cathodic wave (Fig. 1*h*) that is due to further reduction of the aryl nitro group, presumably to form hydroxylamines, which are known to result from reduction of aryl-NO₂ compounds (40). The second cathodic wave is not completely reversible and includes other electrochemical processes that make it appear oddly shaped in comparison with other waves due to

dianion formation in Fig. 1. Scanning to even more negative potentials (past the formation of dianion) produces two multi-electron waves that are due to further reduction of the protonated 1-Fc/4-NO₂ dianion to ultimately form amines.

1-Fc/Py shows a one-electron reversible oxidation due to formation of a radical cation, similar to the other ferrocenyl azines discussed thus far (A in Fig. 2a). However, 1-Fc/Py was the only ferrocenyl azine that exhibits a reversible cathodic reduction for the formation of the both the radical anion and dianion and provides values for $E_{0,\bullet-}^{\circ} = -1.549$ V vs. SCE and $E_{\bullet-/2-}^{\circ} = -1.995$ V vs. SCE, respectively. This is typical for pyrene-containing molecules (41). Reversing the potential after the formation of the radical anion (B) results in a completely reversible wave. Continuing into the positive potential region results in the CV showing two one-electron reversible waves for the reduction and oxidation of 1-Fc/Py (dashed line in Fig. 2a). No oxidation waves were observed for 2-Py/H or 1-pyrenecarboxaldehyde up to +1 V whose electrochemical behavior were examined for comparison to 1-Fc/Py. Formation of the azine (i.e., 1-Fc/Py and 2-Py/H) results in a negative potential shift for the formation of the pyrene radical anion in comparison to 1-pyrenecarboxaldehyde. It must be noted that in the case of the azines, it is the C=N bond that is reduced, but the C=O bond is reduced in 1-pyrenecarboxaldehyde. In general, the azomethine group is more easily reduced than the carbonyl group from which it is derived (40). Thus a shift to more positive reduction potentials is expected by replacing the oxygen of a C=O bond with a nitrogen. In the case of the azines, the observed shifts relative to the parent carbonyl compounds is to more negative potentials, suggesting that the effects of replacing the C=O with C=N are offset by the conjugative or inductive effects of the azine unit and its second substituent. For 1-Fc/Py, the negative shift in reduction potential indicates that there is some electronic communication through the azine moiety with the electron donating ferrocenyl group of 1-Fc/Py having a larger effect (shift of -0.2 V) than the phenyl ring of 2-Py/H (shift of -0.12 V). Reduction to the dianion shows only a small effect due to azine formation.

An additional process is also observed in the CVs of the pyrene-containing molecules. The wave for the formation of the dianion is followed very closely by a third reversible reduction wave that can be clearly identified in the CV of 2-Py/H (Fig. 2b). In the cases of 1-Fc/Py and 1-pyrenecarboxaldehyde, the formation of dianion is coincidental with the third reduction process. This results in a wave that appears as a single reversible reduction wave (at approximately -1.9 V), but it is not completely reversible since the cathodic and anodic peak-current ratios are greater than unity. At faster scan rates, the peak-current ratio does approach unity, indicating that the rate of the third reduction process is slow enough to be outrun by the scan rate. It was noticed that the appearance of the third reduction process was dependant on the quality of the solvent used for the experiment (i.e., [H₂O]). In meticulously dried solvent, the third reduction process for 2-Py/H was almost not observable. As well, addition of an acid (TFE) to the electrochemical solution of 2-Py/H, caused an increase in the current for the third reduction. This third reduction process is due to the reduction of the product derived from protonation of the dianion by solvent molecules or any residual water present. The formation of this

Azine				
X	Y	$E^{o}_{.+/0}$ (V) ^{<i>a,b</i>}	$E_{0/-}^{o}(V)^{a}$	$E^{\circ}_{\cdot -/2-} (\mathbf{V})^a$
Fc	4-NO ₂	0.612	-0.956	-1.642^{d}
Fc	Anth	0.583	-1.437^{c}	f
Anth	Н	e	-1.403^{c}	f
Anth	Anth	e	-1.232^{c}	-1.822
9-Anthraldehyde		e	-1.207^{c}	f
Fc	Ру	0.576	-1.549	-1.995
Ру	Н	e	-1.462	-1.859
1-Pyrenecarboxaldehyde		e	-1.338	-1.929
Fc	4-CN	0.577	-1.645	-2.029^{d}
Fc	Pyrd	0.579	-1.767	-2.115^{d}
Fc	4-OCH ₃	0.553	-2.158	-2.439^{d}
Fc	Fc	0.572	-2.303^{g}	f
Acetylferrocene		0.691	-2.262	f

Table 1. Electrochemical data for the oxidation and reduction of ferrocenyl and related azines in 0.1 M TEAP–DMF solution.

"Reported in V vs SCE.

^hOxidation potential of the Fe^{II}/Fe^{III} couple. ^cReversible only at faster scan rates. ^dPeak potential ($E_{p+-/2}$) at 0.1 V s⁻¹ scan rate. ^eNo oxidation process was observed up to +1 V. ^fNo further reduction processes were observed. ^gPeak potential at 0.1 V s⁻¹; see text.

Fig. 2. Cyclic voltammograms of selected compounds measured in 0.1 M TEAP–DMF at 0.2 V s⁻¹: (*a*) 1-Fc/Py; (*b*) 2-Py/H; and (*c*) 1-pyrenecarboxaldehyde. Arrows indicate scan direction. Dashed lines are the CV when the potential is reversed after radical anion formation.



protonated product is also responsible for the minor anodic peaks on the return scan (between -0.5 and -0.8 V, depending on scan rate) due to oxidation of the formed conjugate base for each of the pyrene containing azines. As well, the protonated product is also responsible for the minor peak preceding wave A for 1-Fc/Py (Fig. 2*a*), which is not observed unless the scan goes through the formation of a

Fig. 3. Cyclic voltammograms of selected compounds measured in 0.1 M TEAP–DMF at 0.2 V s⁻¹. Arrows indicate scan direction: (*a*) 1-Fc/Anth; (*b*) 2-Anth/H; (*c*) 2-Anth/Anth; and (*d*) 9-anthraldehyde.



dianion. Protonation would interrupt any conjugation that may exist and result in a minor ferrocenyl-containing product that is easier to oxidize than the original azine.

The anthracenyl-containing molecules exhibit different electrochemical behavior compared with the others. Fig. 3a shows the CV of **1**-Fc/Anth, which features a completely reversible one-electron wave (A) at positive potentials, as well as an irreversible one-electron cathodic wave (B) at slow

Scheme 4.



scan rates (i.e., 0.1–0.5 V s⁻¹) that becomes quasi-reversible at faster scan rates (i.e., 15–65 V s⁻¹). The E_p shifts to more negative potentials with increasing scan rate and does not vary linearly with the logarithm of the scan rate (log v). Also present in the CV for 1-Fc/Anth is an anodic wave (C) with an $E_{\rm p}$ at approximately -0.9 V whose intensity decreases relative to the peak current of the irreversible wave as the scan rate is increased. The E_p of wave C shifts towards more positive values with increasing scan rate. This suggests that the anodic wave C is due to a product formed during the reduction process at wave B. The decrease of relative intensity of wave C compared with wave B with increasing scan rate indicates that the formation of the new species is outrun at faster scan rates. Reversing the scan direction towards more negative potentials after the appearance of oxidation wave C results in a CV that is identical to the one obtained on the initial scan, indicating that the product formed upon azine reduction is oxidized back to the original azine. This electrochemical behavior of 1-Fc/Anth is consistent with electrochemically reversible reduction followed by rapid dimerization. The formed dimer can then be oxidized back to starting azine. Digital simulation of the CV of a reversible reduction followed by dimerization produces similar features (i.e., E_p shifts to more negative values and non-linear E_p vs. $\log v$ as are observed for the experimental data. Similar voltammetric features are observed in the CVs for other anthracenyl-containing model compounds (Figs. 3b-d) 2-Anth/H, 2-Anth/Anth, and 9-anthraldehyde, which do not show any oxidation processes up to +1 V.

The reduction of 9-anthraldehyde (used as a model compound to examine substituted anthracene reduction, Fig. 3d) was examined in 0.1 M TEAP-DMF solution by Lasia and Rami (42). It exhibits similar voltammetric features upon reduction as 1-Fc/Anth and the other anthracenyl azines. The one-electron cathodic wave results from the formation of the 9-anthraldehyde radical anion that quickly couples ($k_d = 1 \times$ $10^5 \text{ M}^{-1} \text{ s}^{-1}$ (42) with a second radical anion to form a dianionic dimer (I in Scheme 4) and results in the observed one-electron irreversible reduction wave. The anodic wave at ~ -0.5 V on the reverse scan results from the oxidation of the dimer back to 9-anthraldehyde (42) and is not reversible upon switching the scan direction once again. In the case of 1-Fc/Anth, 2-Anth/Anth, and 2-Anth/H, the corresponding dimers II, III, and IV (Scheme 4) are proposed to account for the oxidation waves observed at -0.927, -0.614, and -0.772 V vs. SCE at 0.1 V s⁻¹, respectively. Rate constants

Table 2. Electrochemical data and dimerization rate constants for anthracene containing azines.

Compound	$E_{\rm p}~({\rm at}~0.2~{\rm V}~{\rm s}^{-1})^a$	$E^{o a}$	$k_{\rm d}~({ m M}^{-1}~{ m s}^{-1})$
1-Fc/Anth	-1.445	-1.437	5.1×10^{4}
2-Anth/H	-1.397	-1.403	1.5×10^{5}
2-Anth/Anth	-1.224	-1.232	3.3×10^{5}
9-Anthraldehyde	-1.203	-1.207	1.8×10^5

^aIn V vs. SCE.

for dimerization (k_d) can be calculated using known procedures (43) and appear in Table 2. The k_d value for 1-Fc/Anth suggests that the electron donating abilities of the ferrocenyl group act to hinder dimer formation. The rates are approximately equal for the remaining anthracenyl azines.

For 1-Fc/Anth, the electrochemical behavior is governed by two independent moieties, namely the ferrocene and the anthracene groups. The ferrocene moiety has the effect of making the anthracenyl unit more difficult to reduce as evidenced by a shift of 0.24 V to more negative potentials relative to 9anthraldehyde. This indicates that some electronic communication must be occurring through the azine unit. A similar situation is observed for 2-Anth/H. The reduction of 2-Anth/Anth also shows evidence for electronic communication. Although the reduction potential of 2-Anth/Anth occurs at the roughly same potential as 9-anthraldehyde, only one electron is involved in the process. One might expect a two-electron wave for 2-Anth/Anth if the azine moiety prevented any communication between the two anthracene units (i.e., reduction of both anthracene units simultaneously, similar to the situation previously observed for 4,4'-dinitroacetophenone azine (39)).

The electrochemical behavior of acetylferrocene and acetylferrocene azine (1-Fc/Fc) was also examined for comparison with the results obtained for the other 1-Fc/Ar. 1-Fc/Fc shows an anodic wave that consists of two oneelectron reversible oxidations that have slightly different oxidation potentials (Fig. 4b). This results in an oxidation wave that is approximately twice the magnitude of the other oneelectron oxidations (Fig. 5) and appears to have a shoulder on the leading edges of the waves. This is consistent with the electrochemistry observed for 1-Fc/Fc by Osborne et al. (2) who estimates the oxidation potentials of the two ferrocene units to be +0.47 V and +0.56 V vs. SCE in 0.2 M TBAP-CH₂Cl₂. 1-Fc/Fc also shows a reduction wave at very negative potential caused by the reduction of the C=N bond of the azine unit. This reduction occurs into the solvent discharge, which makes determining the standard potential difficult. Reduction of a C=N bond at such negative potentials results in the formation of minor electroactive species, which are oxidized on the reverse scan and have similar structure to the parent azine. These products most likely result from reaction of the azine radical anion with H₂O or electrolyte or some reduced form of the electrolyte. Figure 4 illustrates the CVs of 1-Fc/Fc as well as the reference compound, acetylferrocene. The reduction that occurs in the CV of acetylferrocene is the one-electron reduction of the carbonyl group. All electrochemical data is summarized in Table 1.

The Fe^{II}/Fe^{III} couple in the 1-Fc/Y is subject to a substituent effect as indicated by the oxidation potentials of the two model compounds, ferrocene and acetylferrocene (+0.470 V and +0.691 V vs. SCE in DMF, respectively). The

Fig. 4. Cyclic voltammograms of (*a*) acetylferrocene and (*b*) 1-Fc/Fc measured in 0.1 M TEAP–DMF at 0.2 V s⁻¹. Arrows indicate scan direction. Dashed line is the CV in the positive potential region only.



oxidation potentials of the ferrocene unit can be used to probe the effects of adding an azine unit and any possible contribution from the aryl group to the electrochemical behavior of the iron core. The CVs showing the reversible oxidation of 1-Fc/Ar to 1-Fc/Ar⁺⁺ at 0.2 V s⁻¹ are shown in Fig. 5. As expected, the ferrocenyl unit becomes easier to oxidize (less positive potentials) with more electron donating substituents and vice versa. All $E_{\bullet+/0}^{\circ}$ are within 59 mV of each other, indicating only a modest substituent effect on the oxidation. This reinforces the notion of little to no conjugation through the azine unit, producing only small substituent effects, particularly on the Fe core. A more illustrative example of the extent of communication through the azine unit is the oxidation of 1-Fc/Fc that shows two oxidation processes that occur at slightly different potentials. If there was no conjugation through the azine unit, we would expect that the oxidation potentials would be coincidental and that the observed wave would appear as if it were a completely reversible twoelectron reduction process. That is, both ferrocene units would be oxidized simultaneously. Thus the oxidation of 1-Fc/Fc would be similar to the simultaneous double oneelectron reduction of 4,4'-dinitroacetophenone azine (39). Since the oxidation of 1-Fc/Fc appears as two processes at slightly different potentials, there must be some electronic communication through the azine moiety that results in the second oxidation being slightly harder to accomplish (i.e., occurs at more positive potential) than the first.

The heterogeneous rate constants (k_{het}) for electron transfer can be calculated (43, 44) for the compounds investigated and are listed in Table 3. The calculated k_{het} are within the expected range ($10-10^{-3}$ cm s⁻¹) for reversible or quasireversible electrode kinetics. Rate constants for compounds 1-Fc/Fc, 2-Anth/Anth, 2-Anth/H, and 9-anthraldehyde could not

Fig. 5. Cyclic voltammograms of the reversible oxidation waves for the ferrocenyl azines measured in 0.1 M TEAP–DMF at 0.2 V s⁻¹ scan rate: (*a*) 1-Fc/Fc; (*b*) 1-Fc/4-NO₂; (*c*) 1-Fc/Anth; (*d*) 1-Fc/Py; (*e*) 1-Fc/4-CN; (*f*) 1-Fc/Pyrd; and (*g*) 1-Fc/4-OCH₃.



be determined in this way because they do not exhibit suitable reversible waves, a requirement for the calculation.

The 1-Fc/Ar compounds offer the opportunity to calculate the HOMO–LUMO energy gap (listed in Table 3). The energy difference between oxidation and reduction potentials is the HOMO–LUMO energy gap and is an indication of the electron donor–acceptor properties of the compound. The variation of $\Delta E_{\text{HOMO-LUMO}}$ as a function of the substituent (values differ by more than 30 kcal mol⁻¹) illustrates the "fine tuning" possible for azine electronic properties simply by changing the substituent(s) attached to the azine unit.

To further our examination of the electronic nature of azines, the photochemical behavior of a series of azines containing a chromophoric group (specifically anthracene) was investigated. This allowed for the evaluation of the effect of the ferrocene group on the photochemical characteristics of these azines. Azine photochemistry is governed by E/Zisomerization of the azomethine bonds (45-51), which has been shown to be a general property of the 2,3-diaza-1,3butadienes. The photochemistry and photophysics of 2-Anth/Anth has been thoroughly investigated by Appenroth et al. (48–51). **2**-Anth/Anth can exist as three isomers, E/E, E/Z, and Z/Z, where the E/Z and Z/Z isomers can be selectively produced, starting from the thermodynamically stable E/E form, by irradiation with wavelengths $\lambda = 488$ and 436 nm, respectively. It was found that neither of the three isomers fluoresce at room temperature and only the Z/Z isomer fluoresced at 77 K (51). The fluorescence spectrum of (Z/Z)-2-Anth/Anth contained the same structural features as anthracene and its quantum yield of fluorescence in ethanol was determined to be $\Phi_f = 0.090$ using an excitation wavelength of 350 nm at 77 K.

To investigate the luminescent properties, the fluorescence spectra of the anthracenyl-containing azines were recorded

Compound	$E^{\mathbf{o}}_{\boldsymbol{\cdot}+/0} (\mathbf{V})^a$	$E_{0/-}^{o}(\mathbf{V})^{a}$	$k_{\rm het}~({\rm cm~s^{-1}})^b$	$\Delta E_{\rm HOMO-LUMO}$ (kcal mol ⁻¹) ^c
1-Fc/4-NO ₂	0.612	-0.956	$4.9 \times 10^{-2} d$	36.2
2			$5.0 imes 10^{-2} e$	
1-Fc/Anth	0.583	-1.437	$3.1 \times 10^{-2} e$	46.6
1-Fc/Py	0.576	-1.549	1.9×10^{-2} d	49.0
5			$2.5 imes 10^{-2} e$	
2 -Py/H		-1.462	$2.4 \times 10^{-2 d}$	_
1-Pyrenecarboxaldehyde		-1.338	$2.7 imes 10^{-2}$ d	_
1-Fc/4-CN	0.577	-1.645	$1.9 imes 10^{-2}$ d	51.2
			$3.1 \times 10^{-2} e$	
1-Fc/Pyrd	0.579	-1.767	$1.4 imes 10^{-2}$ d	54.1
-			$1.6 \times 10^{-2} \ ^{e}$	
$1-Fc/4-OCH_3$	0.553	-2.158	$1.1 imes 10^{-2}$ d	62.5
2			$2.0 \times 10^{-2} e$	
1-Fc/Fc	0.572	-2.303	_	66.3
Acetylferrocene	0.691	-2.262	$2.4 imes 10^{-2}$ d	68.1
-			$1.3 imes 10^{-2}$ e	

Table 3. Heterogeneous rate constants and HOMO–LUMO energy gap for ferrocenyl and related azines.

^aReported in V vs SCE.

 $^{\textit{b}}\textsc{Average}$ value for scan rates between 0.05 and 0.5 V s $^{-1}.$

"Energy difference between the HOMO and LUMO energy levels determined from electrochemical data.

^dValue calculated for a reduction process.

eValue calculated for an oxidation process.

Fig. 6. The emission spectra of 1-Fc/Anth, 2-Anth/H, and 2-Anth/Anth in EPA at 77 K using a 350 nm excitation wavelength: (*a*) 2-Anth/H; (*b*) (dashed line) 2-Anth/Anth; (*c*) 1-Fc/Anth.



in EPA both at room and low temperature (77 K). Figure 6 shows the fluorescence spectra of **1**-Fc/Anth, **2**-Anth/H, and **2**-Anth/Anth at 77 K. None of the azines showed fluorescence at room temperature, and only weak fluorescence at low temperature when an excitation wavelength of 350 nm was used. Such behavior was observed previously for several different azines including **2**-Anth/Anth (48, 51), where

the E/E isomer was shown to be non-fluorescent. The samples were then exposed to radiation of wavelength 410-490 nm to induce isomerization to the Z/Z isomer and the fluorescence was reexamined. Once again, little to no emission was observed at room temperature. In contrast, the emission intensity at 77 K was dramatically increased, approximately 12-70 times relative to the samples before irradiation. The low-emission intensity at room temperature can be attributed to efficient energy dissipation in the excited state via E/Z isomerization of the azomethine bonds. This isomerization process becomes less important at 77 K with a concomitant enhancement of fluorescence since the azine molecules are now contained in the solid glass of the frozen EPA solution. The emission observed for 1-Fc/Anth, 2-Anth/H, and 2-Anth/Anth contains similar structural features as that of anthracene (52).

Appenroth et al. (51), attributed the observed emission of (Z/Z)-2-Anth/Anth to the anthracene chromophore that is twisted out of the molecular plane of the azine moiety in the Z/Z isomer (53, 54). The twisting results from steric interactions between the azine nitrogen and the anthracene unit. This results in an interruption of any conjugation that may be occurring. The E/Z isomer of 2-Anth/Anth did not show any emission at either temperature despite twisting of one of the anthracene units. The situation is very similar for 1-Fc/Anth and 2-Anth/H. The need for irradiation at 410-490 nm prior to the observation of any emission suggests that the E/E isomers of 1-Fc/Anth and 2-Anth/H, the thermodynamically most stable and initial structures, do not fluoresce and any fluorescence must come from one of the other two isomers. Similar to 2-Anth/Anth, long-wavelength irradiation induces isomerization of the C=N bonds and results in fluorescence not observed for the E/E isomers. Emission from the E/Z or Z/Z isomers of 1-Fc/Anth and 2-

intensities of 1-Fc/Anth,	2-Anth/H and 2-Anth	Anth in EPA at
room temperature and 77	7 K.	
	Before irradiation	After irradiation

Table 4. Quantum yields (Φ_f) and total normalized fluorescence

Azine $\Phi_{\rm f}{}^a$ 77 K 77 K r.t. r.t. 1-Fc/Anth 0.176 0.3 3.4 20 242.1 2-Anth/H 0.042 0.08 5.1 1 58.4 2-Anth/Anth 0.090 0.14 7.2 1.7 123.7

Note: Fluorescence intensities are normalized relative to the area under the room temperature emission curve of **2**-Anth/H after irradiation at 410–490 nm.

^aQuantum yields in EPA at 77 K using 350 nm excitation wavelength relative to that of **2**-Anth/Anth (51). The concentrations of the fluorescence samples were adjusted so that absorption at 350 nm was equivalent.

Anth/H cannot, however, be distinguished since it is unclear whether both C=N bonds need to be in the Z configuration or only the C=N bond nearest the anthracenyl group.

The fluorescence quantum yields (Φ_f) of 1-Fc/Anth and 2-Anth/H were determined by comparison to the $\Phi_{\rm f}$ previously determined for 2-Anth/Anth (51) under similar experimental conditions. The determined quantum yields at 77 K are listed in Table 4 along with the normalized fluorescence intensities. Table 4 shows that, in frozen solution where the isomerization is prevented, the fluorescence of 1-Fc/Anth is twice that of 2-Anth/Anth and four times that of 2-Anth/H. The emission intensity of 2-Anth/Anth is approximately twice that of 2-Anth/H under all conditions owing to the two anthracenyl groups in 2-Anth/Anth compared with one in 2-Anth/H. The fluorescence intensity of 1-Fc/Anth at room temperature after irradiation was significantly higher than the other two azines. This suggests that radiationless deactivation processes are less favoured for 1-Fc/Anth than for 2-Anth/H and 2-Anth/Anth in fluid solution, and that the ferrocene group may in fact hinder the E/Z isomerization that is the main deactivation mechanism at room temperature. In addition, fluorescence quenching by ferrocene does not appear to dominate, either at room temperature or 77 K, in comparison to the observed fluorescence of 2-Anth/H and **2**-Anth/Anth. This suggests that (Z/Z)-**1**-Fc/Anth (or (E/Z)-**1**-Fc/Anth) does not exhibit significant electronic communication between the two azine substituents either by throughbond or through-space interactions since ferrocene is known to be a good fluorescence quencher (15, 55). Any fluorescence observed before irradiation presumably results from minor amounts of E/Z or Z/Z isomers that may be present in the initial solution, formed by thermal processes.

To extend the solid-state analysis of azines, crystals of $1-Fc/4-NO_2$, 1-Fc/4-CN, 1-Fc/Pyrd, and 1-Fc/Anth suitable for X-ray analysis were grown by slow evaporation of a solution of the azine in an appropriate solvent. All C=N bonds are in their *E* configurations as expected. The average Fe—C bond distances of the ferrocene moiety are all similar (2.030–2.040 Å) and fall within the range commonly found for ferrocene compounds (2, 4, 56) but are shorter than those found in ferrocene itself (2.045 Å) (57). This may be due to any of the conjugative effects of the attached azine, which pulls electron density from the cyclopentadienyl ring and results in the shortening of the average Fe—C bond lengths. All the cyclopentadienyl rings are planar (mean deviation of





0.0002-0.0025 Å) and parallel to each other (angle between rings of $0.9-3.5^{\circ}$). The C—C of the cyclopentadienyl rings, N—N, and C=N bond lengths are similar to those determined for other ferrocenyl azines (2, 4, 12).

One striking feature of the determined 1-Fc/Ar structures is the twisting of the molecules through the azine moiety as indicated by >C=N-N=C< dihedral angles of 99.1-160.9° (see Supplementary material). This is in complete contrast with the structure of ferrocenealdehyde-4-nitrobenzaldehyde azine, reported by Houlton and co-workers (12), illustrated in Scheme 5, whose X-ray structure shows an almost complete planarity of the C₅H₄CHNNCHC₆H₄NO₂ fragment to produce an extended π system. The similar azine 1-Fc/4- NO_2 (Scheme 5), which differs only by the addition of two methyl groups, produces a significantly different orientation. This suggests that 1-Fc/Ar should not exhibit any conjugation through the azine unit. The electrochemical results suggest, however, that there is significant conjugative interactions in the 1-Fc/Ar in solution. The twisting of the molecules observed in the solid state, therefore, may not be a good reflection of their orientation in solution and may be caused by packing effects in the solid. The same argument was proposed by Glaser and co-workers (22, 25) to explain the nonplanarity of the acetophenone azines in the solid state.

Conclusions

The electrochemical behavior of the 1-Fc/Ar is governed by the ferrocenyl and aryl group attached to the azine moiety. All the 1-Fc/Ar showed a reversible oxidation between +0.62 and +0.55 V vs. SCE as a function of the aryl substituent. Electron withdrawing groups resulted in more positive oxidation potentials with only a slight substituent effect on the Fe^{II}/Fe^{III} oxidation, as evidenced by the small variation (59 mV) in potentials. The reduction potentials of 1-Fc/Ar were determined and electron donating groups showed more negative reduction potentials, whereas less negative potentials were observed for electron withdrawing substituents. For 1-Fc/Ar, where the aryl group was a substituted benzene ring, the effect of introducing an electron donating ferrocenyl group on azine reduction results in the ferrocene having similar electron donating characteristics as a methoxyphenyl or dimethylaminophenyl group compared with the reduction potentials determined for similar systems (39). The reduction and oxidation potentials determined for 1-Fc/Ar suggest that there is some electronic communication between the two substituents of the azine moiety in comparison with model compounds. Therefore, we suggest that the azine unit does allow for limited conjugation in the 1-Fc/Ar as it did for the acetophenone azines (39). The nonplanarity of the 1-Fc/Ar observed in the solid-state structures, suggesting no conjugation, may not be an accurate reflection of their orientation in solution.

The photochemistry of 1-Fc/Anth, 2-Anth/Anth, and 2-Anth/H is governed by E/Z isomerization processes and no emission is observed for these compounds either at room temperature or at 77 K. Fluorescence at 77 K is observed after long wavelength irradiation where the thermodynamically most stable E/E isomer is converted to the E/Z and Z/Zisomers from which emission occurs. Any conjugative interactions in the E/E isomer is interrupted upon formation of the E/Z or Z/Z isomer, allowing for fluorescence of the anthracenyl group. The ferrocenyl group in 1-Fc/Anth has only a slight effect on the anthracenyl fluorescence, enhancing it relative to 2-Anth/Anth and 2-Anth/H, and no evidence for intramolecular or inductive quenching by ferrocene was observed under the experimental conditions. The donor-acceptor properties of ferrocenyl azines, however, can be easily manipulated by altering the aryl substituent on the azine unit, making them good candidates for materials applications.

Experimental

Materials

All chemicals used were purchased from Aldrich and used as received unless otherwise stated. For electrochemical experiments only, acetylferrocene, 9-anthraldehyde, and 1pyrenecarboxaldehyde were recrystallized from suitable solvents prior to use. N,N-dimethylformamide(DMF) was distilled under reduced pressure over calcium hydride prior to use. Argon was flushed over the DMF during the transfers into the electrochemical cells. Tetraethyl ammonium perchlorate (Kodak) was recrystallized three times and dried under vacuum at 60°C prior to use and stored in a vacuum dessicator. Ferrocene was sublimed once before use. NMR spectra, recorded on a Varian Gemini 300 MHz (300.075 MHz for ¹H and 75.462 MHz for ¹³C) or Varian Mercury 400 MHz instrument (400.0854801 MHz for ¹H and 100.6015500 MHz for ¹³C), are herein referred to as 300 or 400 MHz for ¹H and 75 or 100 MHz for ¹³C. All chemical shifts are reported in parts per million downfield from tetramethylsilane. Melting points were recorded using a Gallenkamp melting point apparatus and are uncorrected. IR data was recorded on a PerkinElmer System 2000 FT-IR. Mass spectra analysis was performed with a Finnigan MAT 8200 mass-data system. Gas chromatography analysis was performed on a Hewlett-Packard 5890 Series II gas chromatograph equipped with a 10 m HP5 column and an FID detector. UV-vis data were collected on a Varian Cary 100 spectrometer. Fluorescence spectra were recorded using an ISA Spex 3 Fluorimeter.

Electrochemistry — cyclic voltammetry

Experiments were performed using either a Princeton Applied Research (PAR) 283 or 263 potentiostat interfaced to a personal computer. PAR M270 software was used to conduct the experiments as well as analyze the derived data. Measurements were conducted in an all-glass cell kept at 25°C. All glassware was predried in an oven and assembled, hot while flushing with argon. The working electrode was glassy carbon (Tokai) and the counter electrode was a platinum flag. The

reference electrode was a silver wire housed in a glass tube sealed with a porous ceramic tip and filled with a 0.1 M solution of tetraethylammonium perchlorate (TEAP). The same reference electrode was used in all experiments. Concentrations of 2 mM of azine in 0.1 M TEAP in DMF were used. Ferrocene, tetracyanoethylene, or 4-nitroacetophenone azine (39) were used in all experiments as internal references to a saturated calomel electrode ($E^{\circ} = 0.470, -0.319,$ and -0.973 V vs. SCE in DMF, respectively). Positive feedback IR compensation was used in all experiments to minimize the effects of uncompensated solution resistance.

Fluorescence

Fluorescence spectra were recorded on an ISA Spex 3 Fluorimeter interfaced to a personal computer. EPA (2:5:5 mixture of ethanol - diethyl ether - isopentane) was prepared from spectroscopic grade solvents and stored in a tightly sealed bottle. Azine solutions were prepared by dissolving the appropriate amount of azine in EPA so that the UV-vis absorbance at 350 nm was the same for all samples and kept below 0.07. Samples were kept in the dark as much as possible during preparation, transport, and storage. Azine solutions were then placed in quartz tubes, purged with argon gas to remove oxygen and sealed with a rubber septa. The samples were placed in the fluorimeter inside a low-temperature sample holder filled with liquid nitrogen (the same samples and apparatus was used for room temperature spectra but without the liquid nitrogen). The samples were checked for any cracks in the frozen solvent and the fluorescence or excitation spectra were recorded. Samples were removed from the liquid nitrogen and allowed to warm to room temperature between runs. Any condensation that accumulated on the tubes during the warming process was removed before immersing into the liquid nitrogen again. The liquid nitrogen was frequently changed in the sample holder to remove interference from ice particles which form at the nitrogen-air interface. Photolysis with light of wavelength 410–490 nm was performed using the setup described below for the long wavelength photolysis. The fluorescence samples were irradiated in the same quartz tubes used for recording the spectra and placed back in the fluorimeter. The samples were irradiated until no increase in the cold emission intensity was observed, approximately 4 h.

Long wavelength photolysis

Photolysis with light of wavelength 410–490 nm was performed using a high-pressure mercury lamp surrounded by a filter solution of $CuSO_4 \cdot 5H_2O$ (2.7 M NH₃) and NaNO₂ (58) in a quartz reaction chamber. Photolysis was performed on the fluorescence samples whose preparation is described above.

Synthesis of acetylferrocene azines (1-Fc/Ar)

The symmetric azines 1-Fc/Fc and 2-Anth/Anth were synthesized according to a prescribed procedure and the spectral characterization and other physical data matched that previously reported (2, 59). The asymmetrical azines were synthesized by adding the appropriate substituted ketone or aldehyde (1 equiv) to the corresponding acetylferrocene (diethoxyphosphinyl) hydrazone (1 equiv) in benzene–NaH (1.3 equiv). Both the preparation of the acetylferrocene (diethoxyphosphinyl) hydrazone and azine were prepared according to the published procedures (22, 39).

Preparation of diethyl phosphorohydrazidate

Hydrazine hydrate (20 equiv) was added dropwise to a stirred solution of anhydrous K_2CO_3 (15 equiv) and triethylbenzyl ammonium chloride (0.1 equiv) in CCl_4 – CH_2Cl_2 (4:7) at 20–25°C. A solution of diethylphosphite (1 equiv) in CH_2Cl_2 was then added at 20–30°C. The stirring was continued for 6 h after which the K_2CO_3 crystals were filtered off and rinsed with CH_2Cl_2 . The solvents were removed and the residue was kept under high vacuum for several hours. The resultant pale yellow liquid was used without further purification.

Preparation of acetylferrocene(diethoxyphosphinyl)hydrazone

Diethyl phosphorohydrazidate (1 equiv) and acetylferrocene were dissolved in benzene and heated at reflux for 5 h. The benzene was removed by rotary evaporation to yield a crystalline sample. The solid was then purified by recystallization from hexanes-benzene (2:1). The purity of the sample was verified by GC and NMR.

Acetylferrocene azine (1-Fc/Fc) (2)

mp 234–235°C. ¹H NMR (300 MHz, $CDCl_3$) δ : 2.16 (s, 6H), 4.17 (s, 10H), 4.34 (t, 4H), 4.71 (t, 4H). Anal. calcd. for xxxx: 452.0637; found: 452.0632.

9-Anthraldehyde azine (2-Anth/Anth) (60)

mp 273–275°C. ¹H NMR (300 MHz, CDCl₃) &: 7.60 (m, 4H), 8.09 (d, 2H), 8.60 (s, 1H), 8.80 (br d, 2H), 10.15 (br s, 1H). Anal. calcd. for $C_{30}H_{20}N_2$: 408.1626; found: 408.1621.

The following are, to the best of our knowledge new compounds or the complete spectral data has not yet been reported. X-ray crystallographic data is also available for some 1-Fc/Ar.

Acetylferrocene(diethylphosphinyl)hydrazone

¹H NMR (300 MHz, CDCl₃) δ: 1.36 (dt, 6H), 2.05 (s, 3H), 4.18 (m, 11H), 4.55 (m, 2H), 6.35 (br d, 1H).

Acetylferrocene-4-nitroacetophenone azine (1-Fc/4-NO₂)

mp 178–180°C. UV–vis (DMF) λ_{max} (nm) (ϵ , M⁻¹ cm⁻¹): 323 (21 170). FT-IR (CCl₄, cm⁻¹): 3105, 3080, 2920, 1592, 1512, 1342, 855, 821. ¹H NMR (300 MHz, CDCl₃) & 2.23 (s, 3H), 2.38 (s, 3H), 4.23 (s, 5H), 4.45 (t, 2H), 4.81 (t, 2H), 8.05 (d, 2H), 8.27 (d, 2H). ¹³C NMR (75 MHz, CDCl₃) & 161.75, 155.95, 148.15, 144.58, 127.26, 123.54, 82.56, 70.55, 70.45, 69.55, 69.25, 67.75, 67.65, 15.95, 14.95. MS *m*/*z* (%): 389 (M⁺, 100), 324 (9), 270 (18), 185 (31), 121 (31). Anal. calcd. for C₂₀H₁₉N₃O₂Fe: 389.0826; found: 389.0827.

Acetylferrocene-4-cyanoacetophenone azine (1-Fc/4-CN)

mp 156–157°C. UV–vis (DMF) λ_{max} (nm) (ϵ , M⁻¹ cm⁻¹): 296 (25 050). FT-IR (CCl₄, cm⁻¹): 3100, 2960, 2924, 1603, 1573, 1563, 1476, 1364, 1292, 1131, 1106, 1017. ¹H NMR (300 MHz, CDCl₃) δ : 2.20 (s, 3H), 2.31 (s, 3H), 4.19 (s, 5H), 4.40 (t, 2H), 4.74 (t, 2H), 7.68 (d, 2H), 7.97 (d, 2H). ¹³C NMR (75 MHz, CDCl₃) δ : 161.50, 156.15, 142.82, 132.09, 121.04, 118.81, 112.60, 82.89, 70.57, 69.62, 67.88, 15.99, 14.81. MS m/z (%): 369 (M⁺, 100), 304 (15), 185 (57), 129 (29), 121 (37). Anal. calcd. for $C_{21}H_{19}N_3Fe$: 369.0928; found: 369.0825.

Acetylferrocene-4-methoxyacetophenone azine $(1-Fc/4-OCH_3)$

This compound was prepared by adding acetylferrocene (1 equiv) to the corresponding *p*-methoxyacetophenone (diethoxyphosphinyl)hydrazone (1 equiv) (22, 39) in refluxing benzene containing NaH (1.3 equiv). A small amount of product was then isolated by preparative HPLC. ¹H NMR (300 MHz, CDCl₃) & 2.18 (s, 3H), 2.27 (s, 3H), 3.84 (s, 3H), 4.22 (s, 5H), 4.40 (br s, 2H), 4.77 (br s, 2H), 6.92 (d, 2H), 7.83 (d, 2H). MS m/z (%): 379 (M⁺, 100), 309 (28), 185 (11), 121 (18). Anal. calcd. for C₂₁H₂₂N₂OFe: 347.1081; found: 347.1084.

Acetylferrocene-9-anthraldehyde azine (1-Fc/Anth)

mp 169–170°C. UV–vis (DMF) λ_{max} (nm) (ϵ , M⁻¹ cm⁻¹): 266 (59 070). FT-IR (CCl₄, cm⁻¹): 3087, 3054, 2926, 2854, 1606, 1474, 1384, 1362, 1292, 1107, 1003, 909. ¹H NMR (300 MHz, CDCl₃) δ : 2.54 (s, 3H), 4.46 (s, 5H), 4.47 (t, 2H), 4.84 (t, 2H), 7.53 (m, 4H), 8.03 (d, 2H), 8.52 (s, 1H), 8.79 (d, 2H), 9.66 (s, 1H). ¹³C NMR (75 MHz, CDCl₃) δ : 156.63, 131.44, 130.64, 130.08, 128.93, 126.86, 125.43, 125.32, 70.80, 70.63, 69.56, 68.11, 16.76. MS *m*/*z* (%): 430 (M⁺, 100), 365 (66), 324 (20), 203 (31), 185 (29), 121 (64). Anal. calcd. for C₂₇H₂₂N₂Fe: 430.1132; found: 430.1137.

Acetylferrocene-1-pyrenecarboxaldehyde azine (1-Fc/Py)

mp 178–179°C. UV–vis (DMF) λ_{max} (nm) (ϵ , M⁻¹ cm⁻¹): 380 (34 460). FT-IR (CCl₄, cm⁻¹): 3099, 3049, 2984, 2962, 2927, 1742, 1607, 1475, 1361, 1291, 1242, 1107. ¹H NMR (300 MHz, CDCl₃) & 2.58 (s, 3H), 4.30 (s, 5H), 4.47 (br s, 2H), 4.84 (br s, 2H), 8.15 (m, 7H), 8.71 (d, 1H), 8.93 (d, 1H), 9.49 (br s, 1H). ¹³C NMR (75 MHz, CDCl₃) & 156.48, 148.01, 132.86, 131.30, 130.66, 130.07, 128.69, 128.56, 127.63, 127.48, 126.22, 126.16, 125.88, 125.68, 125.00, 124.62, 123.06, 70.84, 69.58, 68.06, 16.55. MS *m*/*z* (%): 454 (M⁺, 100), 389 (31), 348 (12), 227 (27), 201 (18), 185 (18), 129 (21), 121 (40). Anal. calcd. for C₂₉H₂₂N₂Fe: 454.1132; found: 454.1139.

Acetylferrocene-4-acetylpyridine azine (1-Fc/Pyrd)

mp 123–124°C. UV–vis (DMF) λ_{max} (nm) (ε, M⁻¹ cm⁻¹): 285 (21 700). FT-IR (CCl₄, cm⁻¹): 3100, 3089, 3038, 2959, 2923, 1608, 1475, 1409, 1364, 1291, 1122, 1107, 1065, 1019, 1002, 889. ¹H NMR (300 MHz, CDCl₃) δ: 2.19 (s, 3H), 2.38 (s, 3H), 4.19 (s, 5H), 4.40 (br s, 2H), 4.74 (br s, 2H), 7.72 (br s, 2H), 8.66 (br s, 2H). ¹³C NMR (75 MHz, CDCl₃) δ: 161.26, 155.75, 150.08, 145.67, 120.63, 71.04, 70.44, 69.39, 67.67, 15.98, 14.44. MS *m/z* (%): 345 (M⁺, 100), 280 (18), 185 (38), 121 (20). Anal. calcd. for C₁₉H₁₉N₃Fe: 345.0928; found: 345.0932.

Acetophenone-9-anthraldehyde azine (2-Anth/H)

This compound was prepared by adding 9-anthraldehyde (1 equiv) to acetophenone (diethoxyphosphinyl)hydrazone (1 equiv) (39) in refluxing benzene containing NaH (1.3 equiv). mp 95–97°C. UV–vis (EPA) λ_{max} (nm) (ϵ , M⁻¹ cm⁻¹): 257 (105 700). FT-IR (CCl₄, cm⁻¹): 3086, 3055, 3031, 1624, 1611, 1519, 1453, 1444, 1364, 1294, 1021, 889. ¹H NMR

(400 MHz, CDCl₃) & 2.65 (s, 3H), 7.52 (m, 7H), 8.03 (m, 4H), 8.54 (s, 1H), 8.79 (d, 2H), 9.71 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) & 165.47, 157.86, 138.27, 131.37, 130.65, 130.37, 130.26, 128.99, 128.51, 127.05, 127.00, 125.77, 125.36, 125.27, 15.95. MS m/z (%): M⁺, 322 (76), 204 (100), 177 (56), 118 (18), 77 (66). Anal. calcd. for C₂₃H₁₈N₂: 322.1472; found: 322.1470.

Acetophenone-1-pyrenecarboxaldehyde azine (2-Py/H)

This compound was prepared by adding 9-anthraldehyde (1 equiv) to acetophenone (diethoxyphosphinyl)hydrazone (1 equiv) (39) in refluxing benzene containing NaH (1.3 equiv). mp 115–117°C. UV–vis (DMF) λ_{max} (nm) (ϵ , M⁻¹ cm⁻¹): 380 (41 500). FT-IR (CCl₄, cm⁻¹): 3084, 3050, 1610, 1580, 1496, 1444, 1364, 1294, 1235, 1185, 850. ¹H NMR (400 MHz, CDCl₃) & 2.68 (s, 3H), 7.47 (m, 3H), 8.08 (m, 5H), 8.22 (m, 4H), 8.72 (d, 1H), 8.94 (d, 1H), 9.52 (br s, 1H). ¹³C NMR (100 MHz, CDCl₃) & 165.30, 157.61, 138.39, 133.11, 131.25, 130.61, 130.22, 130.18, 128.86, 128.78, 128.49, 127.44, 127.19, 126.99, 126.42, 126.21, 126.03, 125.81, 124.99, 124.96, 124.59, 122.90, 15.77. MS *m/z* (%): 346 (M⁺, 100), 227 (47), 201 (80), 145 (20), 119 (9), 77 (30). Anal. calcd. for C₂₅H₁₈N₂: 346.1470; found: 346.1465.

X-ray crystallography

Single crystals of 1-Fc/4-NO₂, 1-Fc/4-CN, 1-Fc/Pyrd, and 1-Fc/Anth were grown by slow evaporation of a concentrated solution of the azine in an appropriate solvent. Crystals were mounted on a glass fibre. Data were collected on a Nonius Kappa-CCD diffractometer using COLLECT (Nonius, 1998) software. The unit cell parameters were calculated and refined from the full data sets. Crystal cell refinement and data reduction was carried out using the Nonius DENZO package. The data were scaled using SCALEPACK (Nonius, 1998) and no other adsorption corrections were applied. The SHELXTL 5.1 (Sheldrick, G.M., Madison, WI) program package was used to solve the structures by direct methods, followed by successive difference Fouriers. All nonhydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were calculated geometrically and were riding on their respective carbon atoms. The crystal data for the structures determined in this report are reported in the Supplementary material.²

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²Supplementary material may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada. For information on obtaining material electronically go to http://www.nrc.ca/cisti/irm/unpub_e.shtml. Crystallographic information has also been deposited with the Cambridge Crystallographic Data Centre (CCDC Nos. 178709, 178710, 178711, 178712). Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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