Synthesis, crystal structures and electrochemical properties of ferrocenyl imidazole derivatives

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ABSTRACT

Six ferrocenyl imidazole derivatives substituted with -Cl, -NO₂ and -CH₃ on the 2-position of the 1H-imidazole ring have been synthesized. Of the six compounds, the di-substituted ferrocenes, i.e. compounds 4 (1,1'-ferrocenylmethyl(2-chloroimidazole)), 5 (1,1'-ferrocenyl(2-nitroimidazole)), and 6 (1,1'-ferrocenylmethyl(2-methylimidazole)) are reported for the first time. The structure-property relationships of compounds 4, 5 and 6 were investigated by means of UV-visible, FTIR, ¹H-NMR, ¹³C-NMR spectroscopy and electrochemical studies. UV-visible analysis in acetonitrile showed that the π → π* band of compounds 2 (1-ferrocenylmethyl(2-nitroimidazole)) and 5 appeared at longer wavelength compared to 1 (1-ferrocenylmethyl(2-chloroimidazole)), 3 (1-ferrocenylmethyl(2-methylimidazole)), 4 and 6. This phenomenon is due to the different electronics around the imidazole moieties. In cyclic voltammetry analysis, all compounds exhibited a quasi-reversible redox wave for the ferrocenyl and imidazole moieties. Density functional theoretical (DFT) calculations with the B3LYP/6-311+G(d) basis set were performed on compounds 1-6, and the calculated HUMO-LUMO band gap energies correlated with those obtained from electrochemical and spectroscopic data. The X-ray crystallographic analysis highlighted the effect of electron-withdrawing and electron-donating substituents on the conformation of the cyclopentadienyl rings attached to the ferrocenyl moiety.

1. Introduction

Ferrocenyl derivatives bearing heteroatoms, such as N, P and S, have been of great importance in organometallic chemistry. The synthesis of compounds containing the ferrocenyl unit with various acceptor units such as pyrrole [1], indole [2], thiourea [3], pyridine [4] and imidazole [5] have been previously reported. These particular ferrocenyl derivatives have potential applications in fields such as electrochemistry [6], medicinal science [7], nonlinear optics [8] and materials science [9, 10]. Ferrocenyl alkyl azoles have received considerable attention as a result of the unusual properties of the ferrocene system, and this is due to its unique steric protection, electron-donation properties and chemical stability [11]. The design and fabrication of series of donor-acceptor systems are increasing due to their use in the preparation of optoelectronic materials [16]. The photonic and electronic properties of the donor-acceptor system can be fine-tuned by varying the acceptor, donor or spacer strength [17].

Several synthetic approaches have been exploited for the synthesis of ferrocenylalkyl azoles. Mono- and di-substituted ferrocenyl compounds with N-heterocyclic groups, such as ferrocenylmethylbenzimidazole, have been reported [18]. Ferrocenylmethyl benzimidazole has been prepared according to the classical method, i.e. from the reaction of thionylidibenzenimidazole and ferrocenylmethanol in dichloromethane [19], 1-Ferrocenylethyl benzotriazole has also been synthesized by using 1-ferrocenylethanol and benzotriazole in dichloromethane in the presence of aqueous fluoroboric acid at room temperature [20]. An alternative approach for the synthesis of ferrocenylalkyl imidazoles has been proposed with the use of N,N'-carbonyldiimidazole (CDI) [16]. For example, 1,1'-bis(imidazolylmethyl)ferrocenes have been synthesized by the reaction of diferrocenemethanol with CDI [21] or phosphorous tri-bromide [5]. Simenel et al. [22] reported a simple method for the synthesis of ferrocenyl(alkyl)imidazoles. This method involves the treatment of ferrocenylcarbinols with CDI in methylene dichloride. Additionally, N,N'-diferrocenylimidazol(in)ium salts have been synthesized by condensation of N,N'-diferrocenylimidazolabutadiene with formaldehyde [23]. The electrochemical behaviour of a range of ferrocenylalkyl azoles has been studied and the compounds were found to have low reduction potentials [24, 25]. The oxidation potentials (Eox) for substituted ferrocenylalkyl azoles have been found to be markedly dependent on the degree of...
electron-accepting or electron-donating properties of the lateral substituents [26].

In terms of applications, a number of ferrocenyl imidazole salt derivatives ferrocenyl imidazole salts, have been utilized in various applications. For example, ferrocenylalkyl imidazole salts have been found to play a vital role in many biological systems such as metallo-proteins [27] and anticancer drugs [18]. Ferrocenyl compounds connected to an imidazole ring, such as ferrocenylethyl-N’-(trimethylphenyl)imidazole chloride have been found to show antimicrobial activity [28]. Substituted ferrocenyl imidazoles have also been employed as the catalyst for the synthesis of nitrogen-doped carbon nanotubes (N-CNTs) and N-CNT-metal nanocomposites [11, 29]. These compounds have produced derivatives ferrocenyl imidazole salts, have been utilized in various applications, and -NO2 substituted ferrocenyl imidazole compounds. The synthesis of derivatives ferrocenyl imidazole salts, have been utilized in various applications, and -NO2 substituted ferrocenyl imidazole compounds. The synthesis of ferrocenemethanol and 1,1-diferrocenemethanol for the synthesis of compounds 1–6 is an orange solid, while 1,1'-ferrocenyl(methyl)imidazole [36].

The resonance peaks of the unsubstituted ferrocenes and the substituted ferrocenes occur as a singlet between 4.12-4.23 ppm and as a triplet between 4.22-4.77 ppm, respectively [37]. The peak for C3-H was observed to be more downfield, i.e. 5.34 ppm for 2 and 5.38 ppm for 5, and this due to the electron-withdrawing inductive effect from the -NO2 substituent (Fig. 1 and Scheme 1).

The appearance of a FTIR absorption band between 1248-1360 cm⁻1 was observed in all compounds. This peak marked the appearance of the C-N absorption band while the O-H bands of the starting ferrrocenyl alcohols disappeared. The most important frequencies for the ferrocene moiety are found at 481–510 (νFe-Cp), 821–831 (νC-H), 1440 cm⁻¹ (νC=C) and 3382–3113 cm⁻¹ (νC=O) [37].

2.2. Crystal structures

Crystals of compounds 4 and 5 were grown in a dichloromethane-hexane solution. ORTEP drawings of these compounds together with the atom numbering schemes, are shown in Fig. 3. Selected bond angles and bond lengths for compounds 4 and 5 are listed in Table 2. The asymmetric unit of compound 4 contains one molecule while for compound 5 it contains half a molecule with the other half generated by the inversion centre on the Fe atom. The Cp rings in compound 5 adopt a perfect anti-conformation with a staggering angle of 35.82(4)°. In

Table 1

| Compound | ¹H-NMR (ppm) | ¹³C-NMR (ppm) |
|----------|--------------|---------------|
|          | C3-H | C5/C6-H | C3 | C4 | C5/C6 |
| 1*       | 4.75 | 6.78/6.81 | 81.81 | 120.65 | 127.93/131.22 |
| 2*       | 5.34 | 6.92/7.01 | 80.15 | 144.47 | 124.87/128.04 |
| 3*       | 4.73 | 6.76/6.84 | 82.78 | 144.47 | 124.87/128.04 |
| 4        | 4.76 | 6.85/6.89 | 82.87 | 131.22 | 128.15/130.87 |
| 5        | 5.38 | 7.15/7.66 | 81.57 | 124.97 | 128.23/128.25 |
| 6        | 4.76 | 6.77/6.82 | 83.66 | 143.92 | 128.79/132.46 |

* Values taken from ref [29].
compound 4, the Cp rings of the ferrocene units are slightly twisted from the ideal eclipsed conformation with C-centroid-centroid-C torsion angles of 11.46(8)°. The Cp rings in compound 4 were slightly tilted by an average angle of 2.25(3)°.

The N-C-N imidazole angles are 121.25° (N1-C13-N2) and 113.96° (N1-C7-N2) in compounds 4 and 5, respectively; and are larger than the values for imidazole salts (107.6–108.7°) reported by Gao et al. [22]. This increase in bond angle could be attributed to the electron-withdrawing effect of the -Cl and -NO2 substituents on the imidazole rings [38, 39].

In compound 4, the dihedral angles between the planes of the substituted Cp rings and the imidazole ring plane are 65.58(5)° and 67.28(2)°, respectively, while in compound 5, the dihedral angles are equal with a value of 71.46° (4). This slight change in the dihedral angle is probably due to the steric effect of the substituents on the imidazole moiety and the Cp rings [40]. The crystallographic data and structural refinement parameters for compounds 4 and 5 are shown in Table 3.

2.3. UV-visible absorption spectroscopic studies

The absorption spectra for compounds 1–6 are shown in Fig. 4 and the relevant absorption characteristics are given in Table 4. The spectra obtained in acetonitrile show bands at approximately 328 and 438 nm. The bands at 328 nm represent π-π* transitions from the ferrocenyl to the imidazole moiety, while the bands at 438 nm are ascribed to d-d transitions, probably mixed with d-π* transitions [41]. There is a shift of the π-π* band of compounds 2 and 5, at 328 nm bathochromically to 331 nm, attributed to the stronger electron-withdrawing effect of the nitro group on the imidazole moiety [42, 43]. This shift could also be attributed to the strong electronic communication between the enriched imidazole and ferrocenyl moieties [44].

In order to establish the solvatochromic behaviour of compounds 1, 3, 4 and 6, absorption studies were carried out in different solvents, that is, dimethylformamide (DMF) (polar aprotic), methanol (polar protic), acetonitrile (polar aprotic) and dichloromethane (DCM) (mid-polar aprotic). In all compounds, two bands (d-d transition and charge transfer (CT)) are observed. The data obtained are summarized in Table 5. CT transitions usually display a large solvent-dependent effect [45], resulting in negative solvatochromism as observed in methanol and DMF when compared with DCM (Fig. 5). This could be attributed to possible hydrogen-bonding between the compounds and the polar solvent molecules. It was found that the CT absorption band in compounds 1, 3, 4 and 6 is the same in all solvents; however, a red shift in the π-π* absorption band was observed upon a change in solvent polarity with compound 1 (showing the most significant shift from λmax ≈ 320 nm methanol/DMF to DCM) (Fig. 5). Thus, the electron-withdrawing and electron-donating substituents influenced the dipole-dipole interactions between the compounds and solvents [46]. Similar behaviour has been reported for ferrocenyl imidazole derivatives [47].

2.4. Electrochemical studies

Electrochemical studies of compounds 1–6 were performed in acetonitrile, with NaClO4 (0.5 M) as the supporting electrolyte, at a scan rate of 100 mV/s. Fig. 6 shows the cyclic voltammograms (CV), while the corresponding electrochemical data are presented in Table 6. The CV of the substituted ferrocenylimidazole compounds exhibit the electrochemical oxidation wave of the ferrocene/ferrocenium ion, and this is coupled with a quasi-reversible peak. Compounds 1–6 show one fully or
Fig. 2. $^{13}$C-NMR of compounds (a) 4 (b) 5 and (c) 6.

Fig. 3. ORTEP diagrams, along with the atom-numbering scheme for compounds (a) 4 and (b) 5. The thermal ellipsoids are depicted at 50% probability.
Table 2
Selected bond lengths (Å) and angles (°) for compounds 4 and 5.

|        | 4            | 5            |
|--------|--------------|--------------|
| C(1)-C(11) | 1.50(2)      | 1.496(2)     |
| C(11)-N(1)   | 1.46(8)      | 1.487(8)     |
| N(2)-C(13)-N(1) | 114.0(8)    | 121.7(14)    |
| N(1)-C(11)-C(1) | 112.2(8)    | 132.0(13)    |
| C(1)-C(11)-C(6) | 79.4(2)      | 180.0(13)    |
| C(1)-C(2)-C(4) | 108.1(13)   | 108.13(14)   |
| C(2)-Fe(1)    | 2.04(14)     | 2.042(6)     |
| C(5)-Fe(1)    | 2.034(14)    | 2.036(15)    |

Table 3
Crystallographic data and structural refinement parameters for compounds 4 and 5.

| Compounds | 4            | 5            |
|-----------|--------------|--------------|
| Empirical formula | C18H16Cl2FeN4 | C18H16FeN6O4 |
| Formula weight | 411.07       | 436.22       |
| T(K)       | 173(2)       | 100(2)       |
| λ (Å)      | 0.71073      | 0.71073      |
| Space group | Monoclinic   | Monoclinic   |
| Unit cell dim. (Å/°) | P2₁/a       | C2/c         |
| β          | 102.9480(10) | 102.539(2)   |
| α          | 8.5123(3)    | 10.9972(3)   |
| b          | 15.7406(6)   | 7.5371(2)    |
| c          | 13.1687(5)   | 21.7860(7)   |
| V(Å³)      | 1719.59(11)  | 1762.78(9)   |
| Z          | 4            | 4            |
| σ (Mg/m³)  | 1.588        | 1.644        |
| ρ (g/cm³)  | 1.195        | 0.897        |
| F(000)     | 832          | 896          |
| Crystal size (mm³) | 0.326 x 0.319 x | 0.220 x 0.160 x |
| 0 range (°) | 2.047 – 27.461 | 1.915 – 28.321 |
| Index ranges | -10 ≤ h ≤ 10 | -11 ≤ h ≤ 14 |
|            | -20 ≤ k ≤ 9  | -9 ≤ k ≤ 9   |
|            | -16 ≤ l ≤ 16 | -29 ≤ l ≤ 26 |
| Reflections collected | 22847       | 8361         |
| Independent reflections | 3288       | 2173         |
| Completeness to θ %/°) | s            | 99.9 (25.242) |
| Data/restrs/para | 3288/0/226  | 2173/0/133   |
| GOOF on I²   | 1.073        | 1.035        |
| Final R indices, R₁, wR₂ [I > 2σ(g)] | 0.0289, 0.0811 | 0.0299, 0.0734 |
| R indices (all data), R₁, wR₂ | 0.0305, 0.0824 | 0.0400, 0.0793 |
| Largest diff. peak & hole | eÅ⁻³ | eÅ⁻³ |

Table 4
UV-visible absorption characteristics of compounds 1-6.

| Compounds | λmax/nm | (molar absorptivity/mol⁻¹ cm⁻¹) |
|-----------|---------|--------------------------------|
| d-d        | n-x     |
| 1          | 438 (174) | 328 (89) |
| 2          | none    | 331 (236) |
| 3          | 438 (138) | 328 (142) |
| 4          | 433 (173) | 328 (141) |
| 5          | none    | 331 (241) |
| 6          | 437 (172) | 328 (249) |

Table 5
Absorption wavelengths of ferrocenyli imidazole derivatives in DCM, methanol, DMF and acetonitrile.

| Compounds | λmax/nm (molar absorptivity/mol⁻¹ cm⁻¹) |
|-----------|--------------------------------|
| DCM       | Methanol              | DMF     | Acetonitrile |
| 1          | none            | 438    | 440 | 438 |
| 2          | 334             | 321    | 321 | 331 |
| 3          | 328             | 327    | 327 | 331 |
| 4          | 436             | 436    | 428 | 428 |
| 5          | none            | none   | none | none |
| 6          | 332             | 327    | 327 | 331 |

Fig. 4. UV-visible spectra of 0.005 M solutions of 1-6 in acetonitrile.

Fig. 5. UV-visible spectra of 0.005 M solutions of compound 1 in DMF, acetonitrile, methanol and DCM.

partially reversible one-electron oxidation and one or two quasi-reversible reductions for the imidazole acceptor moieties. The ferrocenyli moieties in compounds 1-6 show larger Epa values than free ferrocene. The Epa values follow the order: 5 > 4 > 2 > 3 > 1 > 6, which can be related to the effect of the substituents on the redox potential of the compounds and, subsequently, the electron transfer process. Compounds 1-6 gave ipa/ipc ratios of approximately 1. As expected, the introduction of electron-withdrawing -Cl and -NO2 substituents led to a more positive shift in the redox potential [48].

The CV curves of compounds 2 and 5 showed poorly resolved ferrocene-based waves (Fig. 6a and b). Probably the use of a coordinating solvent (i.e. acetonitrile) masked irregular features of the CV curves for compounds 2 and 5. The two observed waves for compounds 1, 3, 4 and 6 are associated with the typical symmetrical dimers which produce a mixed valent transition upon reduction or oxidation. Reductions
The molecular orbitals considered were the second highest (HOMO-1) and highest (HOMO) occupied once and the lowest (LUMO) and second-lowest (LUMO+1) unoccupied ones. Fig. 7 shows the frontier molecular orbitals (HOMO and LUMO) of compound 5. Generally, the systems are characterized by relatively low energies for LUMO and LUMO+1 (Table 7). It is evident from Fig. 7 that, in compound 5, the LUMO resides in the imidazole moiety while the HOMO is intense on the ferrocene ring. The high energies obtained for HOMO and HOMO-1 reflect the ability of electron donation (53). Compound 3 has the highest HOMO and HOMO-1 values (-0.171 eV and -0.172 eV, respectively, Table 7), and this is due to the effect of the electron-donating group on the imidazole moiety, which increases the orbital energies of the ferrocenyl receptor (54). These results indicate that more energy is involved during the electron transition in the HOMO relative to LUMO. The difference between $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$ yields the band gap energy ($\Delta E$), which is an important stability index (55). A smaller band gap is a measure of greater prospect for transfer of electrons within a given system (56). Compounds 2 and 5 gave the smallest band gap energies of 0.073 and 0.085 eV, respectively (Table 7). The HOMO–LUMO energy gaps of compounds 1–6 was found to approximately agree with the band gap energies calculated from the electrochemical (Table 7). As illustrated in Fig. 7, excitation from lower to lowest unoccupied orbital reflects a localized density on the functional groups while the electrons are highly occupied in the parent (ferrocene) moiety. The results obtained in Table 7 indicated that the $\Delta E$ corresponds to CT transitions in all the compounds.

3. Conclusion

Novel ferrocene derivatives, namely of compounds 4–6, were synthesized and characterized. The single crystal X-ray crystallographic analysis of compounds 4 and 5 showed the preferred solid-state conformation and symmetry of the di-substituted ferrocenyl moiety. The electrochemical behaviour of the compounds was studied by cyclic voltammetry which shows one fully or partially reversible one-electron oxidation and one or two quasi-reversible reductions for the imidazole acceptor moieties with band gaps similar to those obtained from DFT calculations. The electron transfer process and redox behaviour of compounds 1–6 are affected by the electron-donating and withdrawing substituent on the imidazole moiety. Thus, the optical and electronic properties of the synthesized compounds can be fine-tuned by changing the substituent groups on the imidazole ring.

4. Experimental

2-Nitro-1H-imidazole (≥98.1%), 2-chloro-1H-imidazole (≥98.2%), 2-methyl-1H-imidazole (≥98%), ferrocenemethanol (98%) and 1,1’-ferrocenedimethanol (98%) were supplied by Sigma Aldrich. Sodium borohydride (95%) and glacial acetic acid (99.8%) were supplied by...
Merck chemicals. All other solvents used were of analytical grade and were used as supplied by Sigma Aldrich, unless stated otherwise. TLC with varying solvent polarity was performed on silica gel 60 F254 plates. Silica gel with 0.063–0.2 mm mesh size was used for column chromatography to purify the products obtained. The melting point of each compound was determined using an open-end capillary tube in a Bibby Stuart Scientific SMP3 apparatus. Infrared spectra were obtained with a PerkinElmer Spectrum 100 FTIR spectrometer fitted with a universal ATR accessory. 1H-NMR and 13C-NMR spectra were recorded on a 400 MHz Bruker AVANCE III spectrometer at room temperature using deuterated CDCl3 or DMSO as solvents. Mass spectra of the synthesized compounds were obtained from an Agilent Technologies, 1100 series, ion-trap mass spectrometer. Electronic spectra were recorded on a PerkinElmer Lambda 35 double-beam UV–visible spectrophotometer with 10 mm path length quartz cuvettes in acetonitrile, dichloromethane, and DMF. Cyclic voltammetry measurements were performed with a CHI660E electrochemical workstation (CH Instruments, USA) with a scan rate of 100 mV/s in a three-electrode system consisting of a GCE (3.0 mm diameter) auxiliary electrode, Ag/AgCl reference electrode and a platinum-wire as the working electrode. The half-wave potential (E1/2) values were obtained using \((E_{pa} + E_{pc})/2\), where \(E_{pa}\) and \(E_{pc}\) are the anodic and cathodic peak potentials, respectively. The band gap energies were estimated from the empirical relation \(E_{band} = [(E_{ox} - E_{1/2(ferrocene)}) + 4.8]\) eV or \(E_{band} = [(E_{red} - E_{1/2(ferrocene)}) + 4.4]\) eV. Ferrocene was used as an external standard. It shows two peaks at 0.38 and 0.45 V hence the \(E_{1/2}\) (ferrocene) is equal to 0.42 V. The longest absorption wavelength \(\lambda_{onset}\) was used to calculate the optical gap energy, \(\Delta E\) (Optical), according to the equation \(E_{g} = 1242/\lambda_{onset}\).

4.1. General procedure for the synthesis of compounds 4–6

4.1.1. Representative procedure for 4–6

The prepared 1,1’-ferrocenedimethanol (240.9 mg, 1 mM) and 2-chloro-1H-imidazole (262.3 mg, 2.32 mM) in acetic acid (5 mL) were stirred for 6 hours at 60 °C. Product formation was monitored by using TLC plates with ethyl acetate/hexane (2:1) as eluent. The reaction mixture was extracted with ethyl acetate (50 mL), washed with 15 mL brine solution and dried over anhydrous sodium sulphate. Thereafter, the solvent was removed under reduced pressure to obtain the crude product which was purified by flash column chromatography on silica gel to give

| Compound | LUMO+1 (eV) | LUMO (eV) | HOMO (eV) | HOMO-1 (eV) | \(\Delta E^*\) (eV) | \(\Delta E\) (CV) (eV) |
|----------|-------------|----------|-----------|-------------|----------------|----------------|
| 1        | -0.045      | -0.046   | -0.172    | -0.173      | 0.127          | 0.073          |
| 2        | -0.054      | -0.107   | -0.180    | -0.181      | 0.073          | 0.081          |
| 3        | -0.044      | -0.045   | -0.171    | -0.172      | 0.126          | 0.070          |
| 4        | -0.058      | -0.058   | -0.184    | -0.185      | 0.126          | 0.121          |
| 5        | -0.115      | -0.115   | -0.200    | -0.200      | 0.085          | 0.070          |
| 6        | -0.052      | -0.053   | -0.178    | -0.179      | 0.126          | 0.160          |

* \(\Delta E\) - calculated band gap energy.

Fig. 7. Lobes of the frontier molecular orbitals for the symmetric compound 5 obtained from the M1 theoretical model.
a yellow solid.

4.1.2. Synthesis of 1,1'-ferrocenylmethyl(2-chloroimidazole) (4)

The general procedure described in Section 4.1.1 was followed by using 1,1'-ferrocenedimethanol (246.0 mg, 1 mM) and 2-chloro-1H-imidazole (237.8 mg, 2.20 mM). The product was purified by column chromatography and concentrated under vacuum to obtain yellow crystals as the product. Yield: 60% (245.0 mg), Rf = 3.0, mp = 170–174 °C. IR (cm⁻¹): 439.01, 736.00, 820.00, 1036.00, 1334.37, 1465.70, 1702.04, 2923.79, 3100.43. ¹H-NMR spectra (400 MHz, CDCl₃, 6 ppm): δ = 6.17–4.42 (8H, t, 2 CH₃), 4.76 (4H, s, 2 CH₂), 6.85 (2H, s, imidazole CH=CH), 6.89 (2H, s, imidazole CH=CH) ppm. ¹³C-NMR spectra (400 MHz, CDCl₃, δ ppm): δ = 14.11, 22.67, 29.64, 30.92, 45.87, 69.53, 69.71, 76.74, 77.06, 77.38, 82.63, 120.46, 128.15, 131.22, 206.98. HR-MS (C₁₈H₁₃Cl₂FeN₄). ES: [M⁺] m/z 459.04801.

4.1.3. Synthesis of 1,1'-ferrocenyl(2-nitroimidazole) (5)

The general procedure described in Section 4.1.1 was followed by using 1,1'-ferrocenedimethanol (246.0 mg, 1 mM) and 2-nitro-1H-imidazole (262.3 mg, 2.32 mM). The product was purified by column chromatography and concentrated under vacuum to obtain orange crystals. Yield: 56% (242.2 mg), Rf = 0.59, mp = 245 °C. IR (cm⁻¹): 437.66, 831.62, 916.65, 1023.23, 1143.93, 1237.14, 1270.40, 1353.90, 1432.43, 143.93, 167.77. HR-MS (C₂₀H₂₂FeN₄). ES: [M⁺] m/z calc. 414.00910, found [M⁺ + Na⁺] 436.9902.

4.1.4. Synthesis of 1,1'-ferrocenylmethyl(2-methylimidazole) (6)

The general procedure described in Section 4.1.1 was followed by using 1,1'-ferrocenedimethanol (246.0mg, 1 mM) and 2-methyl-1H-imidazole (190.5 mg, 2.32 mM). The product was purified by column chromatography and concentrated under vacuum to obtain orange crystals. Yield: 55% (241.6 mg), Rf = 2.44, mp = 258 °C. IR (cm⁻¹): 487.66, 691.80, 831.62, 916.65, 1023.23, 1113.93, 1237.14, 1270.40, 1479.86, 1526.93, 1661.18, 2867.87, 3116.37, 3385.49. ¹H-NMR spectra (400 MHz, CDCl₃, 6 ppm): δ = 4.23–4.45 (5H, t, 2 CH₂), 5.39 (4H, s, 2 CH₂), 7.15 (2H, s, imidazole CH=CH), 7.66 (2H, s, imidazole CH=CH) ppm. ¹³C-NMR spectra (400 MHz, CDCl₃, δ ppm): δ = 30.89, 29.62, 39.83, 40.03, 49.28, 49.66, 60.22, 68.77, 69.86, 70.26, 77.08, 77.33, 80.77, 81.57, 124.97, 128.02, 207.32. HR-MS (C₁₈H₁₅FeN₄O₂). ES: [M⁺] m/z calc. 436.05800, found [M⁺ + Na⁺] 459.04801.

4.2. X-ray crystal structures

Crystals of compounds 4 and 5 were attached onto the tip of a glass fibre with epoxy glue and centered in the X-ray beam under a video camera. Crystal evaluation and data were done and collected on a Bruker diffractometer with Mo Kα radiation (λ = 0.71073 Å) equipped with an Oxford Cryostream low-temperature apparatus. Omega scans of 0.5° width with an exposure time of 20 s per frame were used for data collection. The total number of images was based on results from the program COSMO [57] with the completeness of 100% out to 0.75 Å and expected redundancy was expected to be 4.0. The initial cell matrix was determined from three series of scans collected at intervals of 0.5° in a 6° range, with each of the series of scans collected at different starting angles and the APEXI [58] program suite employed for reflection indexing. Cell parameters were retrieved using APEXI [58] and refined by using SAINT [59] on all observed reflections. The structures were solved by the direct method using the SHELXS [60] program and refined. The visual crystal structures were presented using ORTEP-3 [61] and MERCURY [62]. Non-hydrogen atoms were first refined with anisotropic displacement parameter and then by anisotropic refinement with full-matrix least squares.

Ten different DFT models (B3LYP, [63, 64] B3LYP-D2, B3LYP-D3, [65] CAM-B3LYP, [66] BMK, M05-2X, M06, M06-2X, M06-HF and M06-L [67, 68]) with def2-TZVP [69] and 6-311+G(d) [70, 71] basis sets were examined. M06-L [68] plus either basis sets proved to be sufficient and more accurate than the rest of the DFT models studied. Calculations were executed within the Gaussian 09 RevD.01 software [72] and pre/post molecular analyses were carried out in GaussView [73].

4.2.1. Crystallographic data

Crystallographic data (including structure factors) have been deposited with the Cambridge Crystallographic Data Centre and can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif. The supplementary crystallographic data of compounds 4 and 5 are contained in CCDC 1854200 and 1854185 publication number, respectively.

Declarations

Author contribution statement

Ayomide H. Labulo: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Vincent O.Nyamori: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Bernard Omandi: Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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