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Synthesis and properties of azole-substituted ferrocenes

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Abstract

4-Ferrocenyltriazole, 4-(4-ferrocenylphenyl)triazole, 4-ferrocenyltetrazole, and 4-(4-ferrocenylphenyl)tetrazole have been prepared. Redox potentials and decomposition temperatures were evaluated and all the compounds were crystallographically characterized; in most cases, weak intermolecular CH···N hydrogen bonds (H···N dist. = 2.3–2.5 Å) were formed between the azole moieties. Two polymorphs were found for 4-ferrocenyltetrazole, formed with either CH···N or π–π interactions.

Keywords: Ferrocene; Tetrazole; Triazole; Crystal structures; Hydrogen bond; Redox potentials

1. Introduction

Organometallic supramolecular assemblies have attracted special attention in recent decades [1,2]; heteroaryl-substituted ferrocene ligands provide a useful approach towards their synthesis. For this purpose, we have designed a variety of ligands, which are shown in Chart 1 [3,4]. These versatile ligands give topologically diverse assembled structures when combined with various metal salts; the modes of assembly depend on the number and position of the ligands' nitrogen coordination sites.

To extend the study, we designed the azole-substituted ferrocenes shown in Chart 2. Azole substituents provide versatile ligating sites so have the potential to form a variety of metal complexes [5]. Their chemistry has been the subject of intense development with applications in medicine, biology, agriculture, and other fields [6]. We report here the preparation and properties of 4-ferrocenyl-4*H*-[1,2,4]triazole (FcTr), 4-(4-ferrocenylphenyl)-4*H*-[1,2,4]triazole (FcPhTr), 4-ferrocenyl-1*H*-tetrazole (FcTe), and 4-(4-ferrocenylphenyl)-1*H*-tetrazole (FcPhTe). These molecules are expected to be useful for the development of multi-functional metal assemblies such as spin-crossover complexes [7]. As a related example, 5-ferrocenyl-2*H*-tetrazole [8] is known, which is a *C*-substituted tetrazole having an NH proton.

Tetrazoles and their metal salts are known as explosives [9,10], so we used thermogravimetric analysis to evaluate the thermal decomposition behavior of our molecules. To date, only a few crystal structures of *N*-aryl triazoles and tetrazoles have been reported; therefore, our compounds were fully characterized crystallographically, and the importance of weak CH···N hydrogen bonds to their crystal architectures was revealed. Weak intermolecular interactions in organic crystals are of interest from the viewpoint of organic crystal engineering [11,12].

2. Results and discussion

2.1. Preparation

The azole-substituted ferrocenes could be prepared by methods analogous to those used for the preparation of *N*-aryl triazoles, but the yield was generally lower. In particular, the yield of the ferrocenyl derivatives (FcTr and

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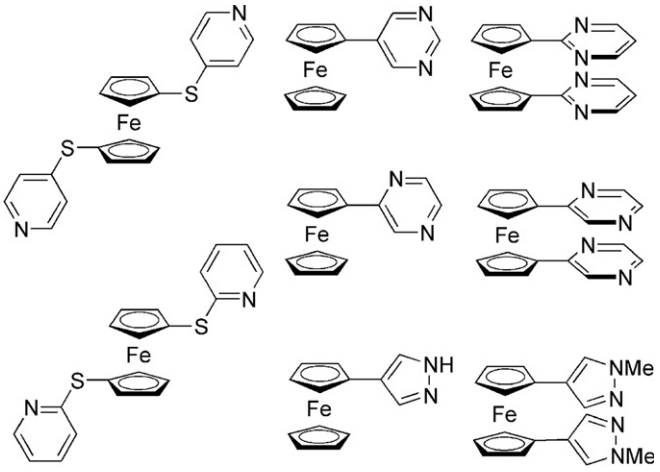


Chart 1.

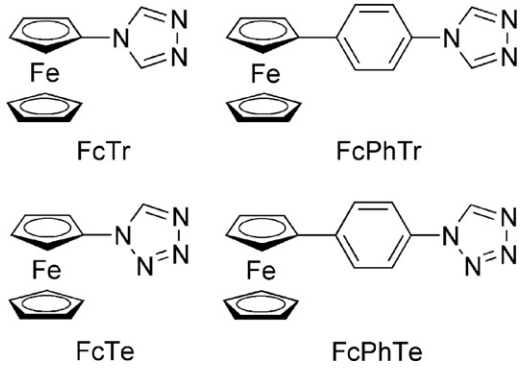
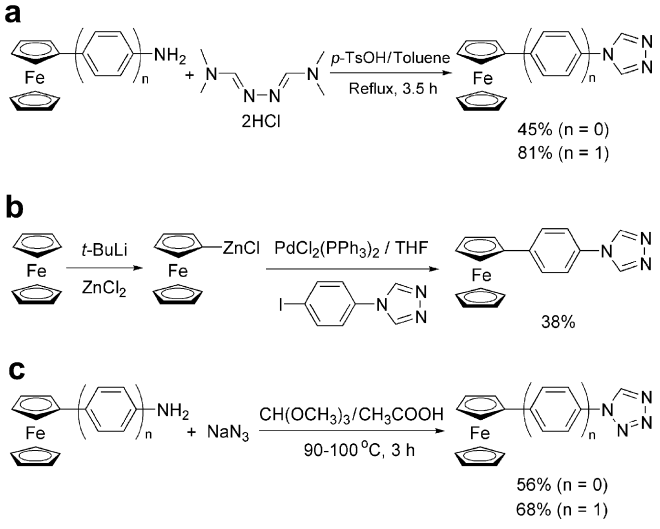


Chart 2.

FcTe) were lower than those of the ferrocenylphenyl ones (FcPhTr and FcPhTe).

FcTr and FcPhTr were prepared most conveniently by the condensation of aminoferrocene or ferrocenylaniline with *N*,*N*-dimethylformamide azine dihydrochloride in the presence of *p*-toluenesulfonic acid (Scheme 1(a); yields 45% and 81%, respectively). *N*-Aryl triazoles are usually prepared in high yields by the condensation of anilines with



Scheme 1.

1,2-diformylhydrazine [13,14]; therefore, we first applied this method but it turned out to be less suitable for ferrocenyl derivatives. Thus, condensation of aminoferrocene with 1,2-diformylhydrazine afforded FcTr, but only in a poor yield (yield 5%), and this reaction produced ferrocenylformamide [15] (yield 37%) as the main product. This method was also applied to the preparation of FcPhTr, but the yield was again low (15%). As an alternative method, FcPhTr could be prepared by Negishi coupling (Scheme 1(b)): the reaction of ferrocenylzinc chloride with 4-(4-iodophenyl)triazole in the presence of a palladium catalyst gave the desired compound in a 38% yield.

FcTe and FcPhTe were prepared by applying a standard method [16], the reaction of amino precursors with sodium azide and trimethyl orthoformate in acetic acid (yields 56% and 68%, respectively, Scheme 1(c)).

In the above reactions, 4-ferrocenylaniline was the starting material for FcPhTe and FcPhTr. 4-Ferrocenylaniline can be synthesized by diazo-coupling of 4-nitrophenyldiazonium salt with ferrocene, followed by reduction [17,18], but we found that the use of Negishi coupling – coupling of ferrocenylzinc chloride with 4-iodoaniline in the presence of a palladium catalyst – was more convenient and resulted in a higher yield (29%) then the conventional method.

2.2. Redox potentials

The electrochemical properties of these compounds were measured by means of cyclic voltammetry in acetonitrile solution. Reversible redox waves of the ferrocenyl moieties were observed in all the compounds, as listed in Table 1 (vs. $FeCp_2/FeCp_2^+$). The half-wave potentials of FcTr and FcTe were 0.21 V and 0.27 V, respectively, and those for FcPhTr and FcPhTe were 0.07 V and 0.09 V, respectively. The higher redox potentials of the former group are attributed to the stronger electron-withdrawing effects of azole groups compared with phenyl groups. The redox potential of FcTe is higher than that of FcTr. This is ascribable to the stronger electron-withdrawing effect of tetrazole, which contains one more nitrogen atom than triazole. This effect becomes less significant when phenylene groups are present, as seen by the more similar redox potentials of FcPhTe and FcPhTr.

2.3. UV–Vis spectra

UV–Vis spectra of the compounds in acetonitrile solution are shown in Fig. 1 and the spectral data are listed

Table 1
Redox potentials (in *V* vs. $FeCp_2/FeCp_2^+$)

	E_p^c	E_p^a	$E_{1/2}$
FcTr	0.17	0.24	0.21
FcTe	0.24	0.30	0.27
FcPhTr	0.04	0.10	0.07
FcPhTe	0.06	0.12	0.09

In 0.1 M nBu_4NClO_4–MeCN.

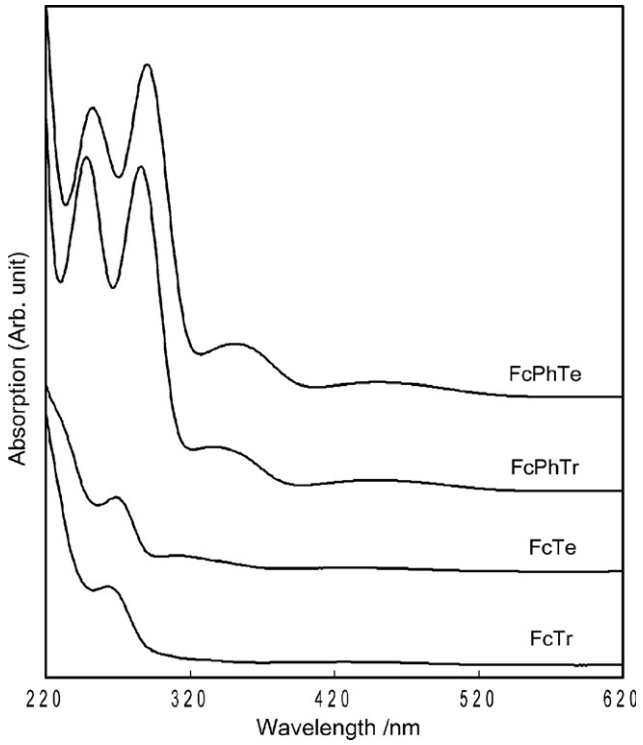


Fig. 1. UV–Vis spectra of azole-substituted ferrocenes in acetonitrile. The spectra are vertically shifted.

in Table 2. As seen in Fig. 1, the spectra of FcTr and FcTe are almost the same, with weak absorptions in the visible region. The absorption bands below 280 nm are assignable to Fe(d)–π^* and π–π^* transitions. Similarly, the spectra of FcPhTr and FcPhTe are almost the same. These compounds were more strongly colored than FcTr and FcTe and exhibit stronger absorption bands at low energies, due to extended conjugation. The bands below 320 nm and around 350 nm are mainly assignable to π–π^* and Fe(d)–π^* transitions, respectively. Very broad weak absorption bands were observed at around 430 nm in FcTr and FcTe, and at around 450 nm in FcPhTr and FcPhTe. These bands are assignable to d–d transitions [19], the latter probably being mixed with Fe(d)–π^* transitions. In both series, the absorption bands for tetrazoles are slightly red-shifted with respect to the triazoles. This is ascribable to the lower LUMO energy of the tetrazole system, which is consistent with the stronger electron-withdrawing effect of the former as revealed by the electrochemical results.

Table 2
UV–Vis absorption data in acetonitrile

Compounds	λ_{max}/nm (ε/M^{-1} cm^{-1})
FcTr	207 (19578), 263 (4078), 426 (126)
FcTe	204 (21118), 269 (4312), 312 (885), 432 (155)
FcPhTr	212 (24249), 248 (16980), 286 (16514), 337 (2200), 449 (504)
FcPhTe	211 (22349), 253 (13608), 290 (15668), 352 (2444), 451 (631)

2.4. Thermogravimetric analysis

To examine the thermal decomposition behavior of these compounds, we performed thermogravimetric (TG) analysis on powder samples. The TG curves are shown in Fig. 2. The temperatures at which weight loss exceeded 5% were 474 K (FcTe), 477 K (FcPhTe), 520 K (FcTr), and 545 K (FcPhTr). The tetrazole ligands were less thermally stable than the triazole ones, as anticipated. The TG curves for the tetrazoles (FcTe and FcPhTe) showed a sudden weight loss at around 480 K, which continued up to about 485 K, of 14% and 10%, respectively. If this is attributable to the evolution of N_2 gas, it corresponds to a loss of ca. 60% of the N atoms from each molecule. The weight loss for triazoles (FcTr and FcPhTr) occurred more gradually at higher temperatures; for these molecules, the loss of one N_2 molecule corresponds to a weight loss of 11% and 9%, respectively, which was seen only above 550 K.

The decomposition temperatures were somewhat higher for ferrocenylphenyl azoles (FcPhTe and FcPhTr) than for ferrocenyl azoles (FcTe and FcTr), which indicates that the presence of the phenylene group increases thermal stability. It has been reported that decomposition temperatures of phenyltetrazoles are about 430–490 K and that the pres-

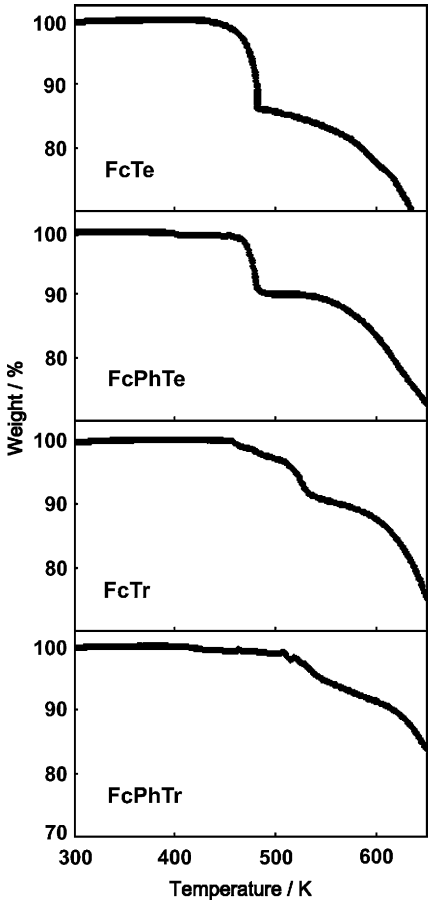


Fig. 2. TG curves for azole-substituted ferrocenes.

ence of an electron-releasing substituent on the tetrazole ring leads to higher thermal stability [10]. The electron-releasing ferrocenyl substituent might contribute to stability but the effect was not remarkable.

2.5. Crystal structures

Structures of all the compounds were determined by X-ray crystallography. Crystallographic parameters are listed in Table 3. In most crystals, significant intermolecular contacts were found between the azole moieties: one of the azole hydrogens has a $C_{azole}H\cdots N_{azole}$ interaction with the N atom of the adjacent molecule (Fig. 3). The H···N distances in the ferrocenyl azoles (FcTr and FcTe) were about 2.3 Å, which is shorter by 0.4 Å than the sum of the van der Waals distances so can be regarded as weak hydrogen bonds [11]. The corresponding distances in ferrocenylphenyl azoles (FcPhTr and FcPhTe) were somewhat longer (about 2.5 Å). Other intermolecular contacts were less significant.

Fig. 4 shows the packing diagram of FcTr. In this molecule, the dihedral angle between the Cp and tetrazole rings is 38.5(1)°. The triazole moieties form a chain arrangement via the CH···N interaction (H···N distance: 2.33 Å) along the *b*-axis, as indicated by dashed lines in the figure. No intermolecular π–π interaction exists, due to the nearly orthogonal intermolecular arrangement of the ferrocenyl moieties.

FcTe afforded two polymorphs, the α-form, from methanol, and the β-form, from acetone. The contrasting packing interactions in these polymorphs are of interest: the CH···N interaction prevails in the α-form, while the β-form shows a π–π stacking interaction. Fig. 5(a) shows

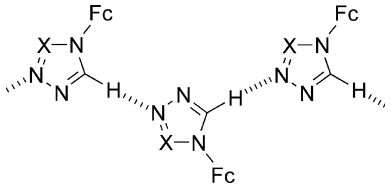


Fig. 3. Schematic illustration of weak hydrogen bonds in FcTr (X = CH) and FcTe (X = N, α-form).

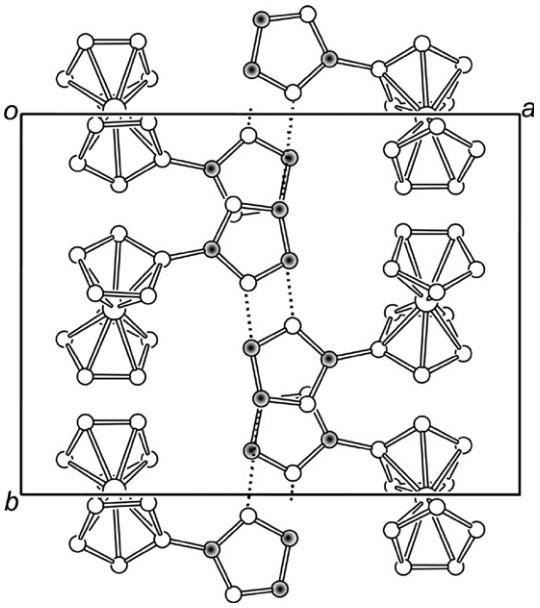


Fig. 4. Packing diagram of FcTr viewed along the *a*-axis. Hydrogen atoms are omitted for clarity. Nitrogen atoms are shaded. CH···N interactions are indicated by dotted lines.

Table 3
Crystallographic data

	FcTr	FcTe (α-form)	FcTe (β-form)	FcPhTr	FcPhTe
Empirical formula	$C_{12}H_{11}FeN_3$	$C_{11}H_{10}FeN_4$	$C_{11}H_{10}FeN_4$	$C_{36}H_{30}Fe_2N_6$	$C_{17}H_{14}Fe_1N_6$
Formula weight	253.09	254.08	254.08	658.36	330.17
Crystal size (mm^3)	$0.50\times0.30\times0.30$	$0.60\times0.20\times0.05$	$0.37\times0.13\times0.06$	$0.40\times0.20\times0.20$	$0.25\times0.13\times0.13$
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
a (Å)	13.4137(7)	10.4150(7)	5.7175(5)	22.801(2)	12.3356(10)
b (Å)	10.2518(5)	7.3714(5)	19.8247(17)	13.4359(14)	6.3641(5)
c (Å)	7.5076(4)	26.7255(18)	8.8152(8)	9.5969(10)	18.1773(15)
β (°)	92.9010(10)		94.646(2)	99.847(2)	97.8140(10)
V ($Å^3$)	1031.08(9)	2051.8(2)	995.90(15)	2896.7(5)	1413.8(2)
Space group	$P2_1/c$	*P*bca	$P2_1/n$	$P2_1/c$	$P2_1/n$
Z value	4	8	4	4	4
D_{calc} ($g\,cm^{-3}$)	1.63	1.645	1.695	1.510	1.551
μ (mm^{-1})	1.433	1.443	1.487	1.040	1.067
F(000)	520	1040	520	1360	680
No. of reflections	7504	14297	7361	21258	8507
No. of observations	2547	2537	2479	7203	3228
Parameters	145	145	145	517	235
Temperature (K)	173	173	173	173	150
Final R_1, R_w ($I > 2\sigma$)	0.0289, 0.0762	0.0322, 0.0797	0.0643, 0.1257	0.0446, 0.0910	0.0400, 0.0865
Final R_1, R_w (all data)	0.0297, 0.0771	0.0397, 0.0872	0.0700, 0.1228	0.0962, 0.1129	0.0771, 0.1008
Goodness-of-fit	1.007	1.03	0.971	0.986	1.022

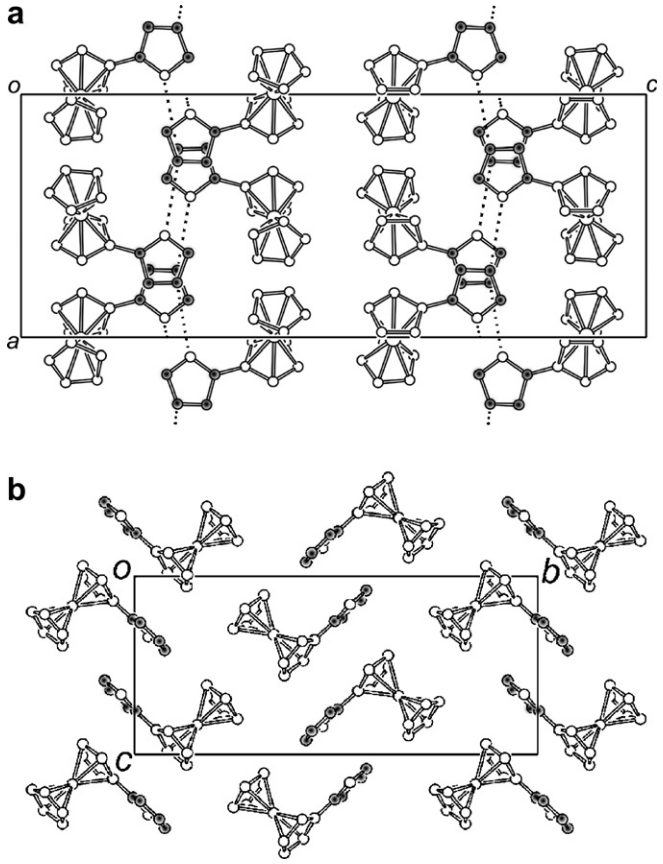


Fig. 5. Packing diagrams of FcTe: (a) α-form and (b) β-form, viewed along the *b*-axes. Hydrogen atoms are omitted for clarity. Nitrogen atoms are shaded. CH···N interactions are indicated by dotted lines.

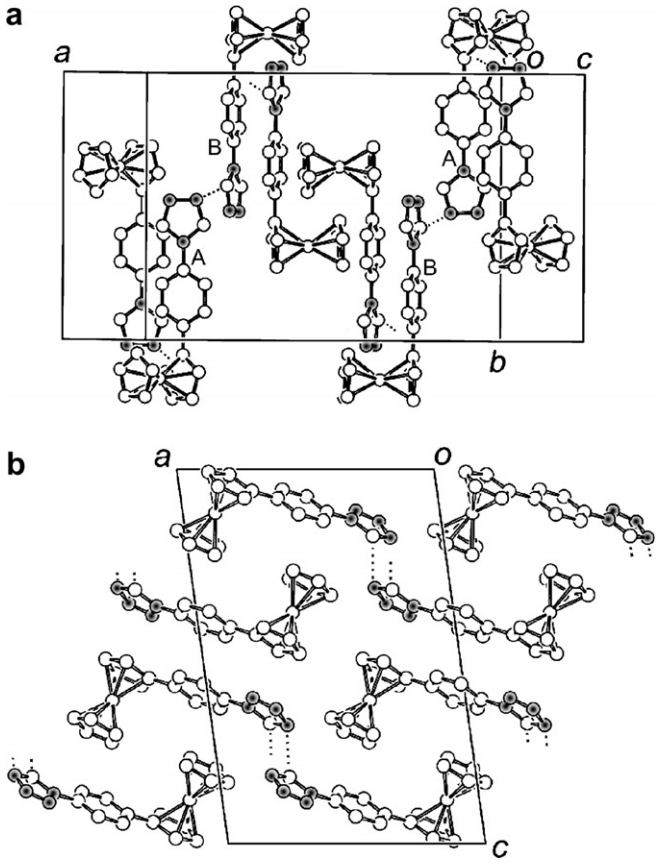


Fig. 6. Packing diagrams of (a) FcPhTr and (b) FcPhTe. Hydrogen atoms are omitted for clarity. Nitrogen atoms are shaded. CH···N interactions are indicated by dotted lines.

the packing diagram of the α-form, the molecular arrangement of which resembles that of FcTr. The tetrazole moieties form a chain arrangement via the CH···N interaction (H···N distance: 2.34 Å) along the *a*-axis, and no intermolecular π–π interaction exists due to the nearly orthogonal arrangement of the ferrocenyl moieties. The intramolecular dihedral angle between the Cp and tetrazole rings is 38.7(2)°. Fig. 5(b) shows the packing diagram of the β-form. The intramolecular dihedral angle between the Cp and tetrazole rings is 12.5(2)°, which is much smaller than for the α-form. The β-form exhibits no chain-like arrangement of the tetrazole moieties, but rather a stacking structure along the *c*-axis, accompanied by intermolecular π–π interactions between the Cp ring and the tetrazole ring. Thus, the polymorphism depends on whether CH···N interactions or π–π stacking interactions dominate.

As seen above, the packing structures of FcTr and FcTe (α-form) are governed by CH···N interactions. However, when phenylene spacers are introduced, the π–π interactions prevail and the CH···N interaction becomes less significant. Fig. 6(a) shows the packing diagram of FcPhTr. The crystal contains two crystallographically independent molecules, denoted A and B, which have different dihedral angles between the phenylene and triazole rings [41.1(2)° and 4.8(2)°, respectively], while those between the Cp and phenylene rings are comparable [18.9(2)° and 19.8(2)°]. The CH···N interaction connects molecules A and B (H···N distance: 2.48 Å); the interaction is local and no network is formed. Some π–π interactions are observed between the molecules. Fig. 6(b) shows the packing diagram of FcPhTe. The dihedral angle between the phenylene and tetrazole rings is 5.3(1)°, and that between the Cp and phenylene rings is 1.3(1)°. The molecules form a dimer-like arrangement via an intermolecular π–π interaction. The C–H···N interaction (H···N distance: 2.53 Å) constructs zig-zag molecular chains along the *b*-axis.

Considering the intramolecular geometries of these molecules, the bond lengths within the azole moieties are as usual and comparable to those observed for *N*-aryl tetrazoles [12,20] and triazoles [21]. The C_{Azole}–$C_{Fc\,or\,Ph}$ bond lengths in the ferrocenyl azoles [1.415(2) Å in FcTr, 1.421(5) Å and 1.4168(17) Å in FcTe] were shorter than those in the ferrocenylphenyl azoles [1.430(4) Å and 1.431(4) Å in FcPhTr, 1.431(4) Å in FcPhTe] and other *N*-aryl azoles. The torsion angles between the azole and adjacent rings vary between 4.8° and 40.6°, suggesting that the torsion angle is susceptible to intermolecular packing forces.

3. Conclusions

Four ferrocene-based triazole and tetrazole ligands have been prepared by standard methods, although the yields were found to be lower than those for *N*-aryl azoles. These molecules are redox-active ligands that might be useful for the preparation of multi-functional metal complexes. X-ray crystallography revealed that weak intermolecular CH···N hydrogen bonds are formed between the azole moieties in most cases, which are important to their crystal architectures. In particular, two polymorphs were found for 4-ferrocenyltetrazole, which provides a good example of the roles of the CH···N interactions and π–π stacking interactions, which were competitive in this case. Preparation of metal complexes with these molecules is underway.

4. Experimental

4.1. General methods

N,*N*-Dimethylformazine dihydrochloride [22] and 4-(4-iodophenyl)-4*H*-[1,2,4]triazole [23] were synthesized by following the reported procedures. Ferrocenylaniline was prepared by an improved method described below. All the other reagents and solvents were commercially available. Zinc chloride was dried under vacuum for 2 days at 120 °C prior to use. All reactions were carried out under a dinitrogen atmosphere. NMR spectra were recorded on a JEOL JNM-ECL-400 spectrometer. Infrared spectra were recorded on a JASCO FT-IR 230 spectrometer as KBr pellets. UV–Vis spectra were recorded on a JASCO V-570 UV–VIS/NIR spectrometer. Cyclic voltammograms were recorded with an ALS/chi electrochemical-analyzer model 600 A. The redox potentials were measured at a scan rate of 0.1 V s^{-1}, in acetonitrile containing 0.1 mol dm^{-3} nBu_4NClO_4 as the supporting electrolyte. An Ag/Ag^+ reference electrode and a platinum working electrode were used, and the potentials were referenced to a $FeCp_2/FeCp_2^+$ couple. Melting points were measured by means of differential scanning calorimetry (DSC) on a TA instruments Q100 calorimeter. TG analysis was performed under a dinitrogen atmosphere at a heating rate of 10 °C/min on a Seiko TG/DTA 220U instrument, in the range 25–400 °C.

4.2. Preparation of 4-ferrocenyltriazole (FcTr)

Method A. *N*,*N*-dimethylformamide azine dihydrochloride (114 mg, 0.53 mmol), aminoferrocene (100 mg, 0.50 mmol), and *p*-toluenesulfonic acid (6.2 mg, 0.036 mmol) were dissolved in toluene (1.2 mL), and the solution was refluxed for 4 h. After cooling to room temperature, the solvent was removed under reduced pressure, and the residue dissolved in chloroform. The solution was filtered through a celite plug to remove insoluble materials. The solution was washed with water; the organic layer was separated, dried over magnesium sulfate, and evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, chloroform:acetone = 9:1, $R_f = 0.29$). Yellow powder (57 mg, yield 45%). ^1H NMR ($CDCl_3$, ppm): $\delta = 4.26$ (s, 5H), 4.28 (t, 2H, $J = 1.8$ Hz), 4.56 (t, 2H, $J = 1.8$ Hz), 8.37 (s, 2H). IR (KBr, cm^{-1}): 3095, 2924, 1651, 1540, 1411, 1240, 1107, 1054, 874, 805, 644, 491. Mp (DSC) = 182.0 °C. Anal. Found: C, 56.74; H, 4.41; N, 16.47%. Calc. for $C_{12}H_{11}FeN_3$: C, 56.95; H, 4.38; N, 16.60%.

Method B. A mixture of aminoferrocene (68 mg, 0.338 mmol) and 1,2-diformylhydrazine (30.2 mg, 0.343 mmol) was heated at 180 °C for 3 h. After cooling to room temperature, the reaction mixture was extracted with chloroform, and the organic layer washed with water. Insoluble materials were removed by filtration; the organic layer was separated, dried over magnesium sulfate, and evaporated. The crude product was purified by column chromatography (silica gel, chloroform:acetone = 1:1). The $R_f = 0.84$ fraction afforded the desired compound (4 mg, yield 5%). The $R_f = 0.21$ fraction afforded ferrocenylformamide [15] (29 mg, yield 37%).

4.3. Preparation of 4-(4-ferrocenylphenyl)triazole (FcPhTr)

Method A. *N*,*N*-dimethylformamide azine dihydrochloride (79.0 mg, 0.37 mmol), ferrocenylaniline (102 mg, 0.37 mmol), and *p*-toluenesulfonic acid (5 mg, 0.03 mmol) were dissolved in toluene (1 mL), and the solution was refluxed for 4 h. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was dissolved in chloroform. The solution was filtered through a celite plug to remove insoluble materials. The solution was washed with water, and the organic layer was separated, dried over magnesium sulfate, filtered, and evaporated. The crude product was purified by column chromatography (chloroform:acetone = 9:1, $R_f = 0.29$). Orange powder (150 mg, yield 81%). ^1H NMR ($CDCl_3$, ppm): $\delta = 4.07$ (s, 5H), 4.40 (t, 2H, $J = 1.8$ Hz), 4.68 (t, 2H, $J = 1.8$ Hz), 7.30 (d, 2H, $J = 8.4$ Hz), 7.61 (d, 2H, $J = 8.8$ Hz), 8.48 (s, 2H). ^1H NMR (DMSO-d_6, ppm): $\delta = 4.04$ (s, 5H), 4.40 (t, 2H, $J = 1.8$ Hz), 4.89 (t, 2H, $J = 1.8$ Hz), 7.61 (d, 2H, $J = 8.8$ Hz), 7.71 (d, 2H, $J = 8.4$ Hz), 9.13 (s, 2H). IR (KBr, cm^{-1}): 3097, 1534, 1512, 1457, 1228, 1080, 997, 886, 844, 822, 646. Mp (DSC) = 190.3 °C. Anal. Found: C, 65.47; H, 4.73; N, 12.55%. Calc. for $C_{18}H_{15}FeN_3$: C, 65.68; H, 4.59; N, 12.77%.

Method B. A mixture of ferrocenylaniline (24.2 mg, 0.0873 mmol) and 1,2-diformylhydrazine (6.3 mg, 0.072 mmol) was heated at 180 °C for 3 h. After usual workup and column chromatography, 4 mg of the desired compound was obtained (yield 15%). When decahydronaphthalene was used as a solvent, the reaction needed *p*-toluenesulfonic acid as a catalyst: the reaction mixture was heated at 180 °C for 1 day, and the yield was 4.2%.

Method C. To a THF solution (5 mL) of ferrocene (1.013 g, 5.45 mmol) cooled to 0 °C, *t*-butyllithium (5 mL, 7.25 mmol, 1.24 mol dm^{-3} *n*-pentane solution) was added

dropwise, and the solution was stirred for 15 min. A suspension of zinc chloride (1.2 g, 8.8 mmol) in THF (13 mL) was added dropwise to this solution and stirred for 30 min. The solution was allowed to warm to room temperature, and stirred for a further 1 h. To this solution were added a THF suspension (6 mL) of dichlorobis(triphenylphosphine)palladium(II) (0.2 g, 0.285 mmol) and a THF solution (15 mL) of 4-(triazole)phenyliodide (1.471 g, 5.43 mmol). The solution was stirred for 2 days at room temperature, and then the reaction was quenched by adding water (2 mL). After usual workup and column chromatography, 0.680 g of the desired compound was obtained (yield 38%).

4.4. Preparation of 4-ferrocenyltetrazole (FcTe)

To a stirred mixture of aminoferrocene (327.7 mg, 0.163 mmol), sodium azide (134.8 mg, 0.209 mmol), and anhydrous trimethyl orthoformate (1.6 mL), was added glacial acetic acid (0.5 mL), and the solution was heated at 90 °C for 3 h. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was dissolved in chloroform, and the solution was washed with water. Insoluble materials were removed by filtration, and the organic layer was separated, dried over magnesium sulfate, filtered, and solvent removed under reduced pressure. The crude material was recrystallized from hexane and further purified by vacuum sublimation. Yellow powder (140.3 mg, yield 56.4%). ^{1}H NMR ($CDCl_3$, ppm): $\delta = 4.28$ (s, 5H), 4.35 (t, 2H, $J = 4.2$ Hz), 4.82 (t, 2H, $J = 1.8$ Hz), 8.71 (s, 1H). IR (KBr, cm^{-1}): 3129, 2926, 1636, 1522, 1411, 1209, 1094, 1030, 814, 666, 485. Mp (DSC) = 165.6 °C. Anal. Found: C, 52.00; H, 4.00; N, 21.93%. Calc. for $C_{11}H_{10}FeN_4$: C, 52.00; H, 3.97; N, 22.05%.

4.5. Preparation of 4-(4-ferrocenylphenyl)tetrazole (FcPhTe)

To a mixture of ferrocenylaniline (99.2 mg, 0.358 mmol), sodium azide (29.1 mg, 0.444 mmol), and anhydrous trimethyl orthoformate (1.0 mL), was added glacial acetic acid (0.5 mL) under stirring. The solution was heated at 100 °C for 3 h. After usual workup, the crude product was purified by column chromatography (silica gel, chloroform, $R_f = 0.16$). Orange powder (80 mg, yield 68%). ^{1}H NMR ($CDCl_3$, ppm): $\delta = 4.07$ (s, 5H), 4.42 (m, 2H, $J = 3.7$ Hz), 4.71 (m, 2H, $J = 3.7$ Hz), 7.61 (d, 2H, $J = 8.8$ Hz), 7.66 (d, 2H, $J = 8.8$ Hz), 8.98 (s, 1H). IR (KBr, cm^{-1}): 3135, 2356, 1606, 1532, 1473, 1211, 1089, 996, 835, 817, 508. Mp (DSC) = 172.5 °C. Anal. Found: C, 61.64; H, 4.34; N, 16.89%. Calc. for $C_{17}H_{14}FeN_4$: C, 61.84; H, 4.27; N, 16.97%.

4.6. Preparation of ferrocenylaniline

To a THF solution (10 mL) of ferrocene (2.24 g, 12.0 mmol) cooled to −10 °C was added *tert*-butyllithium (16 mL, 25.0 mmol, 1.56 mol dm^{-3} *n*-pentane solution) dropwise, and the solution was stirred for 30 min at −10 °C. A suspension of zinc chloride (2.0 g, 14.7 mmol) in THF (20 mL) was added dropwise to this solution and stirred for 30 min. The solution was allowed to warm to room temperature then stirred for a further 1 h. To this solution were added dropwise a THF suspension (20 mL) of dichlorobis(triphenylphosphine)palladium(II) (420 mg, 0.60 mmol) and a THF solution (15 mL) of 4-iodoaniline (3 g, 13.7 mmol). After stirring the solution for 1 day at room temperature, an aqueous solution (20 mL) of sodium hydroxide (2 g), and dichloromethane (50 mL) were added successively to this solution. The solution was filtered through celite and evaporated, the residue dissolved in dichloromethane (500 mL). The solution was washed with water, dried over magnesium sulfate, passed through a short plug of alumina, and evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, hexane:dichloromethane = 1:1). An analytically pure sample of 4-ferrocenylaniline [15] could be obtained by recrystallization from chloroform–pentane (0.95 g, yield 29%).

4.7. X-ray crystallographic analysis

Single crystals suitable for X-ray structure analysis were mostly obtained by slow evaporation of acetone solutions. The α-form of FcTe was obtained from a methanol solution while trying to grow a $CoCl_2$ complex. X-ray diffraction data were collected on a Bruker SMART APEX CCD diffractometer equipped with a graphite crystal and incident beam monochromator using MoKα radiation ($\lambda = 0.71073$ Å). The data were corrected for absorption by using the SADABS program [24]. The structures were solved by direct methods (SHELXS 97 [25]) and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. CCDC-606793 (for FcTr), -615410 (for FcTe, α-form), -602192 (for FcTe, β-form), -602193 (for FcPhTr), and -602194 (for FcPhTe) contain the Supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.08.020.

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