Synthesis, structures and spectroelectrochemistry of methyl-substituted bis(η⁵-indenyl)iron(II) complexes

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Abstract

Several new methyl-substituted indenyl ferrocenes were prepared by metathesis reactions of the indenide (generated from the appropriate indene with BuLi) with ferrous chloride. The indenides used to prepare new ferrocenes were: 2-methyl-, 1,2-dimethyl-, 4,7-dimethyl-, 1,4,7-trimethyl-, and 1,3,4,7-tetramethyl-indenide. These indenyl ferrocenes, along with those prepared from indenide, 1-methylindenide, and 1,3-dimethylindenide, were then characterized by ^{1}H and ^{13}C NMR, UV/visible spectroscopy, cyclic voltammetry and mass spectrometry. The cyclic voltammetry showed an additive relationship between oxidation potential and the number of methyl groups which is also position-dependent, whereas the UV/visible spectra showed two absorptions essentially unaffected by methyl substitution. Additionally, bis(2-methylindenyl)iron(II) and bis(4,7-dimethylindenyl)iron(II) were characterized by X-ray crystallography.
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1. Introduction

The spectroelectrochemistry of ferrocene and many of its cyclopentadienyl derivatives have been extensively studied [1–3]. The same cannot be said of the indenyl analogues for which there are few electrochemical or UV/visible spectroscopic reports [4–6], and certainly no systematic studies. Related systems of particular relevance are the group 4 metallocenes, for which the cyclic voltammetry and UV/visible spectra of many cyclopentadienyl (but not indenyl) derivatives have been reported [7], and the half-sandwich indenyl group 4 complexes which have had some systematic studies carried out [8,9]. We recently reported the spectroelectrochemical properties of trimethylsilyl derivatives of indenyl ferrocenes, but were unable to find consistent trends or rationalize the observations of either the electrochemistry or
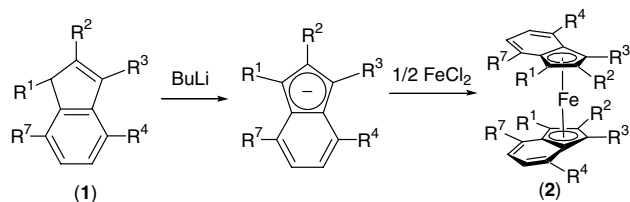
the UV/visible spectroscopy [10]. We therefore sought to simplify the system by using methyl groups, thus eliminating the complication of π-donor/acceptor effects. Previous studies have shown that methyl substituents on cyclopentadienyl groups have the effect of lowering the electron binding energies in the group 4 metallocenes [11] and of similarly lowering the oxidation potential of ferrocenes [2]. Substituent effects on UV/visible spectra, however, are minor in comparison to the effects on electrochemical properties [3]. We report here the preparation, isolation and properties of a number of methyl derivatives of bis(indenyl)iron(II).

2. Results and discussion

2.1. Synthesis and characterization of the methylindenes

Scheme 1 provides the compound numbering system for the indenes and ferrocenes reported in this paper. All

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	R^1	R^2	R^3	R^4	R^7
1a/2a	H	H	H	H	H
1b/2b	Me	H	H	H	H
1c/2c	H	Me	H	H	H
1d/2d	Me	Me	H	H	H
1e/2e	Me	H	Me	H	H
1f/2f	H	H	H	Me	Me
1g/2g	Me	H	H	Me	Me
1h/2h	Me	H	Me	Me	Me

Scheme 1. Synthesis of the methyl-substituted indenyl ferrocenes

of the indenes, except 1,4,7-trimethylindene (**1g**), have been reported previously, however, we report here improved syntheses of 1,2-dimethylindene (**1d**) and 1,3,4,7-tetramethylindene (**1h**) via methylation at the 1 position of the corresponding indenide (2-methylindenide and 1,4,7-trimethylindenide, respectively) with iodomethane. Indene **1g** was similarly prepared from 4,7-dimethylindenide and was characterized by mass spectrometry as well as by ^{1}H and ^{13}C{^{1}H} NMR. The NMR spectra confirmed that the additional methyl group remained in the 1 position during the synthesis and workup procedures.

2.2. Synthesis and characterization of the ferrocenes

The ferrocenes were all prepared by treatment of the indenide (formed by deprotonation of the indene with BuLi) with anhydrous ferrous chloride in THF (Scheme 1). Generally, all of the ferrous chloride has reacted after approximately two hours of stirring at ambient temperature. Purifications of the ferrocenes were carried out by filtration through a Celite column using either diethyl ether or CH_2Cl_2. Compounds **2a** [12], **2b** [4], and **2e** [13] have been reported previously, however, we report here higher yield syntheses as well as additional characterizations (or characterizations in the same solvents that we used for the other compounds). Bis(1,2,4,5,6,7-hexamethylindenyl)iron(II) (**2i**) [6] and the permethylated indenyl ferrocene [(η^5-C$_9$Me$_7$)$_2$Fe] (**2j**) [5,14] have been reported by others.

For the ferrocenes **2b**, **2d** and **2g** (as well as **2i**), the bisplanar chiral nature of the complexes allows the possibility for the formation of both *rac* and *meso* isomers. In each case, a 1:1 mixture of the diastereomers was observed, suggesting that only minor steric interactions occur between the two indenide rings during the synthesis. No attempts were made to separate the isomers and we could not unambiguously assign the NMR spectra to a

particular isomer. The NMR spectra are as expected: methyl substitution on the C$_5$ ring causes a 10–15 ppm downfield shift for the attached C atoms in the 1–3 positions, and a 7–10 ppm downfield shift for the C atoms in the 4 and 7 positions with methyl groups attached.

The parent ion in the EI mass spectra of the ferrocenes was observed for all compounds except **2b**. All of the ferrocenes, except **2h**, also show a peak corresponding to a dimer of the indenyl ligand. It may be that the steric bulk of the tetramethylindenyl ligand in **2h** prevents its dimerization. King [15] has previously reported dimer formation in the mass spectrum of **2a**.

2.3. Spectroelectrochemistry

To a first approximation, the electrochemical oxidation potential is equivalent to the energy of the HOMO while the long wavelength absorption energy corresponds to the energy of the HOMO–LUMO gap [16]. Although the methyl derivatives of group 4 indenyl half-sandwich complexes have been investigated by cyclic voltammetry and UV/visible spectroscopy [8,9], the processes and orbitals involved are quite different from those observed in indenyl ferrocene systems. The cyclic voltammetry of the group 4 complexes gives the energy of the LUMO, rather than the HOMO, as it is a reduction process that is observed and, although the UV/visible spectroscopy provides information on the HOMO–LUMO gap in both systems, it is an LMCT process from the indenyl to a d^0 metal centre in the group 4 complexes [8] rather than a d–d transition of the d^6 Fe atom [5,17]. One must be careful, therefore, when making comparisons between these systems.

We recently reported [10] the spectroelectrochemistry of a variety of trimethylsilyl-substituted derivatives of bis(indenyl)iron(II) in which significant effects on the UV/visible spectra were observed but only minor, non-additive effects were found in the cyclic voltammetry. Quite different effects were observed for the methyl derivatives reported here. We will address the UV/visible spectra first: indenyl ferrocenes exhibit two UV/visible absorption bands (with extinction coefficients of between 300 and 900 L mol^{-1} cm^{-1}), one near 420 nm and the other near 555 nm. Typical UV/visible spectra are shown in Fig. 1. These bands are likely to be d–d transitions since the HOMO is largely metal-based [5,17] and the extinction coefficients are all less than 1000 L mol^{-1} cm^{-1}. For mono-trimethylsilyl-substitution on the C$_5$ ring, we found that the UV/visible absorption peaks change by 10–22 nm while for disubstitution, all of the UV/visible absorption peaks shift to longer wavelength by 40–62 nm [10]. Apparently, the σ* orbitals of the TMS groups have a significant influence on the indenide ring MOs, thus affecting the bands in the UV/visible spectra. For methyl substitution (Table 1), on the other hand, we find that even with
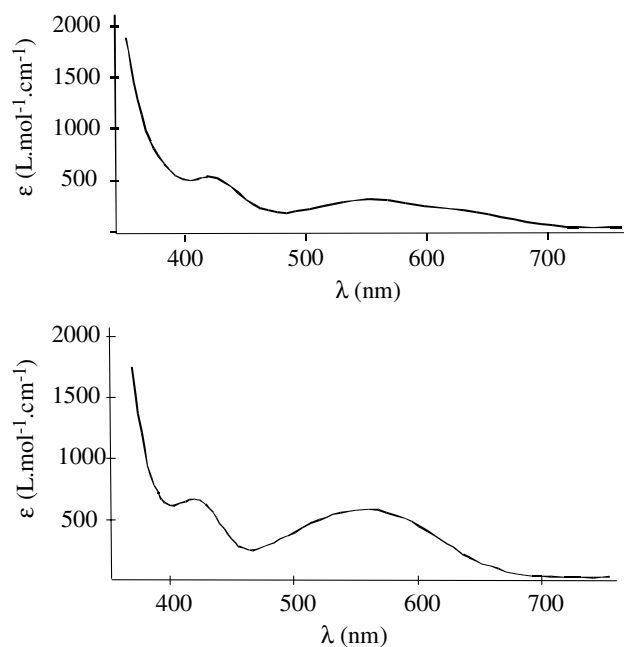
Fig. 1. Typical UV/visible spectra of bis(η^5-indenyl)iron(II) complexes: compound **2c** (top) and compound **2g** (bottom).

Fig. 2. Typical cyclic voltammogram of a bis(η^5-indenyl)iron(II) complex – compound **2g** is shown.

tetramethyl-substitution on each indenide, the UV/visible spectra vary by only 12 nm (416–426 and 548–560 nm). The bis(1,2,4,5,6,7-hexamethylindenyl)iron(II) complex (**2i**) has similarly been reported to have UV/visible absorption maxima within these ranges at 425 and 550 nm [6]. The HOMO and LUMO must, therefore, be affected to the same degree by sigma inductive effects.

Cyclic voltammetry shows a single-electron reversible redox process with a peak potential difference that indicates a slow redox process. A typical cyclic voltammogram is shown in Fig. 2. For mono-trimethylsilyl-substitution, we found that the oxidation potentials change by less than 10 mV while for disubstitution the oxidation potentials decrease by 18 mV (1,2 substitution) and 80 mV (1,3 substitution) from the unsubstituted ferrocene **2a**. It seems that the counterbalancing effect of the σ-donor and π-acceptor properties of the trimethylsilyl groups introduce significant complications and the influence of the trimethylsilyl groups on the oxi-
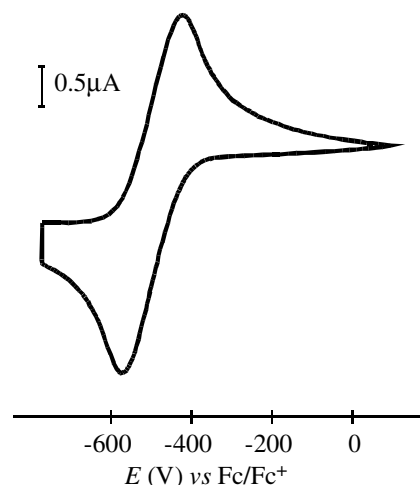
dation potential (energy of the HOMO) of the Fe atom are non-additive and relatively small. In contrast, the CV data for methyl substitution indicates that the sigma effects are large and generally additive: substitution in the 1/3 position (**2b**) gives a 97 mV decrease in oxidation potential per methyl group per indenyl from ferrocene **2a** whereas the 2 position (**2c**) gives a 77 mV decrease, and 4/7 substitution (**2f**) gives a 32.5 mV decrease. Using these values, one calculates an oxidation potential of −452 mV for **2d** (observe −450 mV); −472 mV for **2e** (observe −472 mV); −440 mV for **2g** (observe −451 mV); and −537 mV for **2h** (observe −568 mV). The additivity is not as good for **2h** and it may be that other factors, such as steric effects, are becoming important. We note that the bis(1,2,4,5,6,7-hexamethylindenyl)iron(II) complex (**2i**) has been reported to have an oxidation potential at −690 mV in CH_2Cl_2 [6] which would suggest a contribution of 86.5 mV per methyl group in a 5/6 position. This is likely to be overestimated as a result of non-additivity. The permethylated complex **2j** has been reported to have an oxidation potential of −730 mV in acetonitrile [5]. This is in the right direction, but the different solvent precludes further comparisons. The additive effects observed in the cyclic voltammetry indicates that the methyl groups raise the energy of the metal-based HOMO via σ-donor effects. The relative invariance of the UV/visible spectra indicates that the LUMO is similarly raised in energy for the methyl-substituted indenyl ferrocenes.

2.4. X-ray structural analyses

Crystallographic and refinement data for complexes **2c** and **2f** are given in Table 2 with selected bond distances and angles given in Table 3. The solid-state structures of these compounds were determined to complete their characterization.

Table 1
CV and UV/vis data for the investigated ferrocenes in CH_2Cl_2

Compound	E_0 (mV)[a]	ΔE_P (mV)	λ_{max} (nm) (ε/L mol^{-1} cm^{-1})	λ_{max} (nm) (ε/L mol^{-1} cm^{-1})
2a	−278	170	422 (654)	560 (332)
2b	−375	160	426 (580)	558 (368)
2c	−355	145	418 (530)	552 (304)
2d	−450	105	420 (484)	550 (359)
2e	−472	125	422 (516)	548 (342)
2f	−343	150	416 (827)	556 (430)
2g	−451	157	420 (658)	560 (568)
2h	−568	130	422 (536)	550 (628)

[a] Versus the Fc/Fc$^+$ couple.

An ORTEP of **2c** with the atomic numbering scheme is shown in Fig. 3. As expected, the iron is linearly coordinated by the centroids of the five-membered rings and the indenyl planes are parallel to each other. Fig. 5(a) shows the view down the centroid–centroid axis which illustrates the eclipsed conformation of the indenide rings: The RA of 3.4° is smaller than any previously observed bis(indenyl)iron(II) complex [14,18,19] and indicates that there is minimal steric interaction between the eclipsed methyl groups. Bis(2-menthylindenyl)iron(II) (**3**), which has the same substitution pattern but with bulkier substituents, has an RA of 134° [18]. Other metrical parameters for **2c** indicate that the indenide rings are undistorted, adopt an η^5-coordination mode, and are essentially planar: Δ, HA, and FA values (0.038/0.049 Å, 2.4°/2.8°, 0.4°/2.3°, respectively) are closer to those of bis(indenyl)iron(II) (0.043 Å, 2.2°, and 0.8°, respectively) and bis(heptamethylindenyl)iron(II) (0.030 Å, 2.5°, and 4.4°, respectively) [14] than complex **3** (0.065/0.051 Å, 4.9°/2.5°, and 6.0°/4.1°, respectively) which is distorted by the bulky menthyl groups [18] (see Fig. 4).

The X-ray crystallographic analysis of **2f** revealed two independent molecules, one of which (molecule 2) was found to lie on a crystallographic inversion centre such that the molecule is disordered about this position.

The two molecules are quite similar with both being approximately eclipsed (Fig. 5(b) and 5(c); RA = 14.7° and 17.9°). Δ, HA and FA are similar to that of **2c** except for the fairly large slip-fold parameters, Δ, of molecule 2 (0.056 and 0.061 Å).

3. Conclusions

We have prepared a range of methyl-substituted indenyl ferrocenes, characterized them, and investigated their spectroelectrochemical properties. Unlike the trimethylsilyl-substituted indenyl ferrocenes, an approximately linear dependence on methyl substitution was observed for the CVs of the indenyl ferrocenes while the UV/visible spectra were found to be essentially independent of methyl substitution, especially when compared to the trimethylsilyl derivatives. We conclude, therefore, that sigma inductive effects are similar for the HOMO and LUMO and that σ-donating substituents raise the energy of both orbitals. We expect that these results will assist in the interpretation of spectroelectrochemical properties of other indenyl ferrocenes when both σ and π substituents are involved.

Table 2
Crystal data and structural refinement parameters for **2c** and **2f**

	2c	2f
Empirical formula	$C_{20}H_{18}Fe$	$C_{22}H_{22}Fe$
F_w (g mol^{-1})	314.19	342.25
Temperature (K)	168(2)	163(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Tetragonal	Orthorhombic
Space group	$P4_32_12$	$Pbca$
Unit cell dimensions		
a (Å)	8.2242(12)	12.380(6)
b (Å)	8.2242(12)	15.649(8)
c (Å)	43.278(13)	25.774(14)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
Volume (Å^3)	2927.2(10)	4993(5)
Z	8	12
D_{calc} (mg/m^3)	1.426	1.366
Absorption coefficient (mm^{-1})	1.020	0.903
$F(000)$	1312	2160
Crystal size (mm)	$0.66 \times 0.21 \times 0.21$	$0.54 \times 0.27 \times 0.05$
θ Range (°)	1.88–26.37	2.24–26.41
Index ranges	$-10 \leqslant h \leqslant 10, -10 \leqslant k \leqslant 10, -54 \leqslant l \leqslant 34$	$-15 \leqslant h \leqslant 7, -19 \leqslant k \leqslant 19, -32 \leqslant l \leqslant 31$
Reflections collected	37152	58884
Independent reflections	2974	5081
R_{int}	0.0812	0.0599
Completeness to θ	(26.37°) 99.3%	(26.41°) 99.1%
Absorption correction	None	Semi-empirical
Maximum/minimum transmission	1.0000/0.8485	1.0000/0.8162
Data/restraints/parameters	2974/0/190	5081/0/414
Goodness-of-fit on F^2	0.869	0.784
R indices [$I > 2\sigma(I)$] (R, R_w)	0.0433, 0.0884	0.0274, 0.0674
R indices (all data) (R, R_w)	0.0506, 0.0919	0.0563, 0.0775
Final maximum/minimum $\Delta\rho$ (e Å^{-3})	0.250 and −0.334	0.238 and −0.303

Table 3
Selected bond distances (Å) and angles (°) for **2c** and **2f**

	2c[a]	**2f** (Molecule 1)[a]	**2f** (Molecule 2)[b]
Fe–CNT	1.677, 1.679	1.667, 1.669	1.666, 1.669
Fe–C1	2.050(4), 2.069(4)	2.0510(19), 2.0429(19)	2.052(6), 2.048(4)
Fe–C2	2.063(4), 2.061(3)	2.039(2), 2.038(2)	2.039(4), 2.041(4)
Fe–C3	2.066(4), 2.042(4)	2.048(2), 2.054(2)	2.044(4), 2.051(9)
Fe–C8	2.092(3), 2.112(4)	2.090(2), 2.092(2)	2.101(4), 2.108(7)
Fe–C9	2.103(4), 2.101(4)	2.0957(18), 2.0914(19)	2.110(8), 2.097(4)
CNT–Fe–CNT	178.59	179.28	178.79
C1–CNT–CNT′–C1′	3.5	14.5	18.3
Slip-fold parameter Δ (Å)[c]	0.038, 0.049	0.047, 0.047	0.061, 0.056
Hinge angle HA (°)[d]	2.4, 2.8	1.8, 1.7	2.3, 2.6
Fold angle FA (°)[e]	0.4, 2.3	1.7, 0.4	0.3, 1.2
Rotation angle RA (°)[f]	3.4	14.7	17.9

[a] The second number refers to the equivalent parameter for the "a" ring.
[b] The second number refers to the equivalent parameter for the "c" ring.
[c] Δ = average distance of Fe to C8 and C9 minus average distance of Fe to C1 and C3.
[d] HA = angle between planes defined by [C1, C2, C3] and [C1, C3, C8, C9].
[e] FA = angle between planes defined by [C1, C2, C3] and [C4, C5, C6, C7, C8, C9].
[f] RA = angle formed by the intersection of two lines determined by the centroids of the five- and six-membered rings.
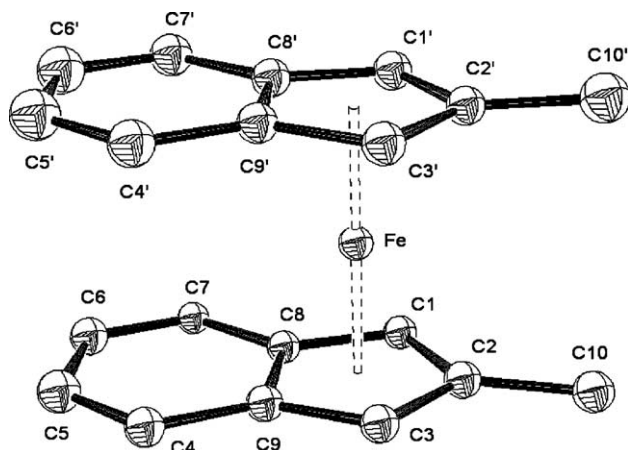

Fig. 3. ORTEP of **2c** indicating the numbering of the atoms. The thermal ellipsoids have been drawn at 40% probability.

4. Experimental

All manipulations and reactions were carried out under an inert atmosphere (Ar or N$_2$) by use of standard Schlenk line techniques. Reagent grade solvents were dried and distilled prior to use: diethyl ether and THF from Na/benzophenone; dichloromethane and petroleum ether (50–70 °C fraction) from CaH$_2$. 1-Methylindene [20], 1,3-dimethylindene [21], and 4,7-dimethylindene [22], were prepared by published procedures. All other reagents were purchased from Aldrich or Sigma Chemical Companies. ^{1}H and ^{13}C{^{1}H} NMR spectroscopy data were collected either on a Varian Unity-300 spectrometer operating at 300 and 75 MHz, respectively. 2D-NMR experiments were performed on a Varian INOVA-500 spectrometer operating at 500 and 125 MHz for ^{1}H and ^{13}C, respectively. Unless otherwise stated, spectra were measured at ambient temperature with residue solvent peaks as internal standards. EI mass spectra were collected on a Kratos MS80RFA mass spectrometer. Elemental analyses were carried out by Campbell Microanalytical Services, University of Otago, Dunedin. UV/visible spectra were obtained on a Hewlett Packard 8452A Diode Array (2 nm resolution) spectrometer using 1 cm cuvets. Cyclic voltammetry was performed using a PAR 173 Potentiostat coupled to a PAR 175 Universal Programmer and a Graphtec WX 1200 chart recorder. All electrochemical measurements were made using a three-electrode cell comprising of a platinum-disk working electrode (1 mm diameter), a platinum-wire auxiliary electrode, and a Ag/Ag$^+$ (0.01 M AgNO$_3$, 0.1 M [Bu$_4$N]PF$_6$-CH$_2$Cl$_2$) reference electrode. All potentials are reported vs the ferrocene/ferrocenium (Fc/Fc$^+$) couple after referencing to in situ ferrocene. Before use, the electrodes were polished with 1 μm diamond paste and cleaned with acetone and distilled water. Electrochemical measurements were made at ambient temperature under an inert atmosphere.
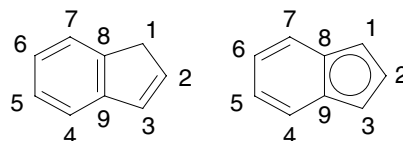
4.1. Preparation of 1,2-dimethylindene (1d)

To a solution of 2-methylindene (2 mL, 14.91 mmol) in diethyl ether (40 mL) at −80 °C was added a solution of n-BuLi (9.32 mL, 1.6 M, 14.91 mmol). The solution was allowed to warm to ambient temperature and stirred for 4 h. The resulting yellow solution was then added
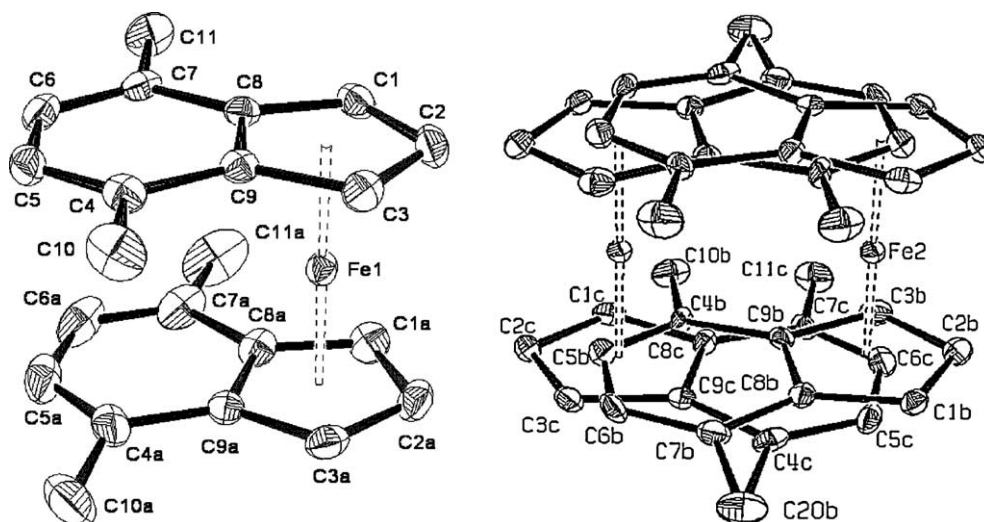
Fig. 4. ORTEPs of molecules 1 and 2 of **2f** indicating the numbering of the atoms and illustrating the disorder in molecule 2. The thermal ellipsoids have been drawn at 40% and 35% probability, respectively.
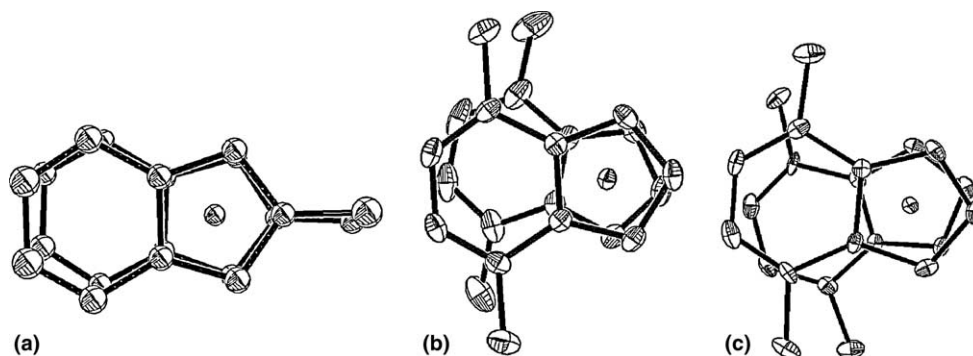

Fig. 5. Views down the CNT–CNT axes: (a) **2c**; (b) Molecule 1 of **2f**; (c) Molecule 2 of **2f**.

drop-wise via cannula to a solution of iodomethane (3.72 mL, 59.64 mmol) in diethyl ether (30 mL) at −80 °C. The solution was stirred overnight at ambient temperature and the reaction quenched by the addition of a saturated aqueous NH_4Cl solution (50 mL). The organic material was extracted with diethyl ether (4 × 20 mL), dried over $MgSO_4$, filtered and the solvent removed with a rotary-evaporator. The resulting yellow oil was distilled at reduced pressure to give 1.405 g (65%) of **1d** as a colourless oil. ^1H and $^{13}C\{^1H\}$ NMR spectra were consistent with the literature [21,23].

4.2. Preparation of 1,4,7-trimethylindene (1g)

To a solution of 4,7-dimethylindene (5.125 g, 35.54 mmol) in diethyl ether (50 mL) at −80 °C was added a solution of *n*-BuLi (22.21 mL, 1.6 M, 35.54 mmol). The solution was allowed to warm to ambient temperature and stirred for 4 h over which time a white precipitate formed. The suspension was then added via cannula to a solution of iodomethane (8.85 mL, 142 mmol) in diethyl ether (50 mL) at −80 °C. The solution was stirred overnight at ambient temperature and the reaction quenched by the addition of a saturated aqueous NH_4Cl solution (50 mL). The organic material was extracted with diethyl ether (4 × 50 mL), dried over $MgSO_4$, filtered and the solvent removed with a rotary-evaporator. The resulting yellow oil was distilled at reduced pressure to give 3.921 g (70%) of **1g** as a colourless oil. ^1H NMR ($CDCl_3$): δ 7.03 (d, $^3J_{HH}$ = 7.8 Hz, 1H, H6), 6.94 (d, $^3J_{HH}$ = 7.8 Hz, 1H, H5), 6.89 (dd, $^3J_{HH}$ = 5.4 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, H3), 6.50 (dd, $^3J_{HH}$ = 5.4 Hz, $^3J_{HH}$ = 1.7 Hz, 1H, H2), 3.60 (qdd, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 1.7 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, H1), 2.45 (br s, 6H, C4–CH_3 and C7–CH_3), 1.37 (d, $^3J_{HH}$ = 7.8 Hz, 3H, C1–CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 146.7 (C8), 142.6 (C9), 141.1 (C2), 130.2 (C7), 128.0 (C3), 127.8 (C5), 127.7 (C4), 126.6 (C6), 45.0 (C1), 18.6 (C4–CH_3), 18.2 (C7–CH_3), 14.7 (C1–CH_3). Mass spectrum: (EI, *m/z* (%)): 158 (54, M$^+$), 143 (31, $C_9H_5Me_2^+$), 128 (100, $C_9H_5Me^+$), 113 (22 $C_9H_5^+$). HR-MS: M$^+$ Calc., 158.10955; Found: 158.11038.

4.3. Preparation of 1,3,4,7-tetramethylindene (1h)

To a solution of 1,4,7-dimethylindene (1.464 g, 9.25 mmol) in diethyl ether (30 mL) at −80 °C was added a solution of *n*-BuLi (5.78 mL, 1.6 M, 9.25 mmol). The solution was allowed to warm to ambient temperature and stirred for 4 h over which time a white precipitate formed. The suspension was added via cannula to a solution of iodomethane (2.30 mL, 370 mmol) in diethyl ether (30 mL) at −80 °C. The solution was stirred overnight at ambient temperature and the reaction quenched by the addition of a saturated aqueous NH_4Cl solution (50 mL). The organic material was extracted with diethyl ether (4 × 30 mL), dried over $MgSO_4$, filtered and the solvent removed with a rotary-evaporator. The resulting yellow oil was distilled at reduced pressure to give 1.012 g (63%) of **1h** as a colourless oil. The ^1H NMR spectrum was consistent with the literature [21]. We report the ^{13}C NMR spectrum here: $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 148.5 (C8), 142.3 (C9), 139.2 (C3), 137.6 (C2), 130.5 (C7), 129.4 (C5), 128.5 (C4), 126.6 (C6), 42.4 (C1), 19.5 (C4–CH_3), 18.5 (C7–CH_3), 17.5 (C3–CH_3), 15.1 (C1–CH_3).

4.4. Preparation of diindenyliron(II) (2a)

To a solution of indene (1.992 g, 17.13 mmol) in THF (95 mL) at −80 °C was added a solution of *n*-BuLi (10.71 mL, 1.6 M, 17.13 mmol). After warming to ambient temperature and stirring for 4 h, the reaction mixture was cooled to − 80 °C and $FeCl_2$ (1.086 g, 8.57 mmol) was added. The reaction mixture was stirred for a further 18 h. The solvent was removed in vacuo and the residue was dissolved in CH_2Cl_2 (40 mL) and filtered through Celite. The Celite was washed with additional CH_2Cl_2 (35 mL) and the solvent was removed in vacuo and purified by vacuum sublimation to give 1.706 g (70%) of **2a** as a black solid. This is a significant improvement over the literature preparation [12]. ^1H NMR (C_6D_6): δ 6.80 (m, 8H, H4-7), 4.48 (s, 4H, H1/3), 3.89 (s, 2H, H2). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 125.5 (C4/7), 122.8 (C5/6), 87.0 (C8/9), 69.9 (C2), 61.9 (C1/3).

4.5. Preparation of rac- and meso-bis(1-methylindenyl)iron(II) (2b)

To a solution of 1-methylindene (0.893 g, 6.86 mmol) in THF (40 mL) at −80 °C was added a solution of *n*-BuLi (4.29 mL, 1.6 M, 6.86 mmol). After warming to ambient temperature and stirring for 2 h, $FeCl_2$ (0.435 g, 3.43 mmol) was added and the reaction mixture was stirred for a further 2 h. The solvent was removed in vacuo and the residue was dissolved in diethyl ether (50 mL) and filtered through Celite. Removal of the solvent in vacuo and further purification by vacuum sublimation yielded 0.485 g (45%) of **2b** as

a black solid. The product was obtained as a 1:1 mixture of *racemic* and *meso* diastereomers. The ^1H NMR spectrum was consistent with the literature [4]. Mass spectrum: (EI, *m/z* (%)): 258 (65, $C_{20}H_{18}^+$), 144 (75, $C_{11}H_{12}^+$), 130 (70, $C_{10}H_{10}^+$), 129 (95, $C_{10}H_9^+$), 128 (100, $C_{10}H_8^+$), 115 (95, $C_9H_7^+$).

Isomer 1: $^{13}C\{^1H\}$ NMR (C_6D_6): δ 127.2 (C7), 125.5 (C4), 123.0 (C6), 122.6 (C5), 87.0 (C9), 86.1 (C8), 74.3 (C1), 72.6 (C2), 60.4 (C3), 11.0 (CH_3).

Isomer 2: $^{13}C\{^1H\}$ NMR (C_6D_6): δ 127.1 (C7), 125.0 (C4), 122.6 (C6), 122.4 (C5), 86.9 (C9), 86.1 (C8), 74.2 (C1), 72.2 (C2), 59.6 (C3), 10.4 (CH_3).

4.6. Preparation of bis(2-methylindenyl)iron(II) (2c)

To a solution of 2-methylindene (0.55 mL, 3.85 mmol) in THF (50 mL) at −80 °C was added a solution of *n*-BuLi (2.40 mL, 1.6 M, 3.85 mmol). After warming to ambient temperature and stirring for 4 h, $FeCl_2$ (0.244 g, 1.93 mmol) was added and the reaction mixture was stirred for a further 16 h. The solvent was removed in vacuo and the residue was dissolved in diethyl ether (25 mL) and filtered through Celite. Removal of the solvent in vacuo followed by recrystallisation from diethyl ether yielded 0.219 g (36%) of **2c** as black crystals. ^1H NMR (C_6D_6): δ 7.00 (m, 4H, H4/7), 6.85 (m, 4H, H5/6), 4.22 (s, 4H, H1/3), 1.73 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 127.45 (s, C4/7), 122.99 (s, C5/6), 86.77 (s, C8/9), 85.57 (s, C2), 63.27 (s, C1/3), 13.54 (s, CH_3). Mass spectrum: (EI, *m/z* (%)): 314 (4, M$^+$), 258 (30, $C_{20}H_{18}^+$), 144 (75, $C_{11}H_{12}^+$), 130 (85, $C_{10}H_{10}^+$), 129 (100, $C_{10}H_9^+$), 128 (90, $C_{10}H_8^+$), 115 (95, $C_9H_7^+$). Anal. Calc. for $C_{20}H_{18}Fe$: C, 76.55; H, 5.78. Found: C, 75.80; H, 5.69.

4.7. Preparation of rac- and meso-bis(1,2-dimethylindenyl)iron(II) (2d)

To a solution of 1,2-dimethylindene (0.541 g, 3.75 mmol) in THF (35 mL) at −80 °C was added a solution of *n*-BuLi (2.34 mL, 1.6 M, 3.75 mmol). After warming to ambient temperature and stirring for 2 h, $FeCl_2$ (0.238 g, 1.88 mmol) was added and the reaction mixture was stirred for a further 2 h. The solvent was removed in vacuo and the residue was dissolved in diethyl ether (30 mL) and filtered through Celite. Removal of the solvent in vacuo yielded 0.433 g (67%) of **2d** as a dark green solid. The product was obtained as a 1:1 mixture of *racemic* and *meso* diastereomers. ^1H NMR ($CDCl_3$): δ 7.17–6.96 (m, 16H, H4-7), 4.29 (s, 2H, *rac*-H3), 3.96 (s, 2H, *meso*-H3), 1.95 (s, 6H, C1–CH_3), 1.79 (s, 6H, C2–CH_3), 1.77 (s, 6H, C1–CH_3), 1.68 (s, 6H, C2–CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 127.2 (C7), 127.1 (C7), 126.1 (C4), 125.9 (C4), 123.1 (C6), 122.7 (C6), 122.4 (C5), 122.3 (C5), 85.7–84.7 (m, C2, C8, C9), 72.6 (C1), 72.3 (C1), 62.7 (C3), 62.0 (C3), 11.7

(C2–CH_3), 11.5 (C2–CH_3), 8.7 (C1–CH_3), 7.8 (C1–CH_3). Mass spectrum: (EI, m/z (%)): 342 (40, M^+), 286 (78, $C_{22}H_{22}^+$), 143 (100, $C_{11}H_{11}^+$), 128 (90, $C_{10}H_8^+$). Anal. Calc. for $C_{22}H_{22}Fe$: C, 77.20; H, 6.48. Found: C, 77.32; H, 5.98.

4.8. Preparation of bis(1,3-dimethylindenyl)iron(II) (2e)

To a solution of 1,3-dimethylindene (0.512 g, 3.55 mmol) in THF (35 mL) at −80 °C was added a solution of n-BuLi (2.23 mL, 1.6 M, 3.55 mmol). After warming to ambient temperature and stirring for 2 h, $FeCl_2$ (0.224 g, 1.78 mmol) was added and the reaction mixture was stirred for a further 2 h. The solvent was removed in vacuo and the residue was dissolved in diethyl ether (30 mL) and filtered through Celite. Removal of the solvent in vacuo yielded 0.359 g (59%) of **2e** as a dark green solid. The ^1H NMR spectrum was consistent with the literature [13]. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 128.7 (C4/7), 123.9 (C5/6), 84.9 (C8/9), 82.1 (C2), 74.4 (C1/3), 11.7 (CH_3). Mass spectrum: (EI, m/z (%)): 342 (5, M^+), 286 (10, $C_{22}H_{22}^+$), 143 (60, $C_{11}H_{11}^+$), 142 (80, $C_{11}H_{10}^+$), 141 (100, $C_{11}H_9^+$), 128 (35, $C_{10}H_8^+$).

4.9. Preparation of bis(4,7-dimethylindenyl)iron(II) (2f)

To a solution of 4,7-dimethylindene (2.09 g, 14.49 mmol) in THF (95 mL) at −80 °C was added a solution of n-BuLi (9.05 mL, 1.6 M, 14.49 mmol). After warming to ambient temperature and stirring for 4 h, $FeCl_2$ (0.919 g, 7.25 mmol) was added and the reaction mixture was stirred for a further 16 h. The solvent was removed in vacuo and the residue was dissolved in diethyl ether (50 mL) and filtered through Celite. Removal of the solvent in vacuo yielded 1.86 g (75%) of **2f** as a dark purple solid. ^1H NMR (C_6D_6): δ 6.57 (s, 4H, H5/6), 4.42 (s, 4H, H1/3), 4.02 (2, 2H, H2), 2.13 (s, 12H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 133.17 (s, C4/7), 121.83 (s, C5/6), 88.95 (s, C8/9), 69.36 (s, C2), 60.05 (s, C1/3), 19.52 (s, CH_3). Mass spectrum: (EI, m/z (%)): 342 (18, M^+), 286 (7, $C_{22}H_{22}^+$), 160 (62), 145 (100, $C_{11}H_{13}^+$), 143 (27, $C_{11}H_{11}^+$). HR-MS: M^+ Calc., 342.10705; Found, 342.10595. Anal. Calc. for $C_{22}H_{22}Fe$: C, 77.20; H, 6.48. Found: C, 76.90; H, 6.40.

4.10. Preparation of rac- and meso-bis(1,4,7-trimethylindenyl)iron(II) (2g)

To a solution of 1,4,7-trimethylindene (0.647 g, 4.09 mmol) in THF (35 mL) at −80 °C was added a solution of n-BuLi (2.55 mL, 1.6 M, 4.09 mmol). After warming to ambient temperature and stirring for 2 h, $FeCl_2$ (0.26 g, 2.04 mmol) was added and the reaction mixture was stirred for a further 2 h. The solvent was removed in vacuo and the residue was dissolved in CH_2Cl_2

(20 mL) and filtered through Celite. Removal of the solvent in vacuo yielded 0.536 g (71%) of **2g** as a dark purple solid. The product was obtained as a 1:1 mixture of *racemic* and *meso* diastereomers.

Isomer 1: $^{13}C\{^1H\}$ NMR (C_6D_6): 136.0 (C7), 133.0 (C4), 123.0 (C6), 121.2 (C5), 90.3 (C9), 86.0 (C8), 74.6 (C1), 74.4 (C2), 58.8 (C3), 21.2 (C7–CH_3), 19.3 (C4–CH_3), 13.8 (C1–CH_3).

Isomer 2: $^{13}C\{^1H\}$ NMR (C_6D_6): 134.8 (C7), 134.6 (C4), 122.6 (C6), 121.8 (C5), 89.5 (C9), 85.6 (C8), 74.1 (C1), 72.9 (C2), 56.7 (C3), 21.4 (C7–CH_3), 19.1 (C4–CH_3), 11.6 (C1–CH_3).

Isomeric mixture: ^1H NMR ($CDCl_3$): δ 6.76–6.61 (m, 8H, H5 and H6), 4.42 (s, 2H, H3), 4.16 (s, 2H, H3), 4.03 (s, 2H, H2), 3.97 (s, 2H, H2), 2.43 (s, 6H, C7–CH_3), 2.33 (s, 6H, C7–CH_3), 2.30 (s, 6H, C4–CH_3), 2.23 (br s, 12H, C4–CH_3 and C1–CH_3), 1.83 (s, 6H, C1–CH_3). Mass spectrum: (EI, m/z (%)): 370 (66, M+), 355 (8, [M–CH_3]$^+$), 314 (11, $C_{24}H_{26}^+$), 157 (100, $C_{12}H_{13}^+$), 141 (46, $C_{11}H_9^+$). HR-MS: M^+ Calc., 370.13835; Found: 370.13892.

4.11. Preparation of bis(1,3,4,7-tetramethylindenyl)iron(II) (2h)

To a solution of 1,3,4,7-tetramethylindene (0.789 g, 4.58 mmol) in THF (40 mL) at −80 °C was added a solution of n-BuLi (2.87 mL, 1.6 M, 4.58 mmol). After warming to ambient temperature and stirring for 2 h, $FeCl_2$ (0.290 g, 2.29 mmol) was added and the reaction mixture was stirred for a further 2 h. The solvent was removed in vacuo and the residue was dissolved in CH_2Cl_2 (20 mL) and filtered through Celite. Removal of the solvent in vacuo yielded 0.648 g (71%) of **2h** as a dark purple solid. ^1H NMR (C_6D_6): δ 6.60 (s, 4H, H5/6), 3.44 (s, 2H, H2), 2.30 (s, 12H, C4/7–CH_3), 1.94 (s, 12H, C1/3–CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 135.6 (C4/7), 122.9 (C5/6), 86.8 (C8/9), 81.1 (C2), 72.5 (C1/3), 21.4 (C4/7–CH_3), 13.3 (C1/3–CH_3). Mass spectrum: (EI, m/z (%)): 398 (100, M^+), 383 (16, [M–CH_3]$^+$), 226 (18, [M–$C_{13}H_{16}$]$^+$), 173 (71). HR-MS: M^+ Calc., 398.16965; Found: 398.16937. Anal. Calc. for $C_{26}H_{30}Fe$: C, 78.39; H, 7.59. Found: C, 77.64; H, 7.49.

4.12. X-ray structure determinations for 2c and 2f

Crystal data and experimental details are given in Table 2. For each compound, a crystal was attached to a thin glass fiber and mounted on a Siemens P4 SMART diffractometer with a Siemens CCD area detector. Multi-scan absorption corrections were determined with SADABS and applied to the data [24]. Data processing was undertaken with SAINT [24] and the structures were solved by direct methods and refined by least-squares methods on F^2 using the SHELXTL program library [25]. Hydrogen atoms were placed in their

calculated positions and refined isotropically riding with the atoms to which they are bonded. Non-hydrogen atoms were refined anisotropically. The absolute configuration of **2c** was tested and found to be correct (Flack parameter = 0.06(3)). Molecule 2 of **2f** lies on an inversion centre such that the methyl groups C20b and C20c lie in an approximately equivalent position.

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre: CCDC nos. 256589 for **2c**; and 256590 for **2f**. Copies of the information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK. Fax. (int. code) +44(1223)336-033 or by e-mail at deposit@ccdc.cam.ac.uk or from the www at http://www.ccdc.cam.ac.uk.

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