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# A Synthetic Route to 1,1',2,2'-Tetra-iodoferrocene which avoids Isomerization and the Electrochemistry of Some Tetrahaloferrocenes.

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**ABSTRACT:** An efficient synthesis of 1,1',2,2'-tetra-iodoferrocene is described which uses 1,1',2,2'-tetrakis-(tri-*n*-butylstannyl)ferrocene as a key intermediate in its synthesis. In an attempt to examine the stepwise mechanism the reaction of the tetra tin substituted ferrocene 1,1',2,2'-tetrakis-(tri-n-butylstannyl)ferrocene with iodine was monitored by <sup>1</sup>H NMR and a series of coexistent intermediate compounds such as 1',1'-bis-(tri-n-butylstannyl)-(2,2'-diodo)ferrocene were observed. The crystal structure of 1,1',2,2'-tetra-iodoferrocene has been determined and it is compared with the structure of the previously reported 1,1',2,2'-tetrabromoferrocene and 1,2,4,1'-tetra-iodoferrocene. The comparative electrochemistry of 1,1',2,2'tetrachloroferrocene, 1,1',2,2'-tetrabromoferrocene and 1,1',2,2'-tetra-iodoferrocene is described. The crystal structure of 1,2,1'-triiodoferrocene is also reported for comparative use to illustrate the scope of the synthetic method.

Iodoferrocenes<sup>1</sup> are key compounds in the synthesis of substituted ferrocenes, particularly where Heck, Sonogashira, Suzuki-Miyaura or Ullmann coupling reactions,<sup>2</sup> is involved because they are highly reactive in such coupling reactions by comparison with the related chloro- and bromo-ferrocenes. They may also be used as precursors for amino-ferrocene synthesis,<sup>3</sup> as well as being synthons for a broader range of copper-mediated reactions.<sup>4</sup> There has been much interest surrounding one iodoferrocene compound, 1,1'-diiodoferrocene, **2**: there are many synthetic methods available to this compound but the simplest is the reaction of 1,1'dilithioferrocene, **1** with iodine, scheme 1a.<sup>5</sup>



Scheme 1. Two synthetic routes to 1,1'-diiodoferrocene.

This was the method of choice for the preparation of 1,1'di-iodoferrocene in our research group in the early 1980's following the early mercuration/exchange work by Rausch on iodo- and 1,2-di-iodoferrocene synthesis.<sup>6</sup> Subsequently, in the early 1990's, in our undergraduate teaching laboratories we used the reaction of 1,1'-dilithioferrocene with 1,2-di-iodotetrafluoroethane as the method of choice as the yields were consistently high (> 90%) and the work up was

easy. Unfortunately, this reagent became prohibitively expensive because of the demise of industrial fluorocarbon synthesis and we only use this reagent when we require clean samples of 1,1'-di-iodoferrocene quickly. In our view this remains the best synthesis as judged by the success of successive years of undergraduate class synthesis. Concurrently we used temperature gradient vacuum sublimation (commercial instrument) to purify di-iodoferrocene, prepared by the iodine quenching route but we were aware of the large number of by-products such as the 1,1<sup>'''</sup>-diiodo-1',1''-biferrocene which are also formed in the synthesis. To counter all these difficulties a new general synthetic method, was developed:<sup>7</sup> as an example, *bis*-(1,1'-tri-*n*-butylstannyl)ferrocene, 3 on treatment with iodine gives diiodoferrocene directly in much higher yield, scheme 1b. However, the purification of the product, in this case, was challenging. The reason for this difficulty is simply that the high solubility in non-polar solvents of both the tin by-products and 1,1'-di-iodoferrocene, coupled with their low polarities, cause crystallisation and chromatographic separation problems. For iodinated products which are less soluble in non-polar solvents the problem disappears; for example, in the preparation of di-iodoanthracenes or iodoferrocene, the synthetic method is ideal. The synthesis of ferrocenylboronic acids may also be used for iodoferrocene preparation -this was considered for a future examination.8 We judged that because the solubility of the haloferrocenes decreases in non-polar solvents with increasing halogenation the method may be suitable for the preparation of tetra-iodoferrocene and more highly substituted iodoferrocenes. To obtain the *tetra*-substituted tin compound cleanly we decided to use the corresponding 1,1',2,2'-tetra-bromoferrocene, **4**, as the precursor for this work, scheme 2,<sup>9</sup> as the ortho lithiation of di-iodoferrocene followed by an iodine quench gives a mixture of iodoferrocenes. (See supplementary information).



A. <sup>n</sup>BuLi; B. CISn(<sup>n</sup>Bu)<sub>3</sub> C. I<sub>2</sub>/CH<sub>2</sub>CI<sub>2</sub>

**Scheme 2**: Planned stepwise preparation of 1,1',2,2'-tetraiodoferrocene from 1,1',2,2'-tetrabromoferrocene.

As previously mentioned, the related 1,2-diodoferrocene was first prepared as early as 1971 by Roling and Rausch,<sup>6</sup> and was later subsequently structurally characterised,<sup>10</sup> but the preparation was low yielding involving mercury intermediates. A new syntheses of this compound have been described more recently using the ortho-metalation method.11 Also, recently, a full review on halogenoferrocene synthesis and reaction chemistry has been published and the reader is directed to this work for a complete understanding of context.12 In this work Butenschön lists eight known iodoferrocenes and therefore it is the object of this work to expand the range of known iodoferrocenes and also to point the direction to obtain the full complement of possible iodoferrocenes. The obvious use of poly-iodoferroces is in their metal-catalysed coupling reactions to give other tetrasubstituted ferrocenes or polymeric arrays of ferrocene with or without spacer groups. These ferrocene arrays may be useful as electrodes in rapid charge batteries of the future. However, it will also be useful to explore the deliberate isomerisation of 1,1',2,2'-tetraiodoferrocene (halogen dance)to furnish new isomers.

### **RESULTS AND DISCUSSION**

In preliminary work, based on our previous work on bromoferrocenes.<sup>13</sup> we had attempted the low temperature alpha-dilithiation of 1,1'-diiodoferrocene in thf followed by iodine quenching. This always resulted in complex mixtures. In addition the syntheses of the 1,1',2,2'-tetra-iodoferrocene was attempted directly from the corresponding tetra-bromoferrocene by a rapid lithium halogen exchange followed by iodine or chloro-tri-(n-butyl) tin quenching. This was carried out either low temperature (ca -50°C) or room temperature. However, in these attempts a complex mixture of products was always obtained which did include the desired 1,1',2,2'-tetra-iodoferrocene but it co-crystallised with 2'-bromo-1,1',2-tri-iodoferrocene and 2,2'-dibromo-1,1'-diiodoferrocene. The NMR spectral data obtained indicated product mixtures even when highly crystalline samples were obtained. A crystal structure investigation confirmed the presence of bromine in the crystal lattice of the product "tetraiodoferrocene". Attempts at compound separation by chromatography proved equally

fruitless even using preparative plate methods. The problem was that the multiple initial halogen lithium exchange reaction was either much slower than anticipated or the intermediate lithium compounds were reacting slowly at low temperature. Despite this we were able to identify many intermediate mixed halogen compounds using NMR. Examples of <sup>1</sup>H NMR spectra of these mixtures are included in the supporting information.

While this was disappointing it is noted that the mixed bromine/iodine compounds may be valuable because coupling reactions with the iodine groups will furnish products still containing bromines which with allow further product functionalisation. This is a moot point since in the interim the synthesis of pure 1,1',2,2'-tetra-lithioferrocene, 5 from 4, was developed which opened the door to a better synthesis of compound **6**. This compound was reacted in *situ* with chloro-tri-n-butyltin to give the tetrakis-{tri-(n-butylstannyl)} ferrocene 6, as a viscous red oil. This compound was not purified during the current synthesis as this leads to a loss in product yield, but it may be isolated as a red oil following chromatography if a pure sample is required. In the cyclopentadienyl region of the proton NMR spectrum the apparent doublet ( $\delta$ , 4.38) and triplet ( $\delta$ , 4.63) pattern so characteristic of a 1,2-symmetrically di-substituted ferrocene is observed. The direct iodination,<sup>6</sup> step C scheme 2, to convert compound 6 to 7 was next examined. The reaction was monitored using NMR and it is clear to see the stepwise formation of the product, 7. If required the reaction could be halted at any stage to produce the intermediate compounds 8, 9, and 10, however their isolation would require chromatography if small scale reactions were used. Some intermediate compounds which are easily discernible in the NMR spectrum are the 1',2,2'-tris-(tri-n-bu-2,2'-bis-(tri-n-butylstannyl)-1-iodoferrocenes 8. tylstannyl)-1,1'-di-iodoferrocenes, 9a and 9b (one isomer shown in fig 1; the other isomer has one resonance overlapped), and 2'-(tri-*n*-butylstannyl)-1,1',2--tri-iodoferrocenes, **10**. It is noted that one isomer of compounds **9** is formed in preference with resonances at  $\delta$  3.87, 4.06 and 4.57.\* (\*as these are in matrix of other compounds the exact chemical shifts of the pure compounds are likely to be slightly different). The spectroscopic changes may be seen in the figure 1.



**Figure 1**: stepwise addition of  $I_2$  solution in CDCl<sub>3</sub> to 1,1',2,2'-tetra-(tri-n-butylstannyl) ferrocene, **6**, 1, to give

1,1',2,2'*-tetra*-iodoferrocene, **7**, 12 at ambient temperature. (400MHz).

Although the third diiodide isomer **9c** (scheme 3) is not assigned in figure 1 it is likely to be present as there are overlapped unassigned resonances present. The final product **7** is easily isolated because it has its predicted reduced solubility in petrol and therefore crystallises easily. Its NMR spectrum again comprises the characteristic apparent doublet ( $\delta$ , 4.46), triplet ( $\delta$ , 4.13) pattern- it is noted that the doublet and triplet resonances exchange places on going from **6** to **7** indicative of the change in the relative shielding and electronegativities of iodine and tin.



**Scheme 3:** Intermediate compounds formed during the preparation route to 1,1',2,2'-tetra-iodoferrocene, **7** by slow addition of aliquots of iodine to compound **6**. (simplified).

The crystal structure of compound **7** is shown in figure **2** together with an isomer **11**, 1,2,4,1'-tetra-iodoferrocene, which had been previously obtained from the *ortho*-lithiation reaction of 1,1'-diiodoferrocene on quenching with iodine. The melting point of compound **7** (ca, 127-128°C) is higher than that of the corresponding tetra-bromoferrocene (110-112°C) but is almost identical to that of 1,1',2,2'-tetra-chloroferrocene, (126-127°C). Compound **11** is one of the product tetra-iodoferrocenes obtained in the *ortho*-lithiation reaction of 1,1'-diiiodoferrocene followed by reaction with iodine. This is formed because of the iodine scrambling process (halogen dance) recently described by Mongin and co-workers.<sup>15</sup>



Figure 2: 1,1',2,2'-tetra-iodoferrocene, **7** (one of the 2 molecules in the asymmetric unit shown) and 1,2,4,1'-tetra-io-doferrocene, **11** (not showing the minor (2%) disordered component).

It is noted that a further tetra-iodoferrocene 1,2,3,4-tetraiodoferrocene is known.<sup>1b</sup> The crystal structure of compound **7** does not show the eclipsed-ring solid state structure associated with 1,1',2,2'-tetra-chloroferrocene and 1,1',2,2'-tetra-bromoferrocene, 1,1',2,2'-tetra-bromoruthenocene and many mixed-halogen, 1,1',2,2'-tetra-substituted ferrocenes including 2'-bromo-1,1',2-triiodoferrocene and 1,1'-dibromo-2,2'-diiodoferrocene. This may simply be due to the bulkier iodine substituents. The two independent molecules of 7 only really differ in the rotation of the cp rings with respect to each other (torsion angles (I- $Cp_{cent1}-Cp_{cent2}-I$  = 64.23(5)° vs 69.31(5)°. They have almost no tilting between the Cp rings (Cp<sub>cent1</sub>-Fe-Cp<sub>cent2</sub> angles = 179.23(8)°, 179.62(10)°) and the iodine atoms lie barely out of the plane of the Cp rings (0.004(6)-0.147(6) Å) However, the two independent molecules do show a clear pattern when they are considered as a pair. This is apparent on inspection in figure 3a, the structure does show an alternating structure based on the pair. Interestingly the view down the axis of the iodine atoms (i.e. top view) figure 3b does show an eclipsed structure overall of the iodine atoms in a non-fully staggered arrangement of the pair. There are several iodine-iodine interactions: the principal ones are listed in table 1.

Table 1: Iodine-iodine interactions.

Iodine close contacts	Distance / Å
I1I3ª	3.6792(4)
I1I3 <sup>b</sup>	3.7409(4)
I3I13c	3.7564(4)
a): 1/2-x,1/2+y,1/2-z;	b): -1/2+x,1/2-y,-1/2+z; c): 1-x,1-
v.1-z	



Figure 3: a): diagram showing the pairwise packing of **7** b) top view showing eclipsed nature of iodine atoms down the cp centroid-Fe direction.

	Com- pound Fc(XY)2 <sup>*</sup>		$E^{\circ}/V$ ( $\Delta E_p/mV$ )	$\lambda_{max}(nm)$ Fc(XY) <sub>2</sub>	$\lambda_{max}(nm)$ [Fc(XY) <sub>2</sub> ] <sup>+</sup>	Ref.
	Х	Y				
7	Ι	Ι	+0.89 (45)	443	799, 566	this work
	Ι	Br	+0.97 (70)	433	778, 626	16
4	Br	Br	+0.99 (30)	435	760, 617	this work
	Br	Cl	+1.01 (60)	436	757, 613	16
	Cl	Cl	+1.00 (80)	436	755, 615	16
Fc	Н	Н	+0.49(60)	441	625	17

**Table 2**. Formal electrode potentials (V, vs. AgCl/Ag (KCl sat.), peak-to-peak separations (mV) and UV-Vis. absorptions (nm) for the redox changes exhibited by **4**, **7** and related tetrahalo-substituted ferrocenes, in CH<sub>2</sub>Cl<sub>2</sub> solution.

#### \*1,2,1',2'-tetra-substiution.

Compound **11** has the single iodine staggered with respect to the other 3 (smallest torsion angle  $(I-Cp_{cent1}-Cp_{cent2}-I) = 48.27(4)^{\circ}$ ) but also has almost no titling of the Cp rings  $(Cp_{cent1}-Fe-Cp_{cent2} \text{ angle} = 179.06(8)^{\circ})$  and the iodine atoms barely lying out of the plane of the Cp rings (0.043(6) - 0.078(6) Å).

Clearly the synthetic method is suitable for the preparation of a broad range of multiply substituted iodo-ferrocenes, provided the corresponding bromoferrocenes are available. As an example, 1,2,1'-triiodoferrocene, **12** was prepared: its structure is shown in fig. 4. It has the single iodine staggered with respect to the other 2 (smallest torsion angle (I-Cp<sub>cent1</sub>-Cp<sub>cent2</sub>-I) = 59.19(4)° but also has almost no titling of the Cp rings (Cp<sub>cent1</sub>-Fe-Cp<sub>cent2</sub> angle = 179.89(10)°) and the iodine atoms barely lying out of the plane of the Cp rings (0.001(6) - 0.083(6) Å).



Figure 4: Crystal structure of 1,2,1'-tri-iodoferrocene.

The redox behaviour of 7 has been studied by cyclic voltammetry and UV-vis thin layer spectro-electrochemistry and compared with that of several other tetra-halo congeners.<sup>16</sup> These compounds all exhibited reversible behaviour (ip<sub>c</sub>/ip<sub>a</sub>  $\approx$  1 and i<sub>p</sub>  $\propto$  v<sup>1/2</sup>; data summarized in Table 2). A quick look at table 2 allows us to notice that the electronegativity trend is only roughly followed, in fact, the Br and Cl

effect is so similar that the I effect is the only one which truly emerges.

Long *et al*,<sup>18</sup> by studying the series of the four mono- and the four disubstituted  $FcX_n$  compounds (X = F, Cl, Br or I, n = 1 or 2), also observed that the effect of Br and Cl was similar. The behaviour of the easily oxidised F-substituted derivatives made these authors note that the redox trend could not be simply explained by invoking the electronegativity of the substituents. As a result, they hypothesised that resonance effects (measured by R in the well-known expression  $\sigma = \alpha F + R$ )<sup>19</sup> played a key role. The authors obtained *two dis*tinct E° vs. R nice fits for either the FcX or the FcX<sub>2</sub> set. By merging our records with the data reported by these authors, we observed that a single nice fit of all the 14 mono-(FcX), di- (FcX<sub>2</sub>) and tetrasubstituted (Fc(XY)<sub>2</sub>) entries could be obtained using  $E^{\circ}$  vs.  $\Sigma \sigma_x$  ( $\sigma_x = \sigma_F$ ,  $\sigma_{CL}$ , etc.), so treating  $\sigma_x$  as a truly *extensive* property. In passing, we may notice that unsubstituted Fc itself also fits in the trend, while this was not so in the fitting shown in the paper by Long. We obtained as the best fit:  $E^{\circ} = 0.078(4) V + 0.478(8) \times \Sigma \sigma_x V$ , scaled vs.  $E^{\circ}(Fc)$ , with  $R_{FIT} = 0.97$ , shown in figure 5.



Figure 5. Best-fit of E° (V) vs.  $\Sigma \sigma_x$  for FcX, FcX<sub>2</sub> and Fc(XY)<sub>2</sub> (X, Y= H, Cl, Br, I)

It may be reasonable concluded that the main role of R specified in the previous work was a well-hidden artefact due to the almost constant values of the inductive/field parameter F for the halogens group. The sum of both inductive/field and resonance effect results in a more efficient parameter. In a discussion of the electronic spectra of the tetrahalo compounds and how they vary upon oxidation, we may outline that some basic features are persistent in the series: the compounds in their neutral form all exhibit a typical absorption in the narrow range 433-443 nm, while the characteristic blue absorption of ferrocenium cover a much wider region, depending on the nature of the halogen. The shape of this absorption also varies considerably, as well as its resolution. Typically, removal of one electron to form the cations [Fc(XY)<sub>2</sub>]<sup>+</sup> makes two well-distinct broad bands to appear in the low-energy region (see figure 6 and 7). The high-energy band covers the range 566-626 nm, while the low-energy one covers the range 755-799 nm.



Figure 6. Spectral changes recorded in a OTTLE cell upon progressive oxidation of **7**.  $CH_2Cl_2$  solution. [NBu<sub>4</sub>][PF<sub>6</sub>] (0.2 mol dm<sup>-3</sup>) supporting electrolyte.



Figure 7. UV-vis spectra of [Fc(XY)<sub>2</sub>]<sup>+</sup> cations

Since the 433-443 nm absorption of the neutral species varies so little, the HOMO-LUMO gap should also remain constant by changing the X, Y halogens. On the other hand, the HOMO is stabilised by their presence, as indicated by the increasing redox potential. This should mean that the HOMO and the LUMO are similarly stabilised by the halogens on the Cp ring and move almost rigidly. At variance, as shown in figure 7, the presence of halogens has a dramatic effect in the spectrum of the cations. There has been considerable interest<sup>20</sup> on the nature of the ferrocenium ground state, being identified as  ${}^{2}A_{1g}$  or  ${}^{2}E_{1g}$  according to the different authors or techniques. Anyway, the <sup>2</sup>A<sub>1g</sub> and <sup>2</sup>E<sub>1g</sub> states are certainly close in energy and is reasonable that the blue-transition of ferrocenium (625 nm in dichloromethane) observed at room temperature could be an unresolved combination of  ${}^{2}E_{1u} \leftarrow {}^{2}A_{1g}$  and  ${}^{2}E_{1u} \leftarrow {}^{2}E_{1g}$  transitions.  ${}^{21}$  Moreover, the degeneracy of the E states is split by spin-orbit coupling and a low symmetry distortion into a doublet, the extent of such splitting being different for  ${}^{2}E_{1u}$  and  ${}^{2}E_{1g}$ . All these facts, together with the vibrational structure, confers a characteristic asymmetric shape to the ferrocenium blue band. By observation of figure 7 and table 2, it appears that in the spectrum of the tetrasubsituted compounds one of the two components of the large "blue" band moves toward lower energies, while another one remain fixed or slightly moves toward higher energies. This phenomenon, which gives the band a large plateau shape, is more evident when iodine is present as a substituent on the Cp ring. A more detailed study will be certainly necessary, but, currently, this seems enough to guess that this could be an "heavy atom effect", which, as defined by IUPAC, is "the spin-orbit coupling enhancement produced by a heavy atom."<sup>22.</sup>

# EXPERIMENTAL SECTION

General: Lithiation reactions were carried out under a nitrogen atmosphere, but all work up procedures were carried out under open atmosphere lab conditions. Commercial n-butyllithium solutions in hexane was used as supplied as were all other synthetic reagents. Tri-1,1',2-bromoferrocene and 1,1',2,2'-tetrabromoferrocene and other tetrasubstituted ferrocenes were available in these laboratories in multigram quantities as were all other ferrocenes used in comparative spectroelectrochemistry. Flash chromatography was carried out on silica gel 60 or neutral alumina. All other reagents and solvents were laboratory grade

In this work we use tri-n-butyltin chloride as a low-cost reagent. This is toxic liquid, and care should be taken to handle this reagent appropriately according to safety data information.

NMR spectra were recorded using a Bruker AC-400 instrument, operating at 400MHz for <sup>1</sup>H and 100Mz for <sup>13</sup>C. d-Chloroform was used as a solvent throughout.

#### Preliminary reactions.

The reaction of 1,1',2,2'-tetra-bromoferrocene with n-butyllithium was carried out either inside a vessel in an externally cooled ice bath or at -60°C as follows:

**Reaction at -60°C**. To a solution of 1,1',2,2'-tetrabromoferrocene (10.01g, 20mmol) in dry THF (200ml) was added n-BuLi (34ml, 2.5M sol, 85mmol) in hexane. After 10 minutes at -60°C the reaction mixture was quenched using either excess iodine (21.6 g, 85 mmol) or chloro-tri-n-butyltin (27.5g, 85 mmol). If the latter quench reagent was used the dried, isolated product oil was dissolved in dichloromethane and then treated with excess powdered iodine over a 5h. period. (The iodine was powdered using a mortar and pestle prior to addition)

**Reaction at 0°C**. To a solution of 1,1',2,2'-tetrabromoferrocene (10.01g, 20mmol) in dry THF (200ml) was added an excess of a 2.5M n-BuLi sol. in hexane, (34ml, 2.5M sol, 85mmol). After 2 minutes the reaction mixture was quenched using either excess powdered iodine (21.6 g, mmol) or chloro-tri-n-butyltin (27.5g, 85 mmol). Again, if the latter quench reagent is used the isolated product is redissolved in dichloromethane and then treated with excess powdered iodine and left to stir in the dark for 5h.

In each case the products were worked up as previously described for the preparation of iodoferrocenes,<sup>6,7</sup> (removal of excess iodine with aqueous sodium thiosulfate solution, separation, filtering and drying over anhydrous magnesium sulfate) and crystallisation from methanol or hexane. Typical NMR spectral data for these reactions are shown in the supplementary data as are figures of crystallographic structures from the structurally characterisation of the products. Typically, however the products obtained were impure or the halides tended to co-crystallise and thus this synthetic method was abandoned.

#### Tetrakis-(tri-n-butylstannyl)ferrocene, 6: in situ.

The first step of the preparation was carried out under a nitrogen atmosphere. The following procedure has been carried out many times on 1-20 mmol scales. A typical midrange scale preparation is reported here:

1,1',2,2'-Tetrabromoferrocene (5.0g, 10mmol) dissolved in a mixture of hexane (150 ml) and diethyl ether (25 mL) was treated with a 4.5 molar excess of n-BuLi (18 ml of a 2.5 molar solution, 45 mmol). After several minutes the characteristic red tetra-1,1',2,2'-lithioferrocene begins to precipitate from solution.<sup>20</sup> After 1hr the reaction is cooled to -30°C and chloro-tri-n-butyltin (14.6g, 45 mmol) was added. After allowing the solution to warm to room temperature and left to stir for a further 1hr the reaction mixture was hydrolysed with water 30 ml and subsequently the organic layer was separated using additional ether as required. The organic layer was then flash filtered through a magnesium sulfate plug and the solvent was removed at low temperature to leave a bright orange-red viscous oil which was characterised by NMR which indicates this is the product tetrakis-(tri-n-butylstannyl) ferrocene and tetra-butyltin (and other stannyl by-products). A small sample (ca 2%) of this solution was used to further study the iodination reaction by NMR.

Tetrakis-(tri-n-butylstannyl)ferrocene, **6**: <sup>1</sup>H NMR: 0.90-1.95 (overlapping m's with, t, 36H, 0.90, 1.05-1.25 (m, 48 H), 2.50(bt,24H), 4.06 (d,4H), 4.34 (t, 2H). <sup>13</sup>C NMR: 13.65, 22.66, 27, 66, 31,59, 76.06 ( $\alpha$  to Sn), 71.95( $\beta$  to Sn), 71.96 (quat.).

#### Preparation of 1,1',2,2'-Tetraiodo-ferrocene, 7.

The product oil containing 6 was dissolved in dichloromethane 150 mL and an excess of iodine (17.5g, 68 mmol) was added and the mixture was stirred in the dark for 6 hr under nitrogen. The mixture was diluted with ether (200 ml), and it was treated with 100 ml of a saturated sodium thiosulfate solution with rapid agitation. The violet color discharged to leave a bright yellow solution on vigorous mixing of the layers. The organic layer was then separated and dried and the solvent was removed again at low (ca 35°C) temperature. On concentration the product begins to precipitate which can be accelerated by addition of a little hexane. The yellow brown product (3.55 g) was separated by filtration. On washing with a little methanol, it turns pale yellow which is indicative of the pure product. The residual solution was examined by t.l.c. in hexane which indicated the presence of 2 coloured compounds a red/orange fraction with a high rf value and a slower eluting pale-yellow band of the product 7. Further product (ca 1.6g) was obtained by cooling the residual solution at -20°C. If this residual solution is chromatographed on silica using hexane the first fraction to elute is the deep orange band. The second product band turns deep green on the column but reverts to a yellow colour on addition of 20% ether to the eluent and thus can be collected and isolated. An independent tlc study (petrol) indicates that two products are co-eluting one of which is extremely sensitive and decomposes on silica. Total yield of **7**: 5.15g, 74%.

**1,1',2,2'-Tetra-iodoferrocene, 7:** -pale yellow solid: <sup>1</sup>H NMR: 4.13 (at, 2H, J = 2.75 Hz), 4.46 (ad, 2H, J = 2.75 Hz), <sup>13</sup>C

NMR,  $\delta$ : 80.23, 80.70, 79.67. m.p.127-128°C. Mass spectrum: parent ion m/e, 689.6013 (observed) 689.5998 (theoretical) (82%); 563.70044 (M<sup>+.</sup>-I, 100%). Calcd for C<sub>10</sub>H<sub>6</sub>FeI<sub>4</sub>: C, 17.42%, H, 0.88; Found: C, 17.52, H, 0.91. \*at = apparent triplet, to indicate second order nature.

NMR study: A sample of the *crude* **6** was dissolved in *d*-chloroform and a solution of iodine also in *d*-chloroform was progressively added, recording the spectrum each time the iodine color discharged. The proton NMR spectral data were used to identify the intermediate compounds. Typical spectra and data are contained in the supplementary material.

## Preparation of 1,2,4,1'-Tetra-iodoferrocene, 11.

A solution of 1,1'-diiodoferrocene (5.0g, 11.4 mmol) in THF (40mL) was slowly added to a cold solution (-70°C) of LiTMP (25 mmol, prepared by addition of n-BuLi (10 ml of 2.5M) solution to a solution of tetramethylpiperidine (3.60g) in THF (100ml) at -78°C. The reaction mixture was warmed slowly to between -35°C and -40°C for 30 minutes. It was the re-cooled and quenched at -70°C with chloro-tri-(n-butyl) tin and the product was isolated. It was treated with excess iodine in dichloromethane. Following excess iodine removal using aqueous sodium thiosulfate solution the organic layer was separated and dried over anhydrous magnesium sulfate. The reaction mixture was examined by tlc: 5 clear coloured product bands were observed which contained from 2-6 iodines on ferrocene (mass spectrometry). The 2<sup>nd</sup>, 3<sup>rd</sup> and 4<sup>th</sup> fractions all contained compound **11**: fraction 4 which also contained 1,1',2-triiodoferrocene furnished crystals suitable for diffraction when recrystallised **11**, (22%) which were subjected to single crystal analysis. <sup>1</sup>H NMR: 4.18 (pt, 2H), 4.20 (pt, 2H), 4.62 (s, 2H). <sup>13</sup>C NMR: 77.31, (C3,5) 83.62, (C7,8), 83.43(C9,10) (N.B q's C1,2 and C 6 not listed). Calcd. for C<sub>10</sub>H<sub>6</sub>FeI<sub>4</sub>: C, 17.42%, H, 0.88; Found: C, 17.31, H, 0.92. (N.B.: compound 11 normally co-crystallises from the reaction mixture with compound 12, see spectra supplementary section.)

1,2,1'-Tri-iodoferocene, 12: (general method) this compound may be readily prepared either by isolation using column chromatography on deactivated neutral alumina from the reaction mixtures reported above in the preparation of compound **11** or by removal of one iodine using one equivalent of n-butyllithium at -50°C in diethyl ether. The reaction mixture is guenched with one equivalent of chlorotri-n-butyltin chloride and then a few mL of water is added. Following the separation, isolation and drying (anhydrous. MgS0<sub>4</sub>) of the organic layer, the solvent is removed, and the resultant oil is redissolved in dichloromethane. This solution is then treated with one equivalent of finely ground molecular iodine, mixed thoroughly, then left to stand overnight in the dark. Following product workup as described for 7 to remove any excess iodine the solid which is obtained following solvent removal was crystallised from hexane. NMR: 4.09 (at, 2H, J = 2.2Hz) 4.36 (at, 2H), J = 2.2Hz, 4.25 (at, 1H, J = 2.6Hz), 4.44(ad, J = 2.6Hz). Calcd. for C10H7I3Fe: C, 21.31%; H, 1.25. Found: C, 21.40; H, 1.19.

N.B This compound may also be prepared via 1,1',2-trilithio ferrocene from 1,1',2-tribromoferrocene by lithium halogen exchange in hexane (with a few mL diethyl ether added) by following the method used for the preparation of 1,1'2,2'-tetrakis-(trimethylsilyl)ferrocene in ref.15. Tri-n-butyltin chloride is used as the quenching reagent instead of the

chlorosilane. The work up method is identical to the one described here.

For the three samples (7, 11 and 12), a suitable crystal was selected and mounted on a MITIGEN holder in oil on a Rigaku FRE+ (45.0 kV, 55.0 mA) equipped with either VHF Varimax confocal mirrors (70µm focus) and an AFC12 goniometer with either an HG Saturn 724+ detector (11) or HyPix 6000 detector (7), or HF Varimax confocal mirrors (100µm focus) and an AFC12 goniometer with an HG Saturn 724+ detector (12). The crystals were kept at T = 100(2) K during data collection. Data were measured using profile data from  $\omega$ -scans using MoK<sub> $\alpha$ </sub> radiation. Cell determination and data collection were carried out using CrystalClear<sup>23</sup> (11 or 12) or CrysAlisPro<sup>24</sup>(7). With the data reduction, cell refinement and absorption correction using CrysAlisPro. Using Olex<sup>25</sup>, the structures were solved with the ShelXT<sup>26</sup> structure solution program and the models were refined with version 2014/7 of ShelXL<sup>27</sup> using Least Squares minimisation. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. For 11 the molecule is disordered with 2 percent in a different position which is observed from the iodine positions. Due to its small percentage the lesser component has all its atoms left isotropic and constrained (EADP). Also, multiple geometrical restraints (SADI) have been employed.

(\*numbering scheme is based on H1-H10 for ferrocene.) **Crystal Data for 7.** C<sub>10</sub>H<sub>6</sub>FeI<sub>4</sub>,  $M_r$  = 689.60, monoclinic, P2<sub>1</sub>/n, a = 12.9066(2) Å, b = 16.0728(2) Å, c = 14.2765(3) Å, V = 111.842(2)°,  $\alpha = \beta = 90°$ , V =2748.99(9) Å<sup>3</sup>, T = 100(2) K, Z = 8, Z' = 2,  $\mu$ (MoK $_{\alpha}$ ) = 10.048 mm<sup>-1</sup>, 66301 reflections measured, 6305 unique ( $R_{int} =$ 0.0454) which were used in all calculations. The final  $wR_2$ was 0.0495 (all data) and  $R_1$  was 0.0212 (I > 2(I)).

**Crystal Data for 11.**  $C_{10}H_6FeI_4$ ,  $M_r = 689.60$ , monoclinic,  $P2_1/c$ , a = 9.0543(2) Å, b = 8.30650(10) Å, c = 18.7509(4) Å,  $V = 94.500(2)^\circ$ ,  $\alpha = \Upsilon = 90^\circ$ , V = 1405.90(5) Å<sup>3</sup>, T = 100 K, Z = 4, Z' = 1,  $\mu(MoK_{\alpha}) = 9.824$  mm<sup>-1</sup>, 16317 reflections measured, 3203 unique ( $R_{int} = 0.0163$ ) which were used in all calculations. The final  $wR_2$  was 0.0395 (all data) and  $R_1$  was 0.0155 (I > 2(I)).

**Crystal Data for 12.**  $C_{10}H_7$ FeI<sub>3</sub>,  $M_r = 563.71$ , monoclinic, C2/c, a = 13.3762(2) Å, b = 18.7591(2) Å, c = 10.5690(2) Å, V = 112.406(2)°,  $\alpha = 'Y = 90°$ ,  $V = 2451.82(7) Å^3$ , T = 100 K, Z = 8, Z' = 1,  $\mu$ (MoK $_{\alpha}$ ) = 8.744 mm<sup>-1</sup>, 15850 reflections measured, 2809 unique ( $R_{int} = 0.0363$ ) which were used in all calculations. The final  $wR_2$  was 0.0588 (all data) and  $R_1$  was 0.0224 (I > 2(I)).

CCDC 1841021,1841020 and 1876226 contains supplementary X-ray crystallographic data for **7**, **11** and **12** respectively. This data can be obtained free of charge via <a href="http://www.ccdc.cam.ac.uk/structures/">http://www.ccdc.cam.ac.uk/structures/</a>, or from the Cambridge Crystallographic Data Centre, Union Road, Cambridge, CB2 1EZ; fax(+44) 1223-336-033 or email: <a href="mailto:de-posit@ccdc.cam.ac.uk">de-posit@ccdc.cam.ac.uk</a>

**Electrochemistry:** In all the experiments  $N_2$ -saturated solutions of the compound under study were used with  $[Bu_4N][PF_6]$  (0.2 M) as supporting electrolyte (Fluka, electrochemical grade) and freshly distilled  $CH_2Cl_2$ . Cyclic voltammetry was performed in a three-electrode cell containing a glassy carbon working electrode, a platinum counter

electrode, and an AgCl/Ag (KCl sat) reference electrode.<sup>28</sup> A BAS 100W electrochemical analyzer was used as polarizing unit. All the potential values are referred to the AgCl/Ag (KCl sat). The UV-vis spectroelectrochemical measurements were carried out using a PerkinElmer Lambda 2 UV/vis spectrophotometer and an OTTLE (optically transparent thin-layer electrode) cell equipped with a Pt-minigrid working electrode, Pt minigrid auxiliary electrode, Ag wire pseudo reference and CaF<sub>2</sub> windows (Labomak). Nitrogen-saturated CH<sub>2</sub>Cl<sub>2</sub> solutions of the compound under study were used with [NBu<sub>4</sub>][PF<sub>6</sub>] (0.2 M) as supporting electrolyte.

# CONCLUSIONS

A simple and effective synthesis of 1,1',2,2'-tetra-iodoferrocene has been described and its crystal structure and electrochemistry has been compared with its chloro- and bromo-analogues. Given the number of applications that the 1,1'-diiodoferrocene has been integral in, it is expected this compound will have a similar impact in the synthesis of technologically useful ferrocene compounds. The synthetic method is applicable to the preparation of more highly substituted iodoferrocenes which we are now examining with collaborating research groups. In addition, a reviewer has suggested the quantitative titration of iodine into compound **6** on a preparative scale which should be useful in the isolation of some or all of the intermediate compounds The alpha-dilithiation of 1,1',2,2'-tetraiodoferroce will now be possible to further extend the number of poly iodoferrocenes accessible as useful reagent compounds.

# ASSOCIATED CONTENT

**Supporting Information**. Additional crystallographic data for compounds **7**, **11** and **12**, additional electrochemical data and NMR data for compounds described is available from......

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#### Author Contributions

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# **ABBREVIATIONS**

THF – tetrahydofuran; BuLi – butyllithium; TLC, thin layer chromatography, ad= apparent doublet, ap, apparent triplet.

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