1, 1´,2,Tri-bromoferrocene, 1, 1´, 2,2´-Tetra-bromoferrocene, 1, 1´, 2,2´-Tetra-bromoruthenocene: Synthesis and Structure: Expanding the Range of Precursors for the Metallocene Chemist's Toolkit.

Ian R. Butler,*[a] Michael Beaumont,[a] Michael I. Bruce[b], Natalia N Zaitseva,[b]

Jonathan A. Iggo,[a] Craig Robertson,[a] Peter N. Horton[c] and Simon J. Coles[c]

a. Department of Chemistry, University of Liverpool, Crown Street, Liverpool, U.K. L69 7ZD.

b. Department of Chemistry, School of Physical Sciences, University of Adelaide, Adelaide, South Australia, 5005.

c. EPSRC National Crystallography Service, University of Southampton, Southampton, U.K. SO17 1BJ.

i.r.butler@liverpool.ac.uk; j.a.iggo@liverpool.ac.uk; michael.bruce@adelaide.edu.au; natalia.zaitseva@adelaide.edu.au; p.n.horton@soton.ac.uk; s.j.coles@soton.ac.uk; Craig.Robertson@liverpool.ac.uk;.

Abstract

The synthesis, characterisation and isolation of 1,1´,2-tribromoferrocene and 1,1´,2,2´-tetrabromoferrocene, which are key synthons are in ferrocene chemistry, are described. These compounds are prepared using the alpha-halide assisisted lithiation method. The crystal structures of 1,1´,2-tribromoferrocene, 1,1´,2,2´-tetrabromoferrocene, 1,1´-dibromoruthenocene and 1,1´,2,2´-tetrabromoruthenocene have been determined and are reported together with a brief discussion of the intramolecular forces involved in the crystal structures.

Keywords: ferrocene; bromoferrocenes; alpha-halide lithiation; multiple-substitution crystal structure.

Introduction

The synthesis and chemistry of 1,1'- and 1,2-disubstituted ferrocene compounds remains an important area of study because of the numerous applications of these compounds in organic synthesis, materials science and medicine. [1-10] Key to the synthesis of such compounds has been the preparation of suitable versatile precursors such as bromoferrocenes. In the case of 1,1'-dibromoferrocene, which is a key precursor, there are now many suitable reaction protocols allowing its practical synthesis. Interestingly, the synthesis of the related 1,1'-di-iodoferrocene has turned full circle with many modifications,[11-12] recently returning to an old method with a new twist which is, essentially, product distillation/sublimation.[13] The fact that 1,1'-di-iodoferrocene is easily sublimable, like many other ferrocenes,[14] circumvents the difficulty in purifying mixtures of these ferrocenes as their high solubility and low polarity can cause problems during chromatography. In the early 1990's sublimation was used extensively in the purification of a wide range of ferrocenes: we found temperature-gradient sublimation to be particularly useful. However in the synthesis of some bromoferrocenes, the high boiling nature of the quenching reagent (e.g. tetrabromoethane) and thus the difficulty of their complete removal interferes in the sublimation process. Another synthetic problem which has been elegantly addressed is the removal of ferrocene from haloferrocene product mixtures using oxidation with ferric chloride.[15-16] We have found this particularly useful when applied to the reported high yielding synthesis of 1,2-dibromoferrocene. In the case of the 1,2-disubstituted compounds we have pioneered the preparation of extremely simple precursors which are easily modified. Examples are the facile syntheses of 1,2-dibromoferrocene, 1,2-di-iodoferrocene and related alpha-substituted haloferrocenes[17-18] which are easy to use in the preparation of a large range of substituted ferrocenes, figure 1.

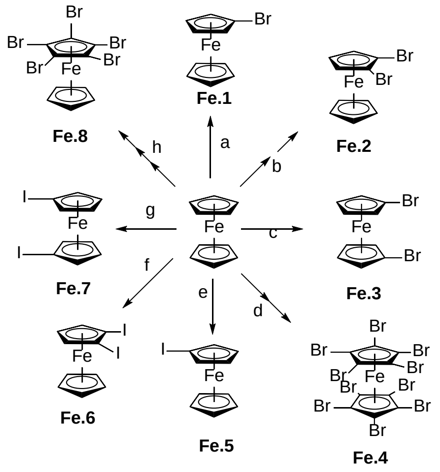

Figure 1: Some important halogenoferrocenes as synthetic precursors a) bromoferrocene, Fe.1, [19] b) 1,2-dibromoferrocene, **Fe.2,**[20] c) 1,1'-dibromoferrocene, **Fe.3,** [21] d) *deca*-bromoferrocene, **Fe.4**,[22] 7e) iodoferrocene, **Fe.5**, [13,23] f) 1,2-di-iodoferrocene, **Fe.6**, [24] g) 1,1'-di-iodoferrocene, **Fe.7**, [25] h) 1,2,3,4,5-*penta*-bromoferrocene, **Fe.8**. [26]

A recent review comprehensively covers those haloferrocenes including bromoferrocenes which have appeared in the literature to date.[27] We now turn our attention to the preparation of tetra-haloferrocene precursors and their derivatives, a subgroup of which are the 1,2,1´,2´-tetra-substituted compounds which have been less studied. We have already published a methodology which allows the preparation of some tetra-substituted phosphinoferrocenes[28] and we had briefly touched upon the search for tri- and tetra-bromoferrocenes, however the yields obtained were rather low and scant attention was paid on their full characterisation. The synthetic route to 1,2-dibromoferrocene may be modified to give products which could be sequentially dimetallated to allow for further synthetic variation, which also includes the general preparation of phosphines, figure 2.[29] There have been several valuable applications of our synthetic methodology recently most notably the work of Weissensteiner[30] and Butenschön[31] which also examine the synthesis of haloferrocenes using the alpha-lithiation method. An important current challenge is the easy synthesis of multimetallic complexes: it should be possible to obtain ligands capable of binding several metals to enhance the efficacy of catalysts for standard reactions such as Mitshunobi, Suzuki and Kumada couplings.

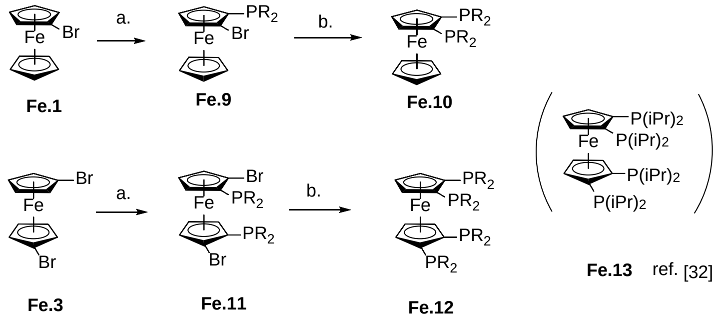

Figure 2: The synthetic utility in making multi-dentate phosphines by the alpha-lithiation and quench technique, a) i) LiTMP, ii) $ClPPh_2$; b) i) n-BuLi, ii) $ClPPh_2$. [29]

Results and Discussion

The synthetic method used in this work is the alpha-lithiation of haloferrocenes which is now part of mainstream ferrocene synthesis, figure 3. This method is suitable for the preparation of more highly brominated ferrocenes. The reaction of 1,1´-dibromoferrocene with lithium 2,2,6,6-tetramethylpiperidide (LiTMP) was carried out in thf and the initial product mixture is a thick oil which could be separated by careful chromatography on active alumina to give 1,1´,2-tribromoferrocene, **Fe.14** and 1,2,1´,2´-tetrabromoferrocene, **Fe.15.** These compounds were purified by crystallisation. Highly pure samples are very pale yellow whereas larger crystals are yellow/brown. Also present in the crude product mixture was a substantial amount of unreacted 1,1'-dibromoferrocene as well as several isomeric and other more highly brominated compounds, (labelled BYPRODUCTS, fig. 3), such as pentabromoferrocenes hexabromo ferrocene etc but we were unable to separate all of these cleanly. The isomerisation takes place because of the shift of lithium on the ferrocene cyclopentadienyl rings as previously observed.[18] The initial isolated yields were relatively low because of this. However, once the main product compounds were identified, all chromatographic fractions containing them in subsequent preparations could be readily identified, combined and purified to afford reasonable quantities.

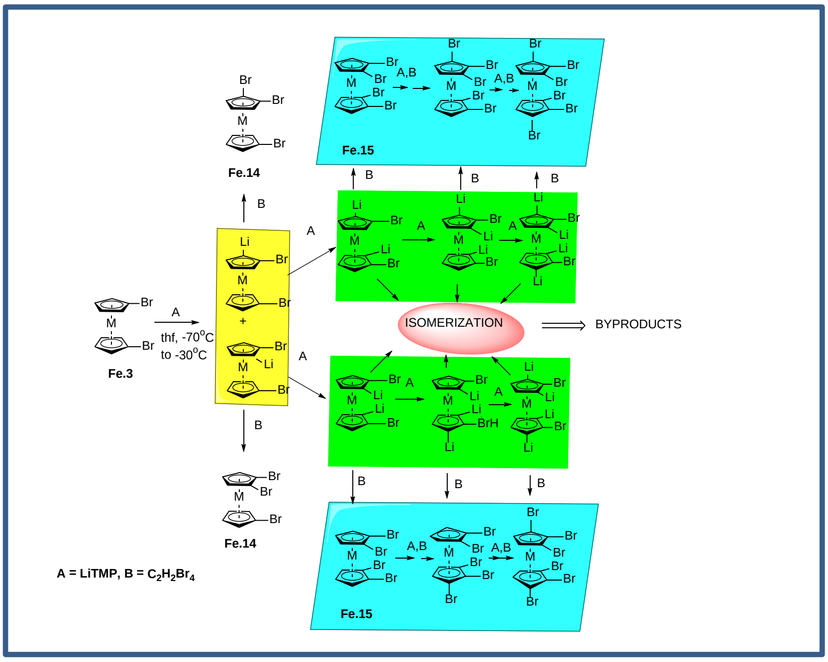

Figure 3: Overview of the complexity of lithiation reactions: Legend: yellow box: mixture of initial lithiated ferrocenes prior to quenching; green boxes: lithiated bromoferrocenes formed as a mixture; blue boxes: product bromoferrocenes, salmon box: isomerized lithiobromoferrocenes leading to formation of isomeric bromoferrocenes.

NMR spectroscopy was used as the primary method for establishing the composition of the reaction mixture. In general, protons adjacent to Br shift further downfield with a greater degree of bromine substitution. Proton chemical shifts mirror those of other ferrocenes previously prepared.[32] The pertinent coupling constants were obtained from 2DJ experiments. In the ^{1}H NMR spectrum of 1,1’,2-tribromoferrocene there is overlap of the (H-4 and H-3'(H-8*) resonances occurred at 400Mz, all other resonances being clearly distinguishable. 1,1´,2,2´-Tetrabromoferrocene shows the expected triplet and doublet resonances in the ^{1}H NMR spectrum. It should be noted here that many other bromoferrocenes (penta-, hexa, hepta and octa-bromoferrocenes) are present and can be readily identified in the slower eluting fractions however clean purification methodology has yet to be devised for these compounds. A full discussion of the crystal structures of all bromoferrocenes with molecular structure calculations on these compounds will be published in a forthcoming paper. Gas phase electron diffraction experiments on bulk samples (gram scale) of compound **Fe.15** have proved difficult due to the partial decomposition during vaporisation. Finally it should be noted that a recent development on the metalation of ferrocene [33] is likely to impact this area of study and should provide complementary syntheses.

The synthetic method is equally applicable to the synthesis of ruthenocenes as exemplified by the preparation of 1,1´,2,2´-tetrabromoruthenocene, **Ru.2.** This compound is isolated as a white crystalline solid following the synthesis from 1,1´-dibromoruthenocene, **Ru.1** which in turn was prepared from ruthenocene. The separation of the other compounds present such as 1,1´,2-tribromoruthenocene and the higher ruthenocenes was not achieved because of the smaller synthetic scale used and chromatography was difficult because of overlapping colourless bands. The crystal structure of **Ru.1** is shown in figure 4 in which the ruthenocene is almost fully eclipsed. As a molecule **Ru.1**, has many similar characteristics to 1,1’-dibromoferrocene (**Fe.3**) with the bromine atoms eclipsed (0.92(1)°), however the packing is quite different, with every cp ring basically lying parallel to all the others, unlike in **Fe.3** which has alternating 90° rotations. The ^{1}H NMR spectrum of **Ru.2** exhibits the characteristic triplet and doublet resonances at 4.60 and 4.87 ppm. These chemical shifts are 0.3 ppm lower field than those in the analogous ferrocene compound.

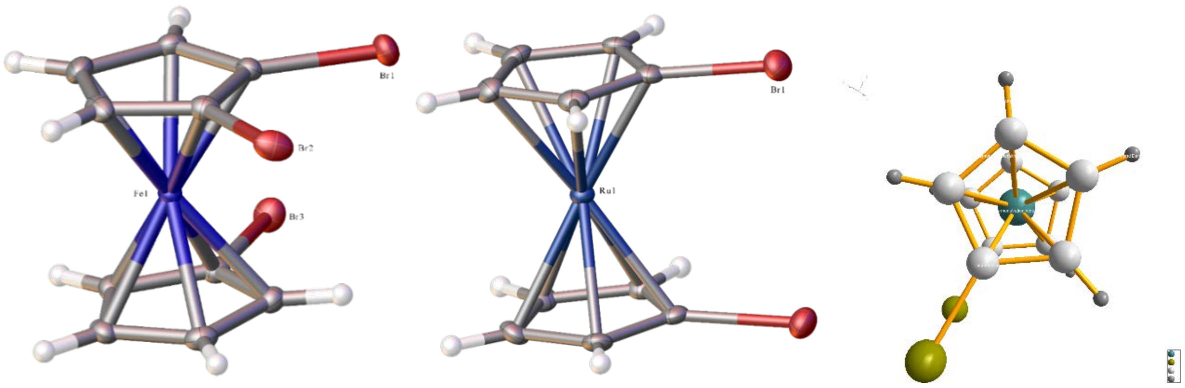

Figure 4: crystal structure of 1,1’,2-tribromoferrocene, **Fe.14**. and 1,1’-dibromoruthenocene, **Ru.1**. (side and top views).

Structural Characterisation

The molecular structure of 1,1’,2-tribromoferrocene, **Fe.14,** (fig. 4) shows the single bromine in a more staggered conformation in relation to the other two (closest Br-C…C-Br torsion angle = 53.71(9)°). There is no internal molecular symmetry with one unique molecule forming the asymmetric unit (shown in figure 4). There is almost no tilting between the Cp rings (Cp_{cent1}-Fe-Cp_{cent2} angle = 178.95(5)°). The molecules form ‘dimers’ with opposing dibromo-Cp rings facing each other in a staggered geometry. These dimers then alternate throughout the structure in a herringbone-like array.

In 1,1´,2,2´-tetrabromoferrocene, **Fe.15,** the bromines are almost eclipsed as often found with these compounds (Br-C…C-Br torsion angle = 1.59(8)°). Also, in common with many symmetric ferrocene structures only half the molecule exists in the asymmetric unit, with the iron atom lying on the 2-fold axis. There is a little more tilt between the Cp rings ((Cp_{cent}-Fe-Cp_{cent} angle = 175.75(6)°), with the bromine substituted sides further apart. The molecules pack head to tail (bromines vs no bromines) in infinite tapes down the b-axis. These tapes them ‘interdigitate’ with a neighbouring tape with the core iron lying effectively in the same plane as an adjacent cp ring (Fe-plane distance= 0.022(6) Å). The tapes also almost self-stack. Each tape is offset such that the iron atom lie almost directly above a carbon of the neighbouring Cp ring (it is C-H bound carbon). This continues up the tapes like a staircase, with the offset always in the same direction. However the tapes alternate in the direction that the bromines point with the adjacent Cp rings in the staggered geometry. They also lie slightly closer than expected (Cp_{cent1}-Cp_{plane2} = 3.3947(17) Å). Overall, from end on these tapes observe a brick-like structure.

The compound number/code scheme structure is shown in figure 5 and the structure of the tetrabromoferrocene, **Fe.15**, together with that of its ruthenocene analogue, **Ru.2** are presented in Fig. 6. With partial packing views of **Fe.3** and **Fe.4** shown in figures 7 and 8 respectiveley.


Fe.14 **Fe.15** **Ru.1** **Ru.2**

Figure 5: Number/code scheme for bromometallocenes.

The molecules have the characteristic eclipsed C_5 ring geometry found for most tetrahalogenoferrocenes (Br-C...C-Br torsion angle = 1.57(17)°). Thus **Ru.2** has an extremely similar molecular structure to **Fe.15** with the only significant difference being a slight increase in M … Cp ring distance (1.808(2)Å (**Ru.2**) vs 1.6482(8)Å (**Fe.15**)), resulting from differences in size of the metal ions [cf. M … Cp in $FeCp_2$ 1.66, $RuCp_2$ 1.82Å]. This has the effect of reducing the tilt in **Ru.2** (Cp_{cent}-Ru-Cp_{cent} angle = 178.88(12)°) and adjacent Cp-rings slightly closer (Cp_{cent1}-Cp_{plane2} = 3.371(5) Å), but otherwise it has an identical packing architecture.

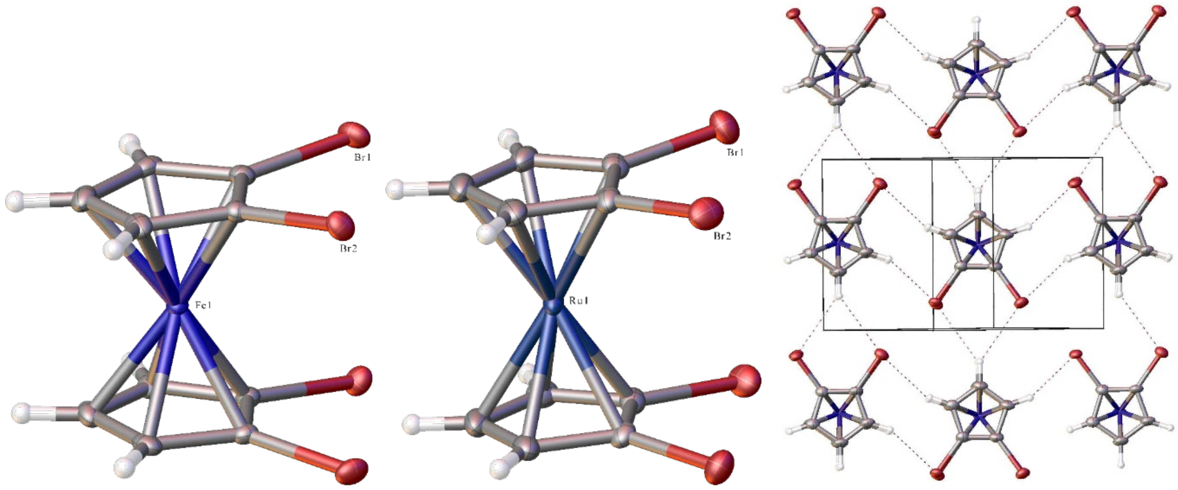

Figure 6. Crystal structures of 1,1´,2,2´-*tetra*-bromoferrocene, **Fe.15**, and of 1,1´,2,2´-*tetra*-bromoruthenocene, **Ru.2**. and top view of **Fe.15** packing with Br-H interactions.

Figure 7: Side view of **Fe.14** showing the dimers and herringbone arrangement of a sheet.

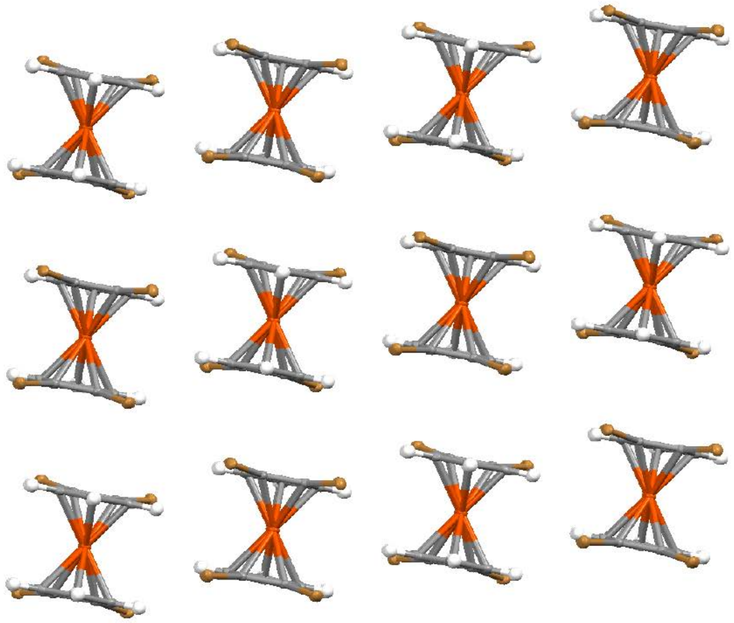

Figure 8: End on view of the tapes in **Fe.15** showing the interdigitation and staircase.

Conclusions and Additional Comments

Oligo-bromoferrocenes and ruthenocenes have been prepared by alpha-lithiation and quench method and fully characterised: this is key to the further syntheses of polysubstituted ferrocenes and ruthenocenes. The use of the product compounds in exchange reactions indicate these are clean reactions and these will be the subject of the next communication. The authors have no conflicts of interest.

Experimental Section

All reaction solvents were dried using standard commercial solvent drying instruments. Other solvents used were commercial grade and used as received. A 2.5M solution of n-butyllithium in hexanes (Aldrich Chemical Co.) was used as received. 2,2,6,6-Tetramethylpiperidine was reagent grade and was used as received. Bulk samples of 1,1´-dibromoferrocene and ruthenocene were available in this laboratory. All reactions were performed under a nitrogen atmosphere, but no special precautions to exclude air were taken during work-up. 1,1,2,2-Tetrabromoethane (Aldrich Chemical Co) was used as the quenching reagent except for 1,1'-dibromoruthenocene where 1,2-dibromotetrafluoroethane (reagent grade, T.C.I Chemicals) was used. Neutral alumina (Brockman grade I) was used for chromatography. NMR data was acquired on a 400MHz (^{1}H)Bruker instrument and $CDCl_3$ was used as solvent and internal standard for all samples.

Preparation of 1,1´,2-Tribromoferrocene, Fe.14, and 1,1´,2,2´-Tetrabromoferrocenes, Fe.15.

1,1´-Dibromoferrocene (34.4g, 100 mmol) in dry thf (200 ml) was slowly added to a well stirred solution of LiTMP [prepared from *n*-BuLi (85ml of a 2.5 M soln. in hexanes) and TMP (30.0g) in thf (800ml)] which was maintained at -70°C. The reaction temperature was raised slowly to *ca* -30°C and it was held at this temperature (1 hr.) before being cooled back to -70°C. 1,1,2,2-Tetrabromoethane (78g, 225 mmol) in thf (100ml) was slowly added to the mixture with vigorous stirring, the reaction mixture remaining cooled throughout. Following the addition, the solution was allowed to warm **slowly** to room temperature over *ca* 1hr, after which it was carefully hydrolysed with water. After separation of the organic layer, drying with $MgSO_4$ and removal of solvent gave an oil [the oil was redissolved in the minimum volume of dichloromethane in a large round bottom flask and alumina was added to this until the solvent absorbed completely on to the alumina. The solvent was then removed on a rotary evaporator at low temperature (protected with a loose cotton wool plug at the neck as bumping generally occurs when the last solvent is removed. The resultant yellow powder was added as a solid to the top of the alumina on the column] which was carefully chromatographed on neutral alumina prepared in petroleum ether 40-60 (column diameter 10 cm, 40 cm depth alumina on 90 cm column) eluting with progressively polar mixtures of hexane and diethyl ether to give seven pale yellow fractions (N.B. although there is banding these bands tend to overlap and as such fractions are collected based on solvent volume alone. Attempted crystallisation of each fraction from methanol gave pure products only from fractions 3, 4 and 6 (NMR). All other fractions gave product mixtures of isomeric bromoferrocenes which either did not crystallise or crystallised as a multi-compound mixture.

Those which gave pure compounds were as follows:

Fraction 3: 1,1´,2-Tribromoferrocene, Fe.14. Pale-lemon crystals, bulk samples are yellow-brown.

^{1}H NMR: 1,1′,2-tribromoferrocene NMR: δ 4.45,(d, 2H, J= 2.73Hz), 4.43, (t, 2H, J = 1.76 Hz), 4.19, (d, 2H, J = 2.05Hz (measurement impaired by overlap)), 4.19,(t, 1H, J = 2.73Hz). Elemental Analysis: Cald ($C_{10}H_7Br_3Fe$), C, 28.41, H, 1.67; found: C, 28.32, H, 1.70%. Mass Spectrum: Calc. 423.74063 Observed : 423.74061; isotope pattern, m/z 419(32%), 421(100), 423(98), 425 (33). Combined yield: 4.2g, (9.9%).

Fraction 4: 1,1′,2,2′-Tetrabromoferrocene, Fe.15. Pale-lemon yellow crystals, darkening in air over time (1yr), bulk samples pale brown and highly crystalline.

^{1}H NMR: δ 4.20, (t, 4H, J = 2.3 Hz), 4.47 .d, 2H, J = 2.3 Hz). ^{13}C NMR: δ 71.85, 73.78, 81.68 (quat.)   M.pt. = 110-112°C, (black oil formed at 198°C, complete decomp. 226°C.) U.V.: λ_{max} : 437.6, 301.35.nm. (cf 1,1′-dibromoferrocene: λ_{max}: 433.5, 302.7). Mass Spec. Theoretical 501.6513, observed, 501.6521, theoretical isotope pattern: m/e 497-505, 497(21%), 499(75), 501(100), 503(68), 505(17). Elemental analysis: calcd ($C_{10}H_6Br_4Fe$): C, 23.94, H, 1.21; found C, 23.89 H, 1.19%. Yield : 7.8g (16%).

Ruthenocenes

1,1′-Dibromoruthenocene was prepared by lithiation of ruthenocene (4.63g, 20 mmol) and TMEDA (1.4g, 12 mmol) with 2.2 mol equiv. of n-BuLi in 91% yield according to the general dilithiation method using ether as a solvent and quenching with 1,2-dibromotetrafluoroethane to give product, 7.1g (91%). ^{1}H NMR: δ 4.53 (t, J = 1.8 Hz, 4H), 4.89 (t, 4H). ^{13}C NMR: δ 72.02, 75.26, 72.54(q).

1,1′,2,2′-Tetrabromoruthenocene, **Ru.2** An identical reaction to that used for the preparation of **Fe.15** was carried out using 1,1′-dibromoruthenocene (4.0g, 10.2mol) as precursor on a 10 mmol scale using thf as a solvent to give 1,1′,2,2′-tetrabromoruthenocene following crystallisation. ^{1}H NMR: δ 4.60 (t, J = 4.4 Hz, 2H), 4.87(d, 4H). ^{13}C NMR: δ 72.69, 76.19, 77.21, 78.48. Yield 1.79 g (ca 32%). m/s: theoretical mass 548.6290, observed, 548.6289. Calcd ($C_{10}H_6Br_4Ru$) C, 21.96, H, 1.11; found C, 22.01, H, 1.15%.

N. B. Mass spectrometry on the initial crude product indicated the presence of small quantities of penta- and hexa-bromoruthenocene. {m/z: 619-632; (625.5365), 699-711 (705.4451), resp.}

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X-ray Crystallography

For the four samples (**Fe.14**, **Fe.15**, **Ru.1** and **Ru.2**), 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) (**Fe.14**, **Fe.15**) or HF Varimax confocal mirrors (100µm focus) (**Ru.1**, **Ru.2**) and an AFC12 goniometer and HG Saturn 724+ detector diffractometer. The crystals were kept at T = 100(2) K during data collection. Data were measured using profile data from ω-scans using MoK_α radiation. Cell determination and data collection were carried out using CrystalClear[i]. With the data reduction, cell refinement and absorption correction using CrystalisPro[ii]. Using Olex2[iii], the structures were solved with the ShelXT[iv] structure solution program and the models were refined with version 2014/7 of ShelXL[v] using Least Squares minimisation. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

Crystal Data for **Fe.14:** $C_{10}H_7FeBr_3$, M_r = 422.74, monoclinic, $C2/c$ (No. 15), a = 12.6299(5) Å, b = 18.1045(6) Å, c = 10.4365(4) Å, β = 113.493(4)°, α = γ = 90°, V = 2188.58(15) Å^3, T = 100(2) K, Z = 8, Z' = 1, μ(MoK_α) = 12.285 mm^{-1}, 12440 reflections measured, 2521 unique (R_{int} = 0.0256) which were used in all calculations. The final wR_2 was 0.0468 (all data) and R_1 was 0.0180 (I > 2(I)).

Crystal Data for **Fe.15:** $C_{10}H_6Br_4Fe$, M_r = 501.64, monoclinic, $P2/n$ (No. 13), a = 8.7231(4) Å, b = 7.1951(3) Å, c = 9.5708(5) Å, β = 95.968(5)°, α = γ = 90°, V = 597.44(5) Å^3, T = 100(2) K, Z = 2, Z' = 0.5, μ(MoK_α) = 14.598 mm^{-1}, 9360 reflections measured, 1372 unique (R_{int} = 0.0232) which were used in all calculations. The final wR_2 was 0.0393 (all data) and R_1 was 0.0156 (I > 2(I)).

Crystal Data for **Ru.1:** $C_{10}H_8Br_2Ru$, M_r = 389.05, monoclinic, C2/c (No. 15), a = 14.0712(5) Å, b = 7.6052(2) Å, c = 9.6732(3) Å, β = 108.684(4)°, α = γ = 90°, V = 980.62(6) Å^3, T = 100(2) K, Z = 4, Z' = 0.5, μ(MoK_α) = 9.692 mm^{-1}, 2009 reflections measured, 2009 unique (R_{int} = 0) which were used in all calculations. The final wR_2 was 0.0690 (all data) and R_1 was 0.0251 (I > 2(I)). [Crystal used was a non-merohedral twin (180° rotation about [-0.71 0.00 0.71] (reciprocal) axis.]

Crystal Data for **Ru.2:** $C_{10}H_6Br_4Ru$, M_r = 546.86, monoclinic, $P2/n$ (No. 13), a = 8.7795(2) Å, b = 7.1969(2) Å, c = 9.8858(3) Å, β = 99.064(2)°, α = γ = 90°, V = 616.84(3) Å^3, T = 100 K, Z = 2, Z' = 0.5, μ(MoK_α) = 14.188 mm^{-1}, 10084 reflections measured, 1427 unique (R_{int} = 0.0371) which were used in all calculations. The final wR_2 was 0.0784 (all data) and R_1 was 0.0295 (I > 2(I)).

CCDC1837233, 1826918, 1890716 and 1826919 contains supplementary X-ray crystallographic data for **Fe.14**, **Fe.15**, **Ru.1** and **Ru.2** respectively. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/structures/, or from the Cambridge Crystallographic Data Centre, Union Road, Cambridge, CB2 1EZ; fax(+44) 1223-336-033 or email: deposit@ccdc.cam.ac.uk.

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