Ferrocenyl anthracenes: synthesis and molecular structure [1]

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Abstract

The synthesis of a series of ferrocenylanthracene derivatives is described, utilising the palladium catalysed coupling reaction of 1,1'-bis(chlorozincio)ferrocene with halo-anthracenes. Bis-1,1'-(9-anthracenyl)ferrocene (1) was characterised by single crystal X-ray diffraction and shows an eclipsed ferrocenyl geometry. X-ray crystallographic studies indicate that there are no clear stacking interactions of either an intra- or intermolecular nature between the anthracenyl rings in the structure. A series of 9- and 10-disubstituted ferrocenylanthracene derivatives has also been prepared. In each case the palladium catalyst (Pd(dppf)Cl$_2$) is recovered in a modified form, e.g. as the [(dppf)PdBr(9-anthracenyl)] complex in the synthesis of bis-1,1'-(9-anthracenyl)ferrocene. The single crystal X-ray structure of one such palladium complex [(dppf)PdBr-{9-(10-chloroanthracenyl)}] (15a) has been determined in a case where chloride/bromide exchange had occurred in the palladium complex intermediate. The potential application of compound 1 as synthon for the construction of a molecular sensing device is discussed.

Cyclic voltammetry and fluorescence studies have been carried out for selected derivatives. © 1997 Elsevier Science S.A.

Keywords: Ferrocenylanthracene; Palladium

1. Introduction

The preparation of stacked ferrocenyl aromatic compounds is of topical interest due to the combination of the well known, sharply defined, redox properties of ferrocene with those of the π-aromatic side chains. Of special interest to our research is the preparation of 1,1'-disubstituted ferrocenes for use in molecular sensor technology. This relies on the physical characteristics of the stacked aromatic groups as probes to detect weakly bound substrates (Scheme 1).

(1)
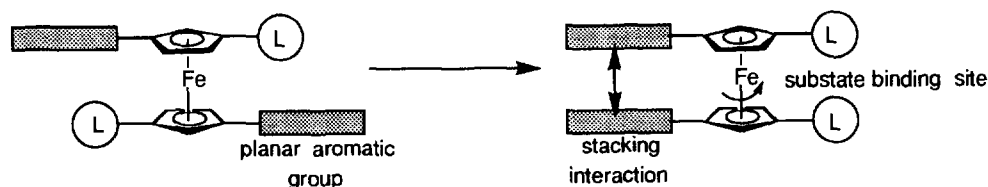1,1'-bis-(9-anthracenyl)ferrocene

(2)
9-anthracenylferrocene
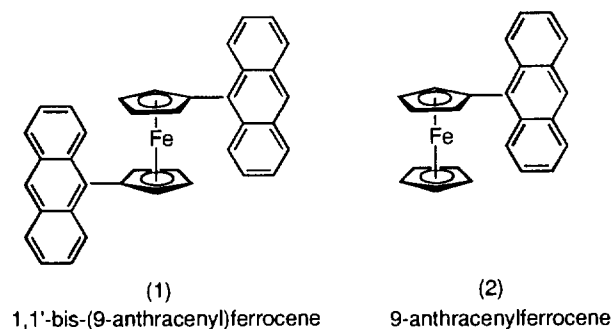
Anthracene coordinated through the 9-position was the initial choice of stacking group due to its size and its extended planarity; the stacking interactions between the two anthracenyl groups, according to Scheme 1, would be maximised when a substrate binds.

The synthesis of 1-ferrocenylanthracene has been previously achieved in 1990, using the reduction of 1-ferrocenylanthraquinone, which in turn was prepared from ferrocene by diazonium salt coupling [1]. Al-
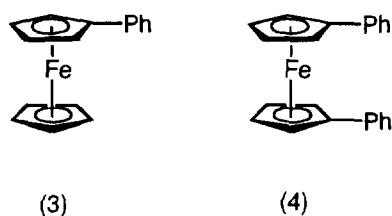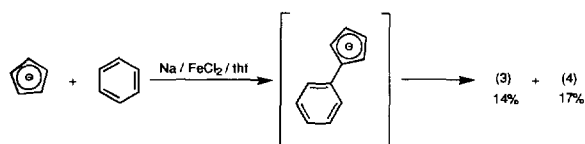
Scheme 1.

though this represents the only reference to the preparation of anthracenylferrocene derivatives in the literature, the development of synthetic strategies for the formation of ferrocenyl aromatics is an area of long-standing interest.

The simplest compound in this general series, phenylferrocene (**3**), was first reported by Pauson in 1954 [2]. This synthesis was undertaken using the known procedure for the preparation of ferrocene, i.e. the reaction of phenyl-substituted cyclopentadienyl-vinylmagnesium bromide (or of alkali metal derivatives of cyclopentadienes) with ferric chloride forming the metallocene structure [3]. Using the same methodology, phenylferrocene and a range of di-, tetra- and hexaphenylferrocenes was subsequently prepared, however at this stage the inaccessibility of phenylcyclopentadiene meant that this was not a feasible large-scale synthetic procedure, thus alternative routes were sought.

Following the observations of Nesmeyanov that ferrocene readily undergoes arylation upon treatment with diazonium salts [4], a range of mono- and bis-substituted aromatic ferrocenes was prepared using aryl–diazonium coupling. Compounds successfully obtained at that time included phenylferrocene (**3**), 1,1'-diphenylferrocene (**4**), *o*-tolylferrocene, *p*-hydroxyphenylferrocene and *o*- and *p*-nitrophenylferrocene [5]. Although diazonium coupling methodology still represents a fundamentally important procedure today, a wide range of alternative synthetic procedures has been developed in the last 30 years or so.

(3)   (4)

In 1966 Beckwith and Leydon demonstrated that reaction of the phenyl free radicals, generated by oxida-

tion of phenylhydrazine with silver oxide [6], with ferrocene (in the form of a co-oxidation of the reaction mixture) afforded phenylferrocene (**3**) and 1,1'-diphenylferrocene (**4**) [7]. The reaction yields were variable, depending upon the nature of the oxidising agent used. Similar transformations were observed with a range of hydrazine derivatives.

Other proven strategies for the preparation of arylferrocenes include couplings via thallation [8], the use of organotin reagents [9] and the decomposition reaction of iron–aryl carbonyl complexes [10]. Prior functionalisation of the cyclopentadienyl rings, similar to the early work of Pauson, is another technique that has been employed. The results of the research work of Bunnett [11] indicated that the coupling of stabilised anions (fluorenyl or indenyl) with aryl halides could be achieved by a radical chain process, initiated from the anion to the aryl halide. This methodology was applied to the cyclopentadienide system in the reaction of sodium cyclopentadienide in liquid ammonia with iodobenzene. Subsequent reaction with anhydrous ferrous chloride afforded a mixture of phenylferrocene (**3**) and 1,1'-diphenylferrocene (**4**) [12], Scheme 2.

The coupling of metallated ferrocenes with haloaromatics, mediated by transition metal catalysts following the early work of Neuse and Bednarick [13] in which poly-ferrocenylenes were isolated, has also been explored for the synthesis of ferrocenyl aromatics [12]. Using this route the palladium catalysed reaction afforded a modest yield of coupled product aryl ferrocenes, but nickel catalysis was found to be ineffective. Finally the work of Negishi et al., utilising organozinc reagents in the selective synthesis of unsymmetric biaryls and diarylmethanes [14], via nickel or palladium catalysed cross-coupling reactions, Scheme 3, has been applied to the synthesis of ferrocenylnaphthalene derivatives by Rosenblum and coworkers in a series of elegant papers [15–18]. The present work explores the extension of these coupling reactions.
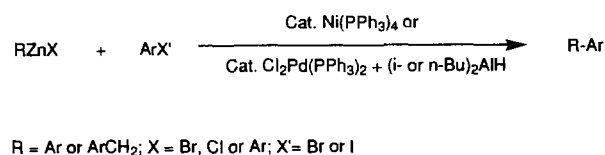
Scheme 2.

R = Ar or ArCH$_2$; X = Br, Cl or Ar; X'= Br or I

Scheme 3.

2. Results and discussion

Ferrocenylnaphthalene derivatives, namely mono- and 1,1′-bis(1-naphthyl)ferrocene, are also known to result from the thermal degradation of the iron–acyl derivative (5) [10], Scheme 4.
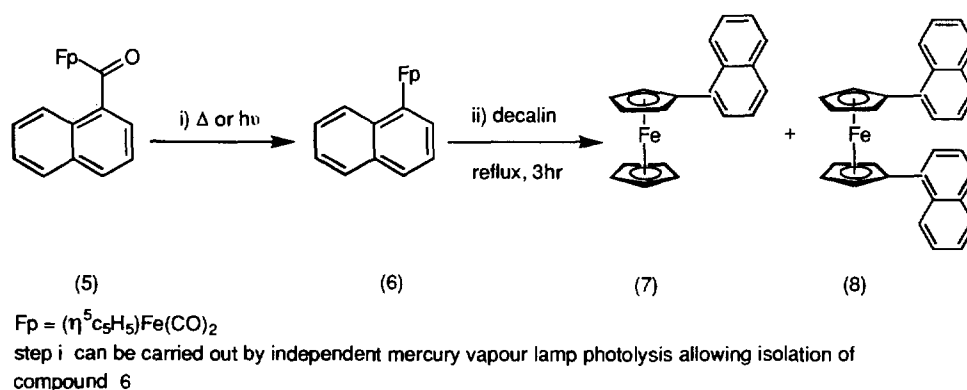
This straightforward synthetic procedure represents the first methodology employed to synthesize a series of ferrocenylanthracenes. The anthracenyl analogue of compound 5, the acyl anthracenyl organometallic dicarbonyl(η-cyclopentadienyl)-(η¹-(9-anthracenyl)meth-1-one)iron (Fp-9-anthracenoyl) (9), was prepared by simple metathesis of 9-anthracenoyl chloride with (η-cyclopentadienyl)dicarbonyliron(II) iodide (FpI), and its thermal decomposition was examined in refluxing decalin. Although both target compounds 1 and 2 were obtained as indicated by ^{1}H NMR after chromatography, the isolated yields were extremely low. It should be noted that the intermediate decarbonylated compound Fp-9-anthracenyl, if desired in its own right, can best be obtained by photolysis. In the thermal decomposition reactions it is simpler to use the iron acyl compounds and thus no attempt was made to isolate the intermediate.

The use of the more classical Ullmann coupling and sodium cyclopentadienide in liquid ammonia coupling reactions was also examined in the synthesis of 1 and 2 before success was achieved using the palladium catalysed arylhalide–ferrocenyl organometallic couplings. Initial studies showed that although the lithioferrocene halo–aryl transition metal mediated coupling employed by Rosenblum for the synthesis of ferrocenylnaphthalenes [12] was reproducible, 9-anthracenylferrocene was formed in less than 5% yield, using analogous chemistry, however the use of palladium catalysed organozinc couplings was found to be extremely effective. In our initial trials, ferrocenyllithium was generated by direct lithiation of ferrocene in THF by treatment with an n-butyllithium solution in hexanes. Kagan and coworker [19] have recently reviewed this area of metallation. The alternate use of t-butyllithium for ex-
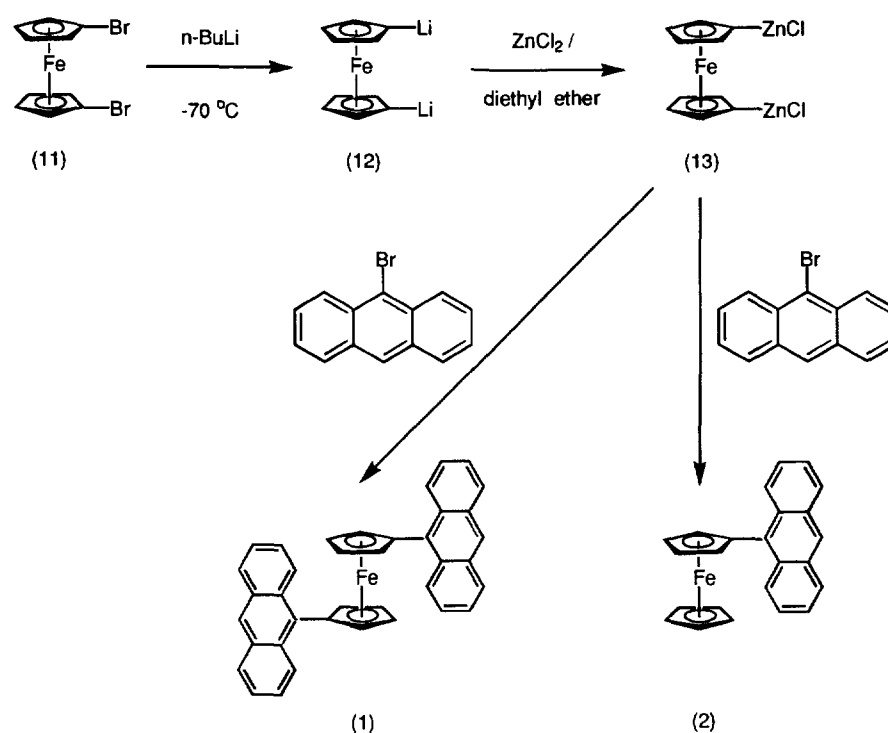
ample is well known to yield high proportions of the mono-lithiated products. We have historically used isolated mono-lithioferrocene rich samples. The product lithioferrocene, which in this case is a crystalline material, was isolated from solution and washed with petroleum ether prior to use. Preliminary experiments using this precursor led to only mono-substituted products proving a predominance of mono-lithioferrocene in this substrate. This was confirmed by reaction of the solid material with DMF to produce mainly (> 90%) ferrocenecarboxaldehyde [20]. Since our primary interest was in the formation of disubstituted derivatives, an alternative route to dilithioferrocenes was sought. Attempts at the use of the readily available dilithioferrocene · TMEDA complex [21] as a precursor were generally ineffective, presumably because of the coordinative ability of the TMEDA ligand towards zinc. Finally, the dilithioferrocene was generated and isolated from the in situ reaction of n-butyllithium in hexane with 1,1′-dibromoferrocene, which is readily available in multigram quantities. The THF re-solvated dilithioferrocene was then treated with a solution of zinc chloride in diethyl ether at 0 °C to form 1,1′-bis(chlorozincio)ferrocene (13), Scheme 5.

The solution was allowed to warm to ambient temperature then after 1 h 9-bromoanthracene (14) was added followed by the palladium catalyst [Pd(dppf)Cl$_2$]. The mixture was then refluxed for 1 h. The ferrocene based catalyst [Pd(dppf)Cl$_2$] was chosen because of its known efficacy in coupling reactions [22]. Generally, two catalyst concentrations were tried, 0.2 mol% and 5.0 mol% with respect to ferrocene. The results obtained are summarised in Table 1.

In general at low catalyst concentration only the 9-anthracenylferrocene (2) derivative was obtained, even using dilithioferrocene and excess bromoanthracene as reagents. No advantage accrued when iodoanthracene was used as a precursor; indeed it is more difficult to remove excess iodoanthracene from the product mixture because, unlike bromoanthracene, it is prone to decomposition on attempted vacuum sublimation. At high

Fp = (η^{5}c$_5$H$_5$)Fe(CO)$_2$

step i can be carried out by independent mercury vapour lamp photolysis allowing isolation of compound 6

Scheme 4.

Scheme 5.

catalyst concentration (5 mol%) the 1,1'-bis(anthracenyl)ferrocene product 1 predominates and thus this is an effective method of synthesis. Experiments with iodobenzene as substrate gave similar results in terms of percentage yield and mono- and bis-substituted product ratios, thus this is a feature of the reaction and not due to the steric bulk of anthracene. The product 2 was isolated following column chromatography, which is necessary because at these high catalyst concentrations a palladium containing by-product characterised as 15 was obtained which had similar physical properties to the product. The latter result is of interest in its own right since it is clear that this must arise from the quenching of the active catalyst, Scheme 6, by oxidative addition with bromoanthracene. Similar results have been reported recently by Brown and

coworkers [23,24] and other palladium complexes have been reported [25–27].

In the case of the coupling reaction with dibromoanthracene as a substrate, some bromide/chloride exchange, presumably metal-catalysed, occurred with the isolation of crystals of the compound 15a present in the recrystallized sample of the catalytic by-product. The extent of the exchange reaction is not clear because a full mass balance of all the catalyst was not possible, however, it is clear that this process occurs during the reaction and not during crystallization. It is not an unexpected result since metal (particularly copper) catalysed halogen exchange is used as an effective synthetic methodology in anthracene chemistry. One of these crystals was subjected to an X-ray single crystal diffraction study as follows.

Table 1
Reaction conditions

	Ferrocene precursor	Catalyst	Mol%	Product	Yield (%)
1	Iron acyl derivative	—	—	2	5
		—	—	1	2
2 [a]	Lithioferrocene (THF)	Pd(dppf)Cl$_2$	0.2	1	30
3 [a]	Lithioferrocene (THF)	Pd(dppf)Cl$_2$	5.0	1	35
4 [a]	Dilithioferrocene (TMEDA)	Pd(dppf)Cl$_2$	0.2	2	5
5 [a]	Dilithioferrocene	Pd(dppf)Cl$_2$	0.2	2	35–40
6 [a]	Dilithioferrocene	Pd(dppf)Cl$_2$	5.0	1	85
				2	5

[a] 9-Bromoanthracene was the substrate.
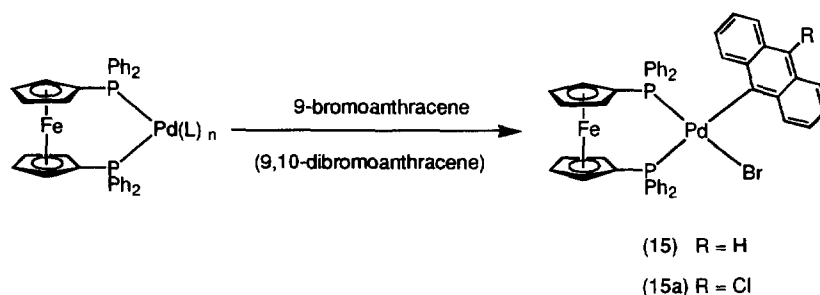
Scheme 6.

2.1. X-ray structures of 1,1'-bis(anthracenyl)ferrocene (1) and bromo(chloroanthracenyl){ferrocene-bis(diphenylphosphine)}palladium(II) (15a)

Single crystals of **1** and the chloroanthracene analogue for the palladium containing by-product **15a** suitable for X-ray work were obtained by recrystallization from dichloromethane/petroleum ether and chloroform/petroleum ether respectively; these compounds were fully characterised by X-ray crystallography.

The molecular structure of compound **1** is shown in Fig. 1, which also indicates the crystallographic atom numbering scheme used. Selected molecular geometry

Fig. 1. Molecular structure of [Fe(C$_5$H$_4$–C$_{14}$H$_9$)$_2$] (**1**) showing the atom numbering. Displacement ellipsoids are drawn at 35% probability. The hydrogen atoms are omitted for clarity.

parameters are presented in Table 2. The structure has an approximately eclipsed (8.2°) ferrocenyl geometry with the anthracenyl groups in the expected 1- and 1'-related positions. The variations in the Fe–C distances are small, 2.023(4)–2.083(4) Å (average 2.047 Å), but seem to be real since the longer distances involve the two carbons [C(5) and C(10)] with anthracenyl substituents. Effects of these substituents on the geometry of the cyclopentadienyl rings are also apparent in the ring C–C distances and C–C–C angles. Thus the distances involving C(5) and C(10) are somewhat longer than the remaining C–C distances [1.419(5)–1.438(5) vs. 1.396(5)–1.414(5) Å], and also the angles at these atoms are narrower than the remaining angles [105.2(4), 105.8(4) vs. 107.6–109.8(4)°]. Both the cyclopentadienyl rings are planar within experimental error and they are also parallel to each other within 6.5(2)°. The bond lengths and angles associated with the anthracenyl rings are normal but they show significant deviations [ca. 0.140(4) Å] from planarity; they are also non-planar with the parent cyclopentadienyl rings as indicated by the dihedral angles [44.3(1), 41.8(1)°] between the respective anthracenyl and cyclopentadienyl moieties. The particular orientations adopted by the side groups and
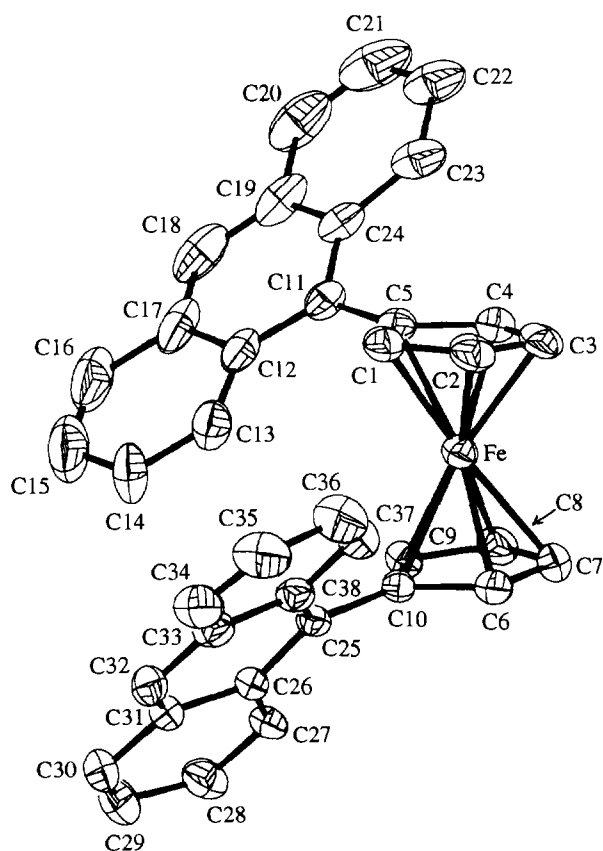
Table 2
Selected bond lengths (Å) and angles (deg) for [Fe(C$_5$H$_4$–C$_{14}$H$_9$)$_2$] (**1**)

Fe–C(8)	2.023(4)	Fe–C(9)	2.023(4)
Fe–C(3)	2.024(4)	Fe–C(4)	2.029(4)
Fe–C(2)	2.043(4)	Fe–C(7)	2.045(4)
Fe–C(1)	2.056(4)	Fe–C(6)	2.061(4)
Fe–C(5)	2.082(4)	Fe–C(10)	2.083(4)
C(1)–C(2)	1.408(5)	C(1)–C(5)	1.426(5)
C(2)–C(3)	1.414(6)	C(3)–C(4)	1.397(5)
C(4)–C(5)	1.429(5)	C(6)–C(7)	1.400(5)
C(6)–C(10)	1.438(5)	C(7)–C(8)	1.414(5)
C(8)–C(9)	1.396(5)	C(9)–C(10)	1.419(5)
C(2)–C(1)–C(5)	109.1(4)	C(1)–C(2)–C(3)	107.8(4)
C(4)–C(3)–C(2)	108.0(4)	C(3)–C(4)–C(5)	109.3(4)
C(1)–C(5)–C(4)	105.8(4)	C(1)–C(5)–C(11)	129.0(4)
C(4)–C(5)–C(11)	125.0(4)	C(7)–C(6)–C(10)	109.3(4)
C(6)–C(7)–C(8)	107.6(4)	C(9)–C(8)–C(7)	108.0(4)
C(8)–C(10)–C(25)	109.8(4)	C(9)–C(10)–C(6)	105.2(4)
C(9)–C(10)–C(25)	127.0(3)	C(6)–C(10)–C(25)	127.2(4)

also the packing of the molecules in the unit-cell seem to result from a clear tendency to avoid significant intra- or intermolecular stacking interactions. There are several interligand short contacts less than the appropriate van der Waals radii sum [H(1) ⋯ H(13) = 2.25, H(4) ⋯ H(23) = 2.28, H(6) ⋯ H(37) = 2.22, H(9) ⋯ H(27) = 2.25 Å] which would explain the large twists of the substituents relative to the parent cyclopentadienyl rings. Intermolecular distances involving the non-hydrogen atoms [≥ 3.370 Å] are appropriate for van der Waals contacts only.

The structure **15a**, together with the crystallographic atom numbering scheme used, is shown in Fig. 2, and selected molecular geometry parameters are presented in Table 3. The two Pd–P distances are significantly different 2.401(2) and 2.272(2) Å, the longer bond being *trans* to the chloroanthracene ligand. The palladium has a square planar geometry with noticeable tetrahedral distortion [*trans* angles 173.8(3) and 171.21(7)°; *cis* angles 85.4(2)–99.82(8)°]. These distortions, particularly the large P(1)–Pd–P(2) angle 99.82(8)°, may be explained by the steric demand of the Fe(Cp)₂ moiety bonded to the two phosphorus atoms. The Pd–P(1)–C(5) and Pd–P(2)–C(10) angles are significantly different at 122.2(3) and 113.9(3)°. Other tetrahedral angles at P(1) and P(2) also show large variations, 101.1(3)–115.9(2)°

and 102.1(3)–117.1(2)° respectively, which may be attributed to close interligand interactions. The Fe–C distances vary from 1.976(9)–2.048(8) Å, mean 2.014 Å, which are somewhat less than the corresponding values in **1**. The C–C distances in the cyclopentadienyl rings are 1.373(11)–1.416(10) Å, mean 1.396 Å and the C–C–C angles are 103.7(7)–109.7(9)°, mean 107.9°. The cyclopentadienyl rings, which are both planar, adopt a staggered configuration in this compound (clearly shown in Fig. 3) and are parallel within 1.5(5)°. The anthracenyl ring is significantly non-planar but the maximum deviation of any atom from the mean plane is much less than in **1** [0.057(8) vs. 0.140(4) Å], which reflects less steric congestion of the anthracenyl moiety in this compound. The intermolecular non-hydrogen contacts [≥ 3.266 Å] suggest that the molecules are held together in the crystal by van der Waals forces only.

Having established a facile synthetic procedure for the synthesis of 9-anthracenylferrocene (**2**) and 1,1'-bis(9-anthracenyl)ferrocene (**1**), the reaction of 1,1'-bis(chlorozincio)ferrocene (**13**) with, 9,10-dibromoanthracene, using varying stoichiometric ratios and catalyst concentrations, was investigated. A series of 9,10-substituted ferrocenylanthracene derivatives has thus been prepared, Scheme 7.

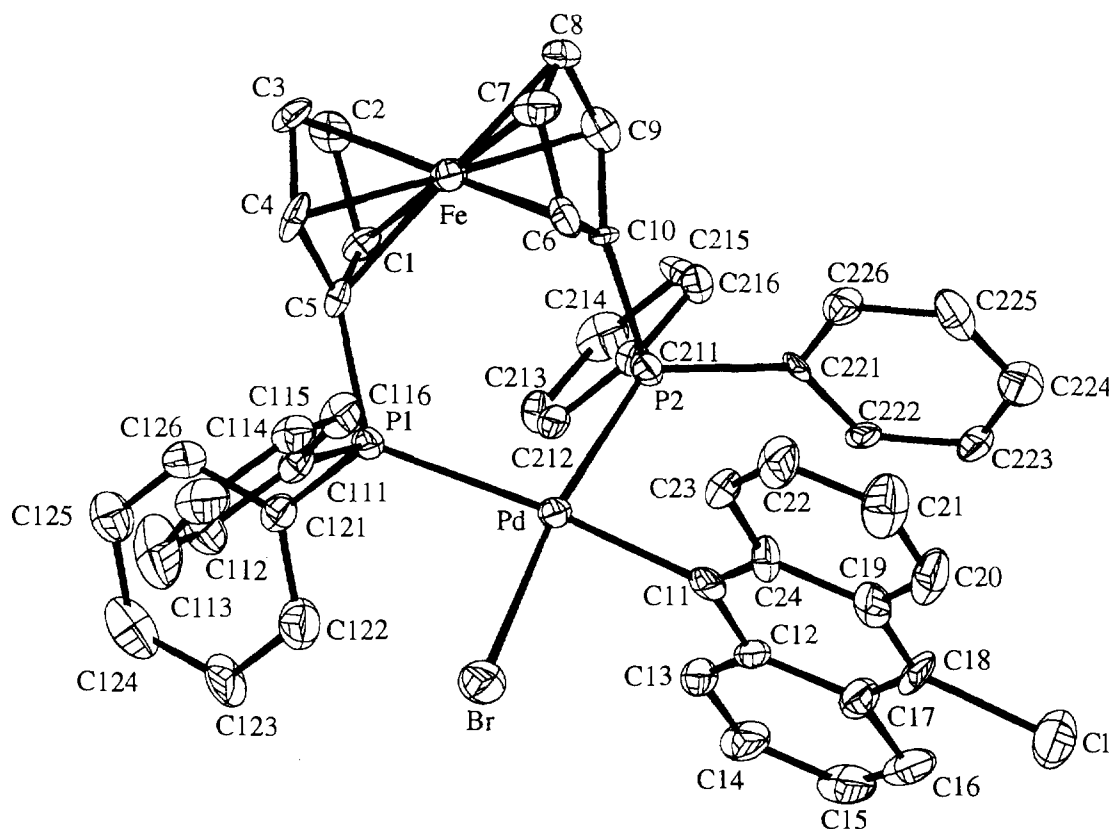The reaction of 9,10-dibromoanthracene (**16**) and

Fig. 2. Molecular structure of [PdBr(C₁₄H₈Cl){Fe(C₅H₄–PPh₂)₂}] (**15a**) showing the atom numbering. Displacement ellipsoids are drawn at 40% probability. The hydrogen atoms are omitted for clarity.
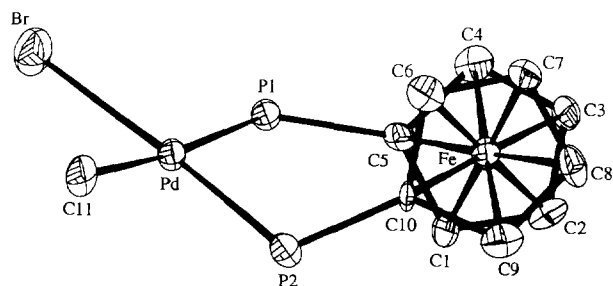
Fig. 3. Staggered arrangement of the two cyclopentadienyl rings in the structure of [PdBr(C$_{14}$H$_8$Cl){Fe(C$_5$H$_4$–PPh$_2$)$_2$}] (**15a**). Only one carbon bonded to Pd from the anthracenyl moiety is included in the figure.

9,10-di-iodoanthracene (**17**) respectively with 1,1′-bis(chlorozincio)ferrocene (**13**) at low catalyst concentrations using a 1:1 ratio of (**16**):(**13**) and (**17**):(**13**) gave

products **18** and **19** respectively as the major products. It was apparent on examination of the NMR spectra however that samples of compound **18** which were crystallized prior to purification by sublimation contained a quantity of the chloride metathesised product **18a** and a quantity of compound **2**. These observations indicate that halide exchange is integral to the catalysis process. The use of a (2.5):1 stoichiometric ratio was found to result in the formation of 9,10-bis(ferrocenyl)anthracene **20**, which was obtained as a red–violet solid. At high catalyst concentrations, in the case where compound **16** was the substrate, a mixture of products arose, from which compounds **21** and **22** could also be tentatively identified by mass spectrometry and NMR data of the product mixtures as the major products, although they were not isolated separately. In experiments in which ferrocene was lithiated using
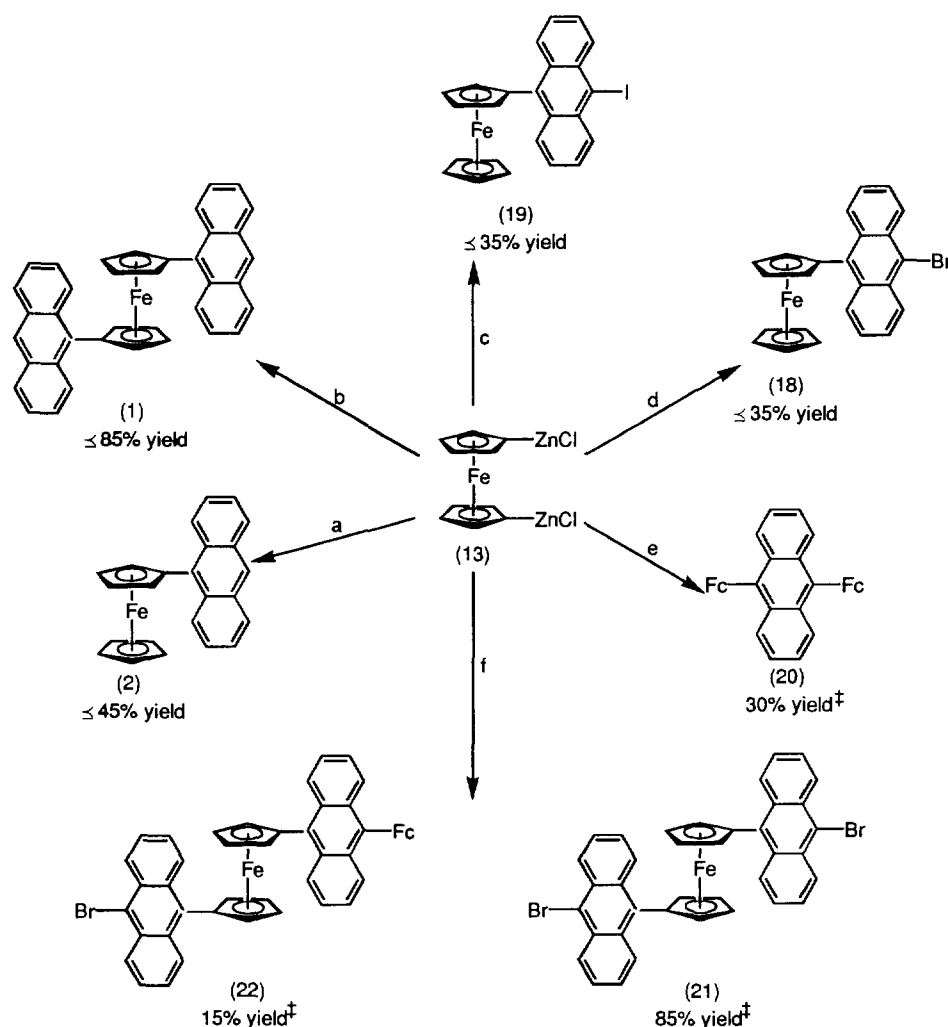
Scheme 7. (a) 0.2 mol% catalyst [13/14 = 1:2.5 ratio], (b) 5 mol% catalyst [13/14 = 1:2.5 ratio], (c) 0.2 mol% catalyst [13/17 = 1:1 ratio], (d) 0.2 mol% catalyst [13/16 = 1:1 ratio], (e) 0.2 mol% catalyst [13/16 = 1:2.5 ratio], (f) 5 mol% catalyst [13/16 = 1:2.5 ratio].

Table 3

Selected bond lengths (Å) and angles (deg) for [PdBr(C$_{14}$H$_8$Cl){Fe(C$_5$H$_4$–PPh$_2$)$_2$} (15a)

Pd–P(1)	2.401(2)	Pd–P(2)	2.272(2)
Pd–Br	2.477(1)	Pd–C(11)	2.053(9)
Fe–C(1)	1.994(9)	Fe–C(2)	2.018(9)
Fe–C(3)	2.026(9)	Fe–C(4)	2.027(9)
Fe–C(5)	2.029(8)	Fe–C(6)	1.976(9)
Fe–C(7)	2.006(9)	Fe–C(8)	2.048(8)
Fe–C(9)	2.009(9)	Fe–C(10)	2.006(8)
C(1)–C(2)	1.409(10)	C(1)–C(5)	1.389(11)
C(2)–C(3)	1.391(12)	C(3)–C(4)	1.391(11)
C(4)–C(5)	1.416(10)	C(6)–C(7)	1.375(10)
C(6)–C(10)	1.410(11)	C(7)–C(8)	1.373(11)
C(8)–C(9)	1.397(11)	C(9)–C(10)	1.405(10)
C(11)–Pd–P(2)	85.9(2)	C(11)–Pd–P(1)	173.8(3)
P(2)–Pd–P(1)	99.82(8)	C(11)–Pd–Br	85.4(2)
P(2)–Pd–Br	171.21(7)	P(1)–Pd–Br	88.84(6)
C(121)–P(1)–C(5)	101.1(3)	C(121)–P(1)–C(111)	103.0(3)
C(5)–P(1)–C(111)	102.4(3)	C(121)–P(1)–Pd	115.9(2)
C(5)–P(1)–Pd	122.3(3)	C(111)–P(1)–Pd	109.9(2)
C(10)–P(2)–C(211)	105.5(3)	C(10)–P(2)–C(221)	102.9(3)
C(211)–P(2)–C(221)	102.1(3)	C(10)–P(2)–Pd	113.9(3)
C(211)–P(2)–Pd	113.8(2)	C(221)–P(2)–Pd	117.1(2)
C(5)–C(1)–C(2)	107.5(8)	C(3)–C(2)–C(1)	109.0(8)
C(4)–C(3)–C(2)	107.2(8)	C(3)–C(4)–C(5)	108.7(8)
C(1)–C(5)–C(4)	107.5(7)	C(1)–C(5)–P(1)	125.4(7)
C(4)–C(5)–P(1)	126.9(7)	P(1)–C(5)–Fe	122.5(4)
C(7)–C(6)–C(10)	111.3(8)	C(8)–C(7)–C(6)	107.1(8)
C(7)–C(8)–C(9)	108.1(8)	C(8)–C(9)–C(10)	109.7(9)
C(6)–C(10)–C(9)	103.7(7)	C(6)–C(10)–P(2)	124.3(6)
C(9)–C(10)–P(2)	132.0(7)	P(2)–C(10)–Fe	125.8(4)

1.5 equiv. of t-butyllithium prior to the transmetallation step followed by an identical coupling procedure using 5 mol% catalyst, the reaction yields were low with mono-substituted ferrocenyl products dominating.

Having prepared a series of anthracenylferrocenes, their physical properties, reaction chemistry and functionalisation were studied, the results of which will be the subject of future communications. Preliminary luminescence studies have been carried out in the case of compounds 9-anthracenylferrocene (2) and 9,10-bis(ferrocenyl)anthracene (20). From the results obtained it can be concluded that the ferrocenyl groups cause fluorescence quenching in the anthracene moiety by a combination of energy and electron transfer. The coupling between the ferrocenyl and anthracenyl units is non-negligible in spite of the orthogonal twisting of 9- or 10-substituted anthracenyl–metallocenyl systems. Dis-

ubstitution leads to particularly noticeable electronic coupling.

Electrochemical characterisation of the compounds 2 and 20 together with 1-naphthylferrocene and ferrocene for reference purposes was carried out using cyclic voltammetry. The results, shown in Table 4, indicate the relationship between structure and the $E_{0.5}$ potential, the ferrocene unit becoming increasingly difficult to oxidise as we progress down the table.

3. Conclusions

In summary, a series of anthracenylferrocene derivatives has been prepared and fully characterised. 1,1'-Bis(9-anthracenyl)ferrocene has been shown to be suitable for a template molecular sensor in terms of its structural and physical properties. Its further functionalisation is currently under investigation. Although the complex (dppf)PdCl$_2$ is a suitable catalyst at high catalyst concentrations, significant halogen exchange does occur in reactions where a halogenated product is desired.

The methodology developed here has also been shown to be transferable to the coupling of other halogenated species onto ferrocenes, such as thiophenes, phenanthrene and dipyridines. These results will be the subject of further communications.

4. Experimental

Unless otherwise stated all experiments were carried out under a nitrogen atmosphere using standard Schlenk line techniques. All reaction solvents were purified prior to use; dichloromethane was distilled from calcium hydride, petroleum spirit (40–60 °C) was dried over sodium wire while tetrahydrofuran (THF) and diethyl ether were distilled from sodium/benzophenone. Dimethylformamide (DMF) was dried over phosphorus pentoxide and distilled from calcium carbonate prior to use.

Column chromatography was carried out using either aluminium oxide (alumina) (150 mesh, 158), Brockmann 1, activated neutral and basic, or silica gel (Kieselgel 230–400 mesh) as specified. All reagents were purchased from either Lancaster or the Aldrich

Table 4

Cyclic voltammetry of selected compounds

Ligand	Ferrocenyl oxidation potential (mV)	Ferrocenyl reduction potential (mV)	$E_{0.5}$ value (mV)
Ferrocene	640	315	478
7	750	460	605
2	738	612	675
20	910	782	846

Chemical Company and used without further purification.

NMR spectra were recorded in deuterated chloroform ($CDCl_3$) on a Bruker AC-250 or SRC WH-400 spectrometer. Elemental analysis for carbon, hydrogen and nitrogen recorded on a Carlo Erba elemental analyser MOD.1106 (using helium as carrier gas).

The electrochemical properties of the compounds prepared were measured using the technique of cyclic voltammetry (CV). All CV measurements were carried out at room temperature in a $10 \, cm^3$ volume electrochemical cell, fitted with a platinum working electrode, a platinum secondary electrode and a reference electrode of silver wire. Dry, degassed dichloromethane containing 0.1 M tetrabutylammonium tetrafluoroborate (TBATFB) as the background electrolyte was used as the solvent. The scan rate applied was $100 \, mV \, s^{-1}$ and the current set at 2 mA. All measurements taken were related to a ferrocene standard, run under identical conditions.

5. Dicarbonyl-cyclopentadienyl(η^1-(9-anthracenyl)meth-1-one)iron (5)

To a sodium amalgam (prepared by the addition of sodium metal (2.5 g, 0.11 mol) in small pieces to a Schlenk tube (approx. 5 cm diameter) containing mercury in 1 cm depth with constant stirring), was added THF (300 ml) followed by Fp dimer, $[Fe(CO)_2Cp]_2$, $(Fp)_2$ (1.37 g, 5.38 mmol) and the reaction mixture was stirred for 1 h. To 9-anthracenoyl chloride (2.00 g, 8.33 mmol) in THF (100 ml), held at $-78\,°C$ was added the NaFp solution, prepared from the Na/Hg amalgam. The reaction mixture was warmed to RT whilst stirring under N_2. The solvent was then removed and the residue columned under N_2 using a silica support. The product, the third coloured fraction collected eluting with diethyl ether/petroleum spirit (60:40), was isolated as a yellow solid (0.70 g, 1.83 mmol) in 34% yield.

(5) $C_{22}H_{14}FeO_3$. Physical characteristics: yellow solid. ^{1}H NMR: ($CDCl_3$) δ_H 4.766 (s, 5H) –Cp protons: 7.46, 7.98 (d), 8.04, 8.32 (bs) –anthracenyl protons. ^{13}C NMR: ($CDCl_3$) δ_H 87.29 –Cp carbons, 124.78, 125.20, 125.54, 125.88, 127.65, 128.60, 133.25 –anthracenyl carbons: 150.00 –acyl carbonyl: 213.56, 215.622 –carbonyl. FAB mass spectrometry data: m/e parent ion, $M - H^+$ 383 (19.5%), 354 (7.0%), 326 (10%), 298 (20%), 205 (100%). Anal. Found: C, 69.13, H, 3.64. $C_{22}H_{14}FeO_3$ Calc.: C, 69.11, H, 3.6%.

5.1. 9-Anthracenylferrocene (2) and 1,1'-bis(9-anthracenyl)ferrocene (1) from dicarbonyl-η^5-cyclopentadienyl(η^1-(9-anthracenyl)-meth-1-one)iron (5)

A solution of compound 5 (0.50 g, 1.27 mmol) in decalin (10 ml) was refluxed for 3 h. After allowing to cool under N_2, the products were purified using a silica column 5 cm in diameter by 6 cm in length. The decalin was first removed from the reaction products by elution with petroleum spirit. Continued elution gave the first fraction which contained ferrocene and anthracene, whilst the second fraction contained traces of the mono-substituted product 2 and bis-substituted (1) products in approximate yields of 5% and 2% respectively. A pure sample of the 9-anthracenylferrocene was isolated by preparative TLC, eluting with petroleum spirit.

5.2. 9-Anthracenylferrocene (2)

$C_{24}H_{18}Fe$. Physical characteristics: orange/red solid. Mass spectrometry data: m/e parent ion $M^{+\cdot}$ 362 (100%), 256 (13%), 239 (11%), 178 (9%), 149 (8%). ^{1}H NMR: ($CDCl_3$) δ_H 4.22 (s, 5H), 4.56 (t, 2H), 4.77 (t, 2H) Fc protons; 7.44 (t, 2H), 7.50 (t, 2H), 7.99 (dd, 2H), 8.40 (s, 1H), 9.17 (bd, 2H) anthracenyl protons. ^{13}C NMR: ($CDCl_3$) δ_H 67.76, 69.84, 73.28, 84.37 –Fc carbons; 124.23, 124.85, 126.77, 127.74, 128.56, 130.68, 131.64, 156.36. Anal. Found: C, 79.51, H, 4.93. $C_{24}H_{18}Fe$ Calc.: C, 79.56; H, 4.97%. Cyclic voltammetry data (measurements taken using tetrabutylammonium tetrafluoroborate (TBATFB) in dichloromethane versus silver wire): ferrocene oxidation potential 738 mV; ferrocene reduction potential 612 mV; $E_{0.5}$ value 675 mV.

5.3. Bis-1,1'-(9-anthracenyl)ferrocene (1)

Physical characteristics: red crystalline solid. Mass spectrometry data: m/e parent ion $M^{+\cdot}$ 538 (33%), 360 (10%), 295 (14%), 239 (100%). Accurate mass 538.1346 ($\Delta = 7.0$ ppm). ^{1}H NMR: ($CDCl_3$) δ_H 4.69 (t, 4H, 4.76 (t, 4H), –Fc protons; 6.95 (t, 4H), 7.32 (t, 4H), 7.96 (d, 4H), 8.42 (s, 2H), 9.08 (bs, 4H) –anthracenyl protons. ^{13}C NMR: ($CDCl_3$) δ 69.53, 75.23, 85.84 ferrocenyl carbons; 124.21, 124.82, 126.93, 127.50, 128.41, 130.71, 131.08, 156.36; anthracenyl carbons. Anal. Found: C, 85.01; H, 5.12. $C_{38}H_{26}Fe$ Calc.: C, 84.76; H, 4.87%.

5.4. Coupling reaction of 1,1'-dilithioferrocene and 9-bromoanthracene using Pd(dppf)Cl$_2$ as catalyst

1,1'-Dilithioferrocene was isolated from 1,1'-dibromoferrocene (3.00 g, 8.72 mmol) in petroleum spirit (10 ml) by reaction with 2.5 M n-BuLi (10.47 ml, 26.20 mmol) at RT for 3 h. The dilithiated species, isolated under N_2 as an orange powder, was washed with petroleum spirit (100 ml) prior to use. To the dilithioferrocene, re-dissolved in THF (100 ml), was added 9-bromoanthracene (5.61 g, 21.80 mmol) and Pd(dppf)Cl$_2$ (5 mol%). The reaction was allowed to reflux for 30 min and stirred at RT for 8 h. The reaction was quenched by the addition of water (100 ml) and the

reaction products were then extracted with dichloromethane (3 × 50 ml). The organic fractions were combined, dried over magnesium sulphate and concentrated under reduced pressure. The reaction yielded starting materials and 9-anthracenylferrocene (2) (< 5%), which were separable by variable temperature sublimation (70–100 °C). No increase in reaction yield was observed when Pd(PPh$_3$)$_4$ was used as an alternate catalyst, under identical reaction conditions.

5.5. Coupling reactions of ferrocenylzinc chloride (from lithioferrocene THF) and 9-bromoanthracene using Pd(dppf)Cl$_2$ as catalyst

To ferrocenyllithium (4.00 g, 20.84 mmol), prepared by reaction of ferrocene and 2.5 M n-BuLi in hexanes and isolated after 12 h from a reduced solvent volume held at low temperature, re-dissolved in THF (100 ml) and held at −10 °C, was added a 1 M solution of zinc chloride in diethyl ether (22.92 ml, 22.92 mmol). After 1 h at RT, 9-bromoanthracene (10.80 g, 41.67 mmol) and Pd(dppf)Cl$_2$ (0.20 mol%) were added and the reaction mixture was then refluxed for 30 min and stirred for 8 h at RT. The reaction mixture was quenched by the addition of water (100 ml) and the reaction products were extracted with dichloromethane (3 × 50 ml). The combined organic fractions were dried over magnesium sulphate and concentrated under reduced pressure prior to purification by column chromatography. The reaction yielded ferrocene, 9-bromoanthracene and 9-anthracenylferrocene (2) in 30–35% yield, which were separated by variable temperature sublimation on a temperature programmed variable sublimation instrument.

Increasing the molar percentage of catalyst used from 0.20 mol% to 5.0 mol% resulted in a yield of 35–38%.

5.6. Coupling reactions of 1,1'-bis(chlorozincio)ferrocene (from lithioferrocene TMEDA) and 9-bromoanthracene using Pd(dppf)Cl$_2$ as catalyst

To a solution of 1,1'-dilithioferrocene · TMEDA (2.00 g, 10.10 mmol) in THF (100 ml) at −10 °C was added a 1 M solution of zinc chloride in diethyl ether (22.22 ml, 22.22 mmol). The reaction mixture was allowed to warm to ambient temperature and was then stirred for 1 h, after which 9-bromoanthracene (7.85 g, 30.30 mmol) and Pd(dppf)Cl$_2$ (5.0 mol%) were added. After a 30 min reflux and subsequent stirring for 8 h, the reaction was quenched by the addition of water (100 ml) and the products extracted with dichloromethane (3 × 50 ml). The combined organic fractions were dried over magnesium sulphate and concentrated under reduced pressure, prior to characterisation. The reaction yielded ferrocene, 9-bromoanthracene (14) and 9-anthracenyl-ferrocene (2), the latter compound in approximately 5% yield.

5.7. Coupling reactions of 1,1'-bis(chlorozincio)ferrocene (from dilithioferrocene) and 9-bromoanthracene using Pd(dppf)Cl$_2$ (0.20 mol%) as catalyst

From 1,1'-dibromoferrocene (3.00 g, 8.72 mmol) in petroleum spirit (10 ml), 1,1'-dilithioferrocene was prepared by reaction with 2.5 M n-BuLi (10.47 ml, 26.20 mmol) at RT for 3 h. The dilithiated ferrocene was isolated as an orange powder under N$_2$ and washed with petroleum spirit (100 ml) prior to use. To the lithiated ferrocene, re-dissolved in THF (100 ml) and cooled to −10 °C, was added a 1 M solution of zinc chloride in diethyl ether (17.44 ml, 17.44 mmol) and the solution was allowed to warm to ambient temperature and stirred further for 1 h. 9-Bromoanthracene (5.61 g, 21.80 mmol) and the catalyst, Pd(dppf)Cl$_2$ (0.20 mol%), were added and the reaction was refluxed for 30 min and stirred subsequently for 8 h at RT. The reaction mixture was then quenched by the addition of water (100 ml) and the reaction products extracted into dichloromethane (3 × 50 ml). The organic fractions were combined, dried over magnesium sulphate and concentrated under reduced pressure. The reaction yielded unreacted ferrocene and 9-bromoanthracene (14) and the product 9-anthracenyl-ferrocene (2); which were easily separable by variable temperature sublimation. The ferrocene and the 9-bromoanthracene sublime at 70–100 °C, whilst the 9-anthracenylferrocene remains as the unsublimed residue at this temperature. Yield of product 45%.

5.8. Coupling reactions of 1,1'-bis(chlorozincio)ferrocene (from dilithioferrocene) and 9-bromoanthracene using Pd(dppf)Cl$_2$ (5.0 mol%) as catalyst

A similar reaction using 3.00 g (8.72 mmol) of 1,1'-dibromoferrocene, 6.73 g (26.16 mmol) of 9-bromoanthracene and Pd(dppf)Cl$_2$ (5 mol%) as starting materials was carried out as above. This yielded ferrocene, 9-bromoanthracene, 9-anthracenylferrocene (2) (5%), bis-1,1'-(anthracenyl)ferrocene (1) in 85% yield by NMR and the catalytic by-product 15.

5.9. [(dppf)PdBr(9-C$_{14}$H$_9$)] (15) formed by the quenching of the active species of Pd(dppf)Cl$_2$ by the addition of 9-bromoanthracene

Physical characteristics: yellow crystalline solid. Mass spectrometry data: m/e parent ion M$^+$ 916/918 (6%, M$^{+\cdot}$ ^{81}Br in Pd isotopic cluster), 837 (15% M$^{+\cdot}$ − Br), 741 (cluster) (12%, M$^{+\cdot}$ − anthracene), 660 (100%, M$^{+\cdot}$ (Br + anthracene)). FAB accurate mass (M$^{+\cdot}$ − Br) 837.0737 ($\Delta = 2.1$ ppm for C$_{48}$H$_{37}$FeP$_2^{106}$Pd). ^{13}C NMR: (CDCl$_3$) δ 65.81, 70.62, 71.40, 71.96, 73.25, 73.30, 73.36, 74.21, 74.43, 74.54, 76.51, 77.02, 77.53, 124.33, 125.36, 126.64, 127.41, 128.16, 128.27, 128.39, 128.44, 128.66, 131.48, 131.65, 133.29. Anal. Found:

C, 63.20; H, 4.21. $C_{48}H_{37}BrFeP_2Pd$ Calc.: C, 62.81; H, 4.03%.

In similar reactions using 9,10-dibromoanthracene as catalyst, the analogous catalytic by-products were obtained. Recrystallization of a small quantity of one of these products from a dichloromethane–ether solution yielded crystals of compound 15a. ^{1}H NMR ($CDCl_3$): δ 3.52 (bs, 2H), 4.10 (bs, 2H), 4.52 (bs, 2H), 4.82 (very bs, 2H), 6.52 (bm, 6H), 7.00 (bm, 2H), 7.15 (td, 2H), 7.26 (m, 4H), 7.50 (m's, 8H), 8.26 (bm, 4H), 8.90 (d, 1H), 9.10 (m, 1H). Mass spectrum: parent ion 950–955 (isotopic cluster $^{35/37}Cl$, ^{106}Pd, $^{79/81}Br$).

5.10. Coupling reactions of 1,1'-bis(chlorozincio)ferrocene (from dilithioferrocene) and 9,10-dibromoanthracene using Pd(dppf)Cl₂ (0.20 mol%) as catalyst

To a solution of bis-1,1'-(chlorozincio)ferrocene, prepared from 1,1'-dibromoferrocene (3.00 g, 8.72 mmol) as previously described in THF (100 ml) at −10 °C was added 9,10-dibromoanthracene [22] (5.86 g, 17.44 mmol) and Pd(dppf)Cl₂ (0.20 mol%). The reaction mixture was refluxed for 30 min and was subsequently stirred for 8 h. Standard work-up, as described in the synthesis of

compound 2, yielded ferrocene, 9,10-dibromoanthracene and compound 18 (30–35%).

5.11. 9-Bromo-10-ferrocenylanthracene (18)

$C_{24}H_{17}BrFe$. Physical characteristics: red/purple solid. Mass spectrometry data: m/e parent ion M$^+$ 440/442. ^{1}H NMR: ($CDCl_3$) δ 4.14 (s, 5H), 4.59 (t, 2H), 4.75 (t, 2H) –Fc protons; 7.04 (td, 2H), 7.45 (td, 2H), 8.40 (dd, 2H), 9.16 (bs, 2H) –anthracenyl protons. Anal. Found: C, 65.51, H, 3.92. $C_{24}H_{17}BrFe$ Calc.: C, 65.34; H, 3.89%.

A similar reaction using 1,1'-dibromoferrocene (3.00 g, 8.72 mmol), 9.10-dibromoanthracene [22] (1.47 g, 4.36 mmol) and Pd(dppf)Cl₂ (0.20 mol%) as starting materials was carried out as above. This yielded ferrocene and 9,10-dibromoanthracene, compounds 18 and 20 in the ratio 7:3.

5.12. Bis-9,10-(ferrocenyl)anthracene (20)

$C_{34}H_{26}Fe_2$. Physical characteristics: red solid. Mass spectrometry data: m/e parent ion M$^+$ 546 (100%), 360 (45%), 302 (42%), 239 (40%), 121 (55%), 56

Table 5
Crystal data and details of data collection and structure refinement for $[Fe(C_5H_4-C_{14}H_8Cl)\{Fe(C_5H_4-PPh_2)_2\}]$ (15a)

	1	15a
empirical formula	$C_{38}H_{26}FE$	$C_{48}H_{36}BrClFeP_2Pd$
formula weight	538.44	952.32
T (K)	293(2)	150(2)
crystal system	monoclinic	monoclinic
space group	$C2/c$ (No. 15)	$P2_1/n$ (No. 14)
a (Å)	27.788(4)	13.293(3)
b (Å)	10.768(3)	10.728(3)
c (Å)	17.471(5)	27.457(3)
β (°)	95.14(2)	98.44(2)
V (Å^{-3})	5207(4)	3873(2)
Z	8	4
D_c (g cm^{-3})	1.374	1.633
μ(Mo Kα) (cm^{-1})	6.06	20.57
$F(000)$	2240	1912
crystal size (mm^3)	$0.12 \times 0.08 \times 0.06$	$0.15 \times 0.06 \times 0.04$
θ range for cell and data collection (°)	2.91 to 24.98	1.82 to 25.05
h_{min}, h_{max}	−31, 27	−12, 15
k_{min}, k_{max}	−11, 9	−12, 10
l_{min}, l_{max}	−18, 19	−30, 27
total reflections collected	10309	14389
total unique reflections (merging R)	3949 (0.0657)	5891 (0.0722)
absorption correction factors	0.894–1.002	0.921–1.005
data/parameters in the refinement	3949/352	5891/439
final R [a] indices	$R_1 = 0.0921$ (0.0485) [b]	$R_1 = 0.1300$ (0.0447) [b]
	$wR_2 = 0.1098$ (0.1031) [b]	$wR_2 = 0.0962$ (0.0838) [b]
largest diff. peak and hole (e Å^{-3})	0.915 and −0.244	0.598 and −0.590
goodness-of-fit	0.830	0.904

[a] $R_1 = \Sigma(F_o - F_c)/\Sigma(F_o)$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; $w = [1/\sigma^2(F_o^2) + (qP)^2]$, where $P = [(F_o^2) + 2F_c^2]/3$ and $q = 0.0466$ and 0.000 for 1 and 15a respectively.
[b] R_1 and wR_2 values for all data; those calculated for data with $F_o^2 > 2\sigma(F_o^2)$ [2192 (1), 2355 (15a)] are given in parentheses.

(32%). Accurate mass: EI peak match on M$^+$ (546.0730000, $\Delta = -2.3$ ppm for $C_{34}H_{26}Fe_2$). ^{1}H NMR: (CDCl$_3$) δ 67.68, 68.86, 73.59, 77.50, ferrocenyl carbons, 123.56, 127.69, 130.73, 156.34 anthracenyl carbons. Cyclic voltammetry data (measurements taken using tetrabutylammonium tetrafluoroborate (TBATFB) in dichloromethane versus silver wire): ferrocene oxidation potential 910 mV; ferrocene reduction potential 782 mV; $E_{0.5}$ value 846 mV. Anal. Found: C, 74.69; H, 4.75. $C_{34}H_{26}Fe_2$ Calc.: C, 74.76; H, 4.80%.

5.13. Preparation of 1,1′-bis(10-bromo-(9-anthracenyl))ferrocene (21) and bis-1-(9-anthracenyl(10-bromo))-1-(9-anthracenyl-(10-ferrocenyl))ferrocene (22)

A similar reaction using 1,1′-dibromoferrocene (3.00 g, 8.72 mmol), 9,10-dibromoanthracene [22] (8.79 g, 26.16 mmol) and Pd(dppf)Cl$_2$ (5.0 mol%) as starting materials was carried out as above. This yielded 1,1′-bis(10-bromo-(9-anthracenyl))ferrocene (21) and bis-1-(9-anthracenyl(10-bromo))-1-(9-anthracenyl(10-ferrocenyl))ferrocene (22) in an 85:15 ratio, based on integration of the ^{1}H NMR spectrum of the reaction mixture. FAB mass spectrometry data: m/e (22) ($C_{48}H_{33}Fe_2Br$), parent ion 800/802 (6.2/8.0%); (21) $C_{38}H_{24}FeBr_2$ parent ion cluster 698(9)/696(18)/694(7); 546 (26%); 440 (100%); 239 (48%).

5.14. Preparation of 1,1′-diphenylferrocene (4) and phenylferrocene (3)

To a solution of 1,1′-bis(chlorozincio)ferrocene, prepared from 1,1′-dibromoferrocene (3.00 g, 8.721 mmol) as previously described in THF (100 ml) held at −10 °C was added iodobenzene (3.60 g, 17.64 mmol) followed by Pd(dppf)Cl$_2$ (2.0 mol%). Following standard workup, phenylferrocene (39%) and 1,1′-diphenylferrocene (53%) were isolated by column chromatography, using a silica support.

5.15. Phenylferrocene (3)

$C_{16}H_{14}Fe$, characterised by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry, data obtained was in accordance with reported literature values [28].

5.16. 1,1-Diphenylferrocene (4)

$C_{22}H_{18}Fe$, characterised by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry, data obtained was in accordance with reported literature values [28].

5.17. X-ray crystallography

Single crystals of 1,1′-bis(anthracenyl)ferrocene (1) and [9-(10-chloroanthracenyl)](1,1′-diphenylphosphino-

ferrocenyl)palladium(II) bromide (15a) suitable for X-ray work were obtained as described above. Crystallographic measurements were made on a Delft Instruments FAST area detector diffractometer positioned at the window of a rotating anode generator with Mo Kα radiation ($\lambda = 0.71069$ Å) by following procedures described in Ref. [29]. The crystal data, details of data collection and structure refinement for both compounds are presented in Table 5. The cell parameters were determined by least-squares refinement of diffractometer angles for 250 reflections.

The structures were solved by standard heavy atom procedures and refined by full-matrix least-squares on F^2 using all unique data with intensities greater than zero. All non-hydrogen atoms were anisotropic. The

Table 6
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for [Fe(C$_5$H$_4$–C$_{14}$H$_9$)$_2$] (1)

Atom	x	y	z	U_{eq}
Fe	1956.6(2)	7774.5(5)	1312.4(3)	41(1)
C(1)	1477(2)	9005(3)	1725(3)	49(1)
C(2)	1949(2)	9488(3)	1813(3)	56(1)
C(3)	2119(2)	9558(3)	1075(3)	60(1)
C(4)	1753(2)	9124(3)	540(3)	50(1)
C(5)	1343(2)	8784(3)	930(2)	42(1)
C(6)	2470(1)	6657(3)	1892(3)	45(1)
C(7)	2568(2)	6807(3)	1125(3)	50(1)
C(8)	2165(2)	6359(3)	656(3)	49(1)
C(9)	1822(2)	5946(3)	1135(2)	41(1)
C(10)	2000(1)	6104(3)	1915(2)	35(1)
C(11)	863(2)	8410(4)	545(3)	50(1)
C(12)	587(2)	7421(4)	822(3)	57(1)
C(13)	715(2)	6739(4)	1503(3)	72(2)
C(14)	449(2)	5801(5)	1746(4)	92(2)
C(15)	15(2)	5451(6)	1318(5)	113(3)
C(16)	−126(2)	6055(6)	666(5)	104(2)
C(17)	144(2)	7062(5)	371(4)	79(2)
C(18)	−9(2)	7689(6)	−296(4)	88(2)
C(19)	245(2)	8708(6)	−549(3)	76(2)
C(20)	69(2)	9386(7)	−1217(4)	100(2)
C(21)	304(3)	10410(7)	−1434(4)	113(2)
C(22)	715(2)	10836(5)	−101(3)	89(2)
C(23)	895(2)	10203(4)	−377(3)	71(2)
C(24)	675(2)	9082(4)	−113(3)	58(1)
C(25)	1782(1)	5619(3)	2605(2)	36(1)
C(26)	1572(1)	4419(3)	2582(2)	37(1)
C(27)	1594(1)	3587(3)	1952(3)	47(1)
C(28)	1375(2)	2449(4)	1941(3)	60(1)
C(29)	1120(2)	2067(4)	2559(3)	69(1)
C(30)	1107(2)	2794(4)	3177(3)	63(1)
C(31)	1336(1)	3975(4)	3222(3)	44(1)
C(32)	1342(1)	4677(4)	3889(3)	51(1)
C(33)	1574(2)	5827(4)	3949(3)	49(1)
C(34)	1611(2)	6513(4)	4657(3)	64(1)
C(35)	1850(2)	7600(5)	4721(3)	73(2)
C(36)	2051(2)	8105(4)	4086(3)	71(2)
C(37)	2021(2)	7511(3)	3398(3)	53(1)
C(38)	1790(1)	6322(3)	3300(2)	43(1)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

hydrogen atoms were included in calculated positions (riding model) with $U_{iso} = 1.2U_{eq}$ of the parent carbon. The four phenyl groups in **15a** were treated as idealised

Table 7
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for [PdBr(C$_{14}$H$_8$Cl){Fe(C$_5$H$_4$–Ph$_2$)$_2$}] (**15a**)

Atom	x	y	z	U_{eq}
Pd	2642.5(5)	7080.5(6)	1414.9(3)	23.3(2)
Fe	1652.9(10)	10840.9(10)	1165.9(5)	25.2(4)
Br	2055.1(8)	5272.0(8)	1858.1(4)	47.2(3)
P(1)	926(2)	7843(2)	1283(1)	23(1)
P(2)	3426(2)	8634(2)	1052(1)	25(1)
C(1)	759(6)	9947(7)	631(4)	27(2)
C(2)	478(7)	11213(8)	632(4)	32(3)
C(3)	213(7)	11509(8)	1090(4)	30(3)
C(4)	286(6)	10420(8)	1368(4)	33(3)
C(5)	614(6)	9443(7)	1082(3)	22(2)
C(6)	2806(6)	10482(7)	1687(4)	28(2)
C(7)	2553(7)	11721(8)	1709(4)	34(3)
C(8)	2701(6)	12250(8)	1270(4)	31(3)
C(9)	3000(6)	11311(8)	696(4)	33(3)
C(10)	3075(6)	10172(6)	1224(3)	17(2)
C(11)	4065(7)	6316(7)	1588(4)	34(3)
C(12)	4415(7)	5450(7)	1262(4)	27(2)
C(13)	3838(7)	5083(7)	797(4)	35(3)
C(14)	4202(8)	4311(8)	487(4)	43(3)
C(15)	5155(9)	3826(8)	595(5)	57(4)
C(16)	5809(9)	4123(8)	1025(4)	48(3)
C(17)	5419(8)	4967(8)	1376(4)	36(3)
C(18)	6022(7)	5345(8)	1792(4)	39(3)
C(19)	5683(7)	6188(8)	2128(4)	34(3)
C(20)	6289(8)	6604(9)	2561(4)	46(3)
C(21)	5930(8)	7461(9)	2862(4)	58(3)
C(22)	4939(7)	7940(9)	2745(4)	45(3)
C(23)	4345(7)	7546(7)	2337(4)	29(3)
C(24)	4682(7)	6686(8)	2017(4)	30(3)
C(111)	376(4)	7741(5)	1856(2)	29(2)
C(112)	−454(4)	6983(5)	1899(2)	36(3)
C(113)	−802(4)	6866(5)	2350(3)	63(4)
C(114)	−320(5)	7506(5)	2758(2)	50(3)
C(115)	511(5)	8264(5)	2716(2)	32(3)
C(116)	859(4)	8381(4)	2265(2)	33(3)
C(121)	29(4)	6958(5)	849(2)	27(2)
C(122)	199(4)	5698(5)	777(2)	46(3)
C(123)	−528(5)	4992(4)	482(2)	49(3)
C(124)	−1425(4)	5546(5)	260(2)	51(3)
C(125)	−1594(4)	6806(6)	333(2)	43(3)
C(126)	−868(5)	7513(4)	627(2)	35(3)
C(211)	3179(4)	8604(5)	383(2)	20(2)
C(212)	2413(4)	7839(4)	150(2)	24(2)
C(213)	2181(4)	7846(4)	−360(2)	34(2)
C(214)	2716(5)	8620(5)	−637(2)	39(3)
C(215)	3483(4)	9386(4)	−404(2)	34(3)
C(216)	3714(4)	9378(4)	106(2)	29(2)
C(221)	4833(3)	8677(5)	1173(2)	22(2)
C(222)	5394(4)	7846(4)	933(2)	32(3)
C(223)	6443(4)	7773(5)	1065(2)	32(2)
C(224)	6930(3)	8533(6)	1437(2)	51(3)
C(225)	6369(5)	9364(5)	1677(2)	45(3)
C(226)	5320(5)	9437(4)	1545(2)	31(3)
Cl	7294(2)	4622(2)	1892(1)	60(1)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

hexagon with C–C distance 1.390 Å and C–C–C angle (internal) 120.0°. All calculations were done on a 486DX2/66 personal computer using the programs SHELXS-86 [30], SHELXL-93 [31], DIFFABS [32] and SNOOPI [33]. Sources of scattering factor data are given in Ref. [30].

Selected bond lengths and angles, and fractional coordinates of the non-hydrogen atoms are given in Tables 2, 3, 6 and 7 respectively. Anisotropic displacement parameters of the non-hydrogen atoms, hydrogen atom parameters and complete lists of bond lengths and angles for complexes **1** and **15a** have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgements

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