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Synthesis and characterization of palladium(II) and platinum(II) complexes with ferrocenylimidazole

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This paper is dedicated to the late Prof. Christopher Imrie.

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ABSTRACT

The synthesis and characterization of ferrocenylimidazole complexes of platinum(II) and palladium(II) are described. Reaction of ferrocenylimidazoles with K_2MCl_4 (M = Pd, Pt) using a biphasic system of dichloromethane and ethanol/water provided the corresponding complexes **2a–2j** in good yields. New synthetic routes for the synthesis of ferrocenylbenzylethers **2k–2o**, bis(4-ferrocenylbenzyl)carbonate [**2p**] and 4-ferrocenylbenzylacetate [**2q**] are also described. These products were obtained by the reaction of 4-ferrocenylbenzyl-1*H*-imidazole-carboxylate and K_2PtCl_4 under various conditions. Compounds **2k–2o** were also obtained by alternative routes which do not involve the use of a platinum salt. The crystal structures of **2b**, **2q** and plausible mechanisms for the formation of **2k**, **2p** and **2q** are reported.

1. Introduction

Transition metal complexes, particularly those containing redox-active fragments such as the ferrocenyl group, are increasingly being investigated for a variety of potential uses, such as those in the field of catalysis and material science [1]. The use of nitrogen-donor ligands has received increasing prominence over the past few years but has not enjoyed the type of systematic investigation that has been done for phosphine donors. Several areas of asymmetric catalysis, where complexes containing nitrogen-donor ligands have shown activity, include hydrogenation and reduction, transfer hydrogenation, hydrosilation, cyclopropanation, Diels–Alder reactions, aldol condensation, alkylation of aldehydes, conjugate additions, Grignard coupling, allylic alkylation and various oxidation reactions [2–4].

Several transition metal complexes with N-donor ligands have been evaluated for catalytic activity. Rajput [5] prepared ferrocenylpyridyl palladium (II) complexes bearing N-donor ligands which were efficient in the carbonylation of nitrobenzene from the corresponding carbamates. Reddy et al. have used N-substituted imidazole derivatives as ligands for palladium and found them highly active for Heck-type reactions [6]. They showed that the catalytic activity was associated with the N-substitution on the imidazole. From a catalytic point of view, the ligating imidazole nitrogen also has a tunable basicity which makes them attractive as ligands for catalysts [7–9]. It was shown that a change in ligand basicity has a marked effect on metal-ligand bond strengths, which in turn affect the catalytic properties [6–9]. Apart from catalysis, the metal binding properties of imidazole-based ligands have been explored in detail due to their presence at the active site of metallo-proteins or enzymes involved in several important metabolic processes [10].

With regard to ferrocenes, several ferrocenyl compounds and metal complexes have been investigated for potential anticancer activity [11]. Furthermore, the introduction of ferrocene into certain molecules enhanced the cytotoxic activity. In this account we report the synthesis and characterization of ferrocenylimidazolate complexes of palladium(II) and platinum(II). Various synthetic routes to 4- ferrocenylbenzylethers are also investigated.

2. Results and discussion

2.1. Synthesis of ferrocenylimidazolate-palladium complexes

The ferrocenylimidazole ligands and potassium tetrachloropalladate were used as starting materials. The ligands were soluble in dichloromethane, whereas the palladium salt was soluble in

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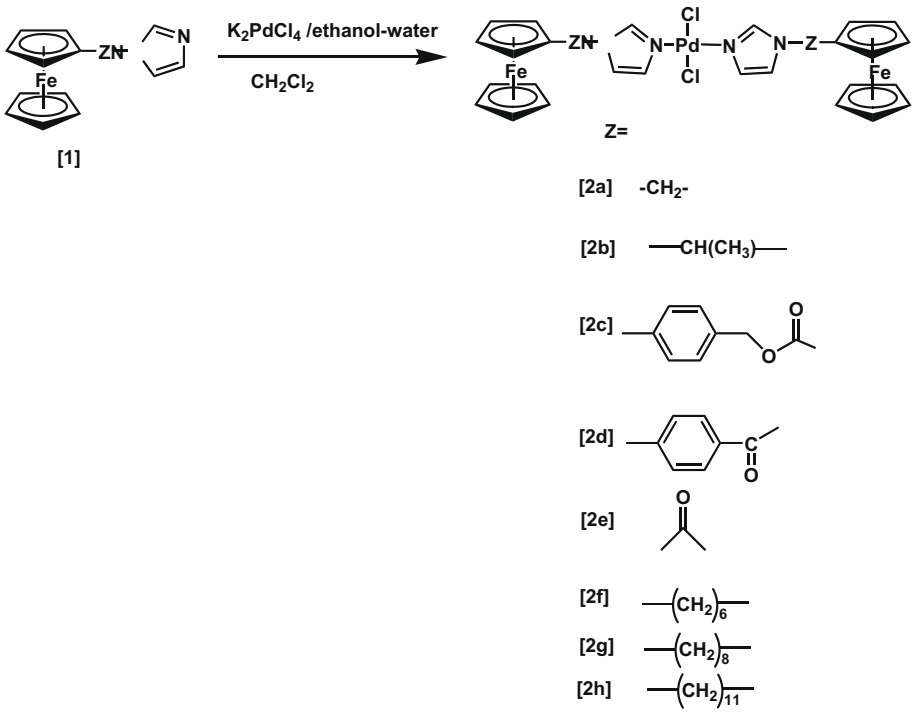


Scheme 1. Synthesis of ferrocenylimidazolate-palladium complexes.

water; this prompted us to use the biphasic system described earlier [12]. The palladium products were formed as insoluble precipitates. The reactions were monitored visually, since the upper brown aqueous layer containing the palladium salt decolourized with time. Scheme 1 outlines the general procedure used and the ferrocenylimidazolate-palladium complexes synthesized. This synthetic route has been reported as giving the *trans* isomer of the palladium complex [5].

The palladium(II) complexes were characterized by ^{1}H NMR, ^{13}C NMR and mass spectrometry. Remarkable downfield chemical shifts were observed for the protons of the imidazole ring in the complexes compared to those of the free ligands. This effect is common in transition metal complexes due to the induction of electron density by the metal which acts as a Lewis acid, and effectively deshielding the ligand protons in close proximity.

The crystal structure of dichlorobis[1-(1-ferrocenyl)ethyl-1*H*-imidazole]palladium [**2b**] (Fig. 1) was obtained with single crystals grown from a mixture of dichloromethane and hexane. The least-squares refinement of the structure gave a final *R* factor of 0.1512, which is the result of the crystals being obtained as plates, and subsequent absorption problems incurred during data collection. However, the structure, in conjunction with the spectroscopic data, provides an insight into some of the interactions within the molecule. The structural refinement data are summarized in Table 1 and selected bond lengths and bond angles are listed in Table 2.

The structure shows a *trans*-configuration of the two 1-(1-ferrocenyl)ethyl-1*H*-imidazole ligands around the palladium(II) metal centre in a square-planar arrangement of the Cl_2N_2 donor atoms. The Cl1–Pd–N2 [89.1(4)°] and Cl2–Pd–N3 [90.3(4)°] angles are close to orthogonality, and the Cl1–Pd–Cl2 angle equals

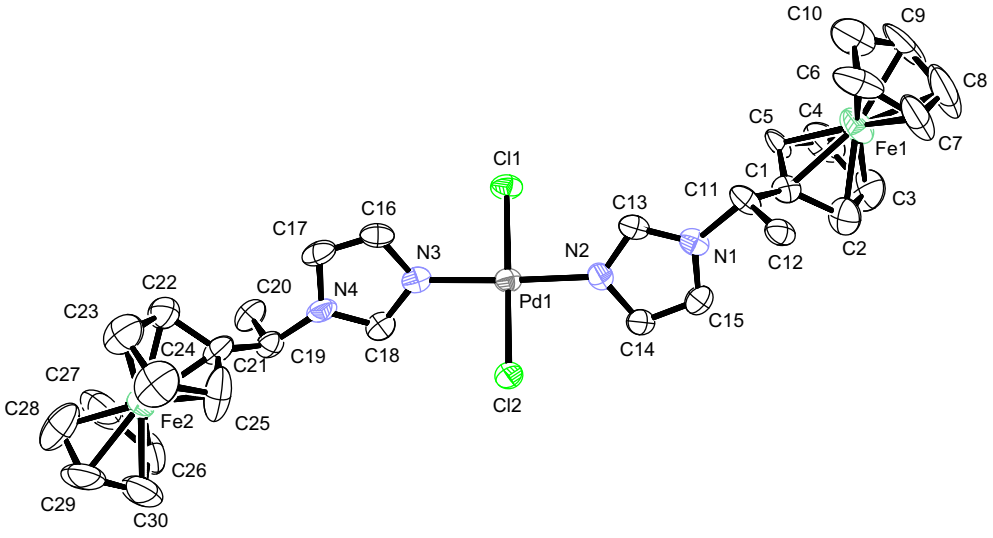


Fig. 1. An ORTEP view of the molecular structure of **2b**.

Table 1
Crystal data and structure refinement for complexes **2b** and **2q**.

	2b	**2q**
Empirical formula	$C_{30}H_{32}Cl_2Fe_2N_4Pd$	$C_{19}H_{18}FeO_2$
Formula weight	737.62	334.18
Temperature (K)	113(2)	273(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	*P*21/*n*	*P*2(1)/*c*
Unit cell dimensions		
a (Å)	10.253(2)	18.8963(4)
b (Å)	8.816 (2)	8.0010(2)
c (Å)	32.359(7)	10.3258(2)
β (°)	90.10(3)	
Volume (Å^3)	2909 (1)	1561.15(6)
Z	4	4
Density (calculated) (mg/m^3)	1.684	1.422
Absorption coefficient (mm^{-1})	1.807	0.970
F(000)	1488	696
Crystal size (mm^3)	0.20 × 0.20 × 0.10	0.29 × 0.27 × 0.19
Theta range for data collection (°)	2.03–27.03	1.08–28.00
Index ranges	$-12 \leqslant h \leqslant 12$ $-11 \leqslant k \leqslant 11$ $-40 \leqslant l \leqslant 40$	$-24 \leqslant h \leqslant 24$ $-10 \leqslant k \leqslant 10$ $-13 \leqslant l \leqslant 13$
Reflections collected	26529	18043
Independent reflections [$R_{(int)}$]	5991 [0.0553]	3772 [0.0438]
Completeness to theta (%)	94.2	100.0
Maximum and minimum transmission	0.8400 and 0.7139	0.8372 and 0.7663
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5991/0/355	3772/80/245
Goodness-of-fit on F^2	1.11	1.119
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.1512$ $wR_2 = 0.34$	$R_1 = 0.0302$ $wR_2 = 0.0866$
R indices (all data)	$R_1 = 0.1710$ $wR_2 = 0.3400$	$R_1 = 0.0393$ $wR_2 = 0.0998$
Largest difference peak and hole (e Å^{-3})	2.11 and −1.63	0.234 and −0.483

179.7(2)°. Both imidazole rings are planar with a dihedral angle of 4.74° between them. The N1C15 and N3C18 rings make dihedral angles of 46.52° and 50.73°, respectively with the square plane around Pd. The average Pd–Cl and Pd–N bond lengths are 2.293(4) and 2.00(1) Å, respectively. All bonds in the imidazole rings are delocalized. The C11 and C19 atoms are sp^3 hybridized with the bond angles N1–C11–C1 = 109(1)° and N4–C19–C21 = 112(2)°. The chirality around C19 is the *R* configuration while that around C11 is the *S* configuration. The configurations could be due to the steric interaction between the methyl group and both the substituted cyclopentadienyl ring and the imidazolium ring.

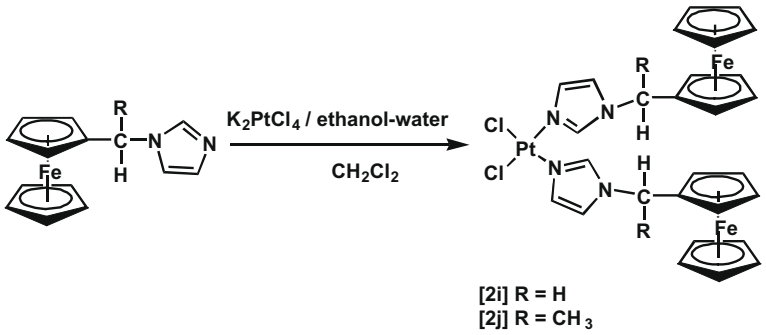
2.2. Synthesis of ferrocenylimidazolate-platinum complexes

The synthetic approach was similar to that used for the palladium complexes (Scheme 2). The biphasic solvent system of ethanol–water and dichloromethane was again utilized. The products were obtained as precipitates which were purified by recrystallisation from a dichloromethane/hexane solution, and characterization was by ^{1}H NMR, ^{13}C NMR and mass spectrometry. The two complexes that were successfully synthesized and purified are shown in Scheme 2. As expected, there were remarkable downfield chemical shifts for the protons of the imidazoles, similar to those observed for the palladium complexes. The palladium complexes readily formed (<6 h) in good yield, while the platinum ones required long reaction times (>12 h) to achieve similar yields. It has been reported the synthetic method reported herein produces complexes exclusively in the *cis* configuration [13]

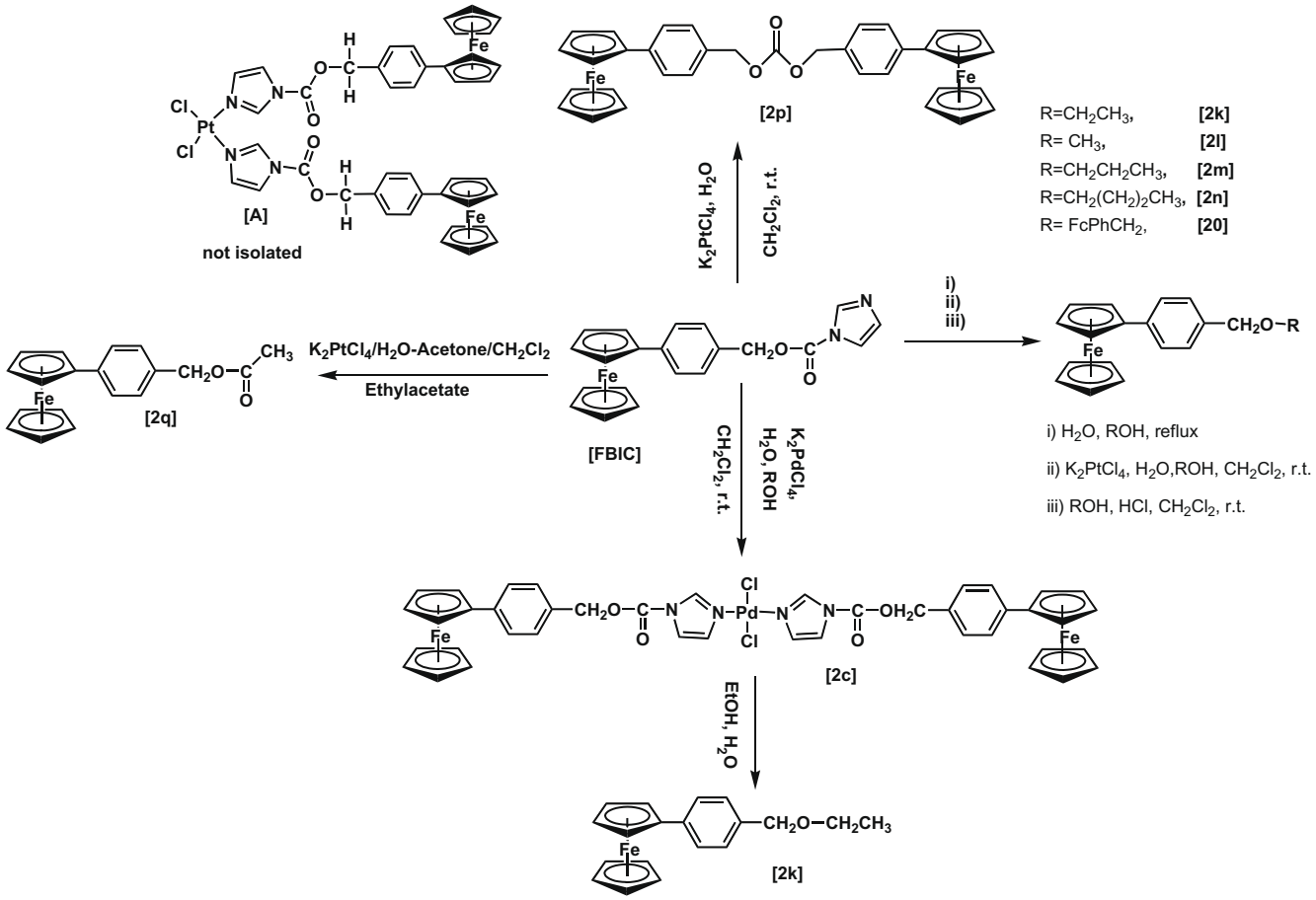
However, the reaction of 4-ferrocenylbenzyl-1*H*-imidazole-1-carboxylate (FBIC) with potassium tetrachloroplatinate (Scheme 3) did not provide us with the expected complex [**A**] as given in the case of palladium in Scheme 1, but [4-(ethoxymethyl)phenyl]ferrocene [**2k**] was isolated instead. If the complex [**A**] formed, it must have been too unstable to isolate and had a short life span. Further investigation was carried out by repeating the reaction under the same conditions but without the potassium tetrachloroplatinate salt. The latter procedure did not show the formation of the ether product, which suggests that the platinate salt was necessary for its formation. The result of this reaction prompted us to investigate a series of alcohols, i.e. methanol, propan-1-ol, butan-1-ol and (4-ferrocenylphenyl)methanol, and the corresponding ethers were obtained in modest yields. A plausible mechanism for this reaction is postulated in Scheme 4. To investigate the mechanism further, the palladium complex [**2c**] (Scheme 1), equivalent to [**A**] (Scheme 3), was chosen as a candidate. The palladium complex [**2c**] was suspended in ethanol–water mixture and refluxed for 5 h, and a yellow-orange solution with a precipitate was obtained. The mixture was filtered and the precipitate was analyzed and found to be the palladium complex [**2c**]. The filtrate, was extracted with dichloromethane, dried, and the solvent removed under vacuum to yield [4-(ethoxymethylphenyl]ferrocene [**2k**] in moderate yield. This implies that the platinum complex [**A**], which may be an intermediate to the formation of **2k,** may have been formed but was too unstable to be isolated, and had a short life span. The lability of the platinum complex [**A**] may be attributed to the higher electron induction of platinum compared to palladium. The electron affinity

Table 2
Selected bond lengths (Å) and bond angles (°) for complexes **2b** and **2q**.

2b				**2q**			
Pd–N3	1.99(1)	N3–Pd–N2	177.1(6)	C20–O1	11.194(2)	O1–C20–O2	122.5(2)
Pd–N2	2.01(1)	N3–Pd–Cl2	90.3(4)	O2–C20	1.343(2)	O1–C20–C22	126.1(2)
Pd–Cl2	2.280(4)	N2–Pd–Cl2	91.3(4)	C20–C22	1.484(3)	O2–C20–C22	111.3(2)
Pd–Cl1	2.305(4)	N3–Pd–Cl1	89.3(4)	C17–O2	1.449(2)	C20–O2–17	116.2(2)
C13–N2	1.34(2)	N2–Pd–Cl1	89.1(4)	C11–C17	1.499(2)	O2–C17–C11	107.4(1)
N2–C14	1.38(2)	Cl1–Pd–Cl2	179.7(2)	C11–C16	1.374(3)		
C14–C15	1.36(2)	C13–N2–C14	107(1)	C15–C16	1.382(2)		
C13–N1	1.34(2)	C15–C14–N2	109(2)	C14–C15	1.382(2)		
N1–C15	1.36(2)	N2–C13–N1	108(2)	C7–C14	1.468(2)		
N3–C16	1.35(2)	C13–N1–C15	110(1)	C6–C7	1.432(2)		
N3–C18	1.35(2)	C14–C15–N1	106(2)	C10–C6	1.417(2)		
N4–C18	1.33(2)	C18–N3–C16	105(1)				
N4–C17	1.39(2)	C18–N4–C17	108(2)				
C16–C17	1.32(3)	N4–C18–N3	110(2)				
N4–C19	1.46(2)	C17–C16–N3	112(2)				
N1–C11	1.49(2)	C16–C17–N4	106(2)				



Scheme 2. Synthesis of ferrocenylimidazolate-platinum complexes.



Scheme 3. Reaction of 4-ferrocenylbenzyl-1*H*-imidazole-1-carboxylate (FBIC) with alcohols under various conditions.

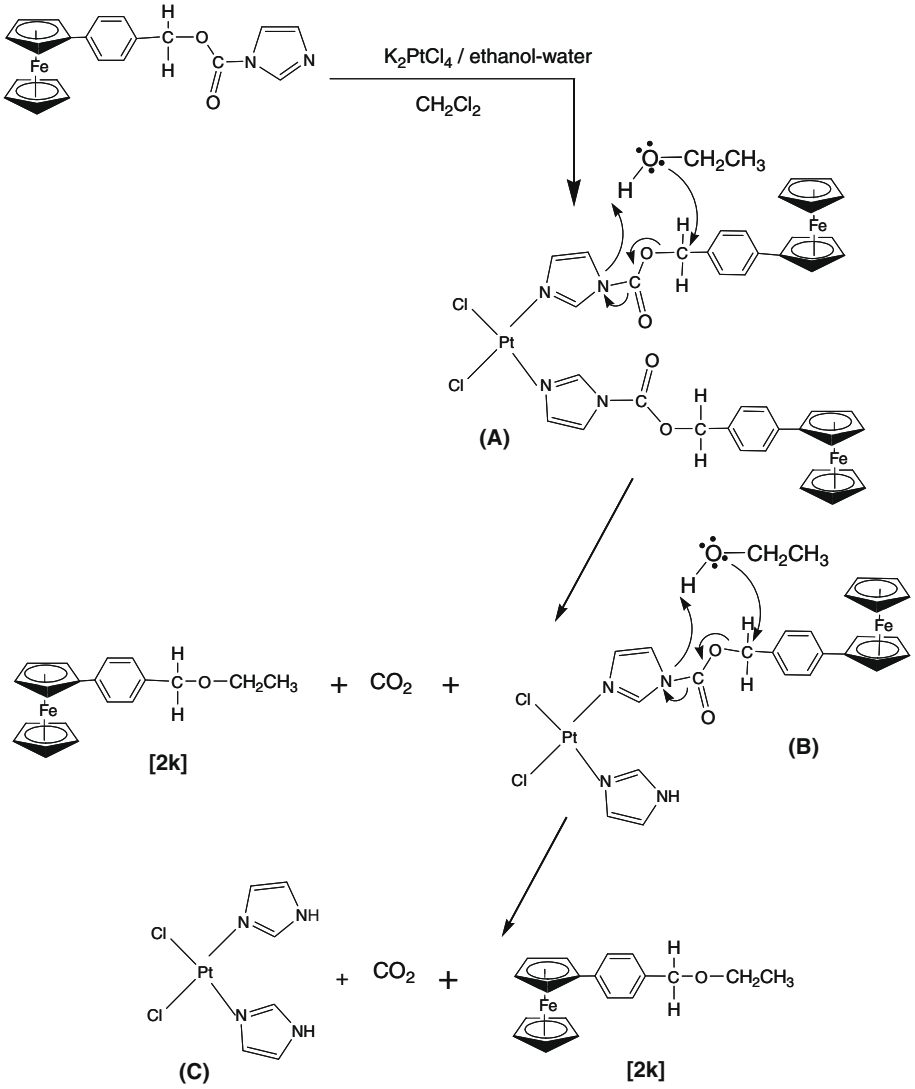
of these two transition metals, which are in the same family, increases down the group. The induction effect of the platinum is strong enough to make nucleophilic attack by the alcohol possible at room temperature, whereas the palladium complex does so only at an elevated temperature.

2.3. Catalyst-free synthesis of ferrocenylbenzyl ethers

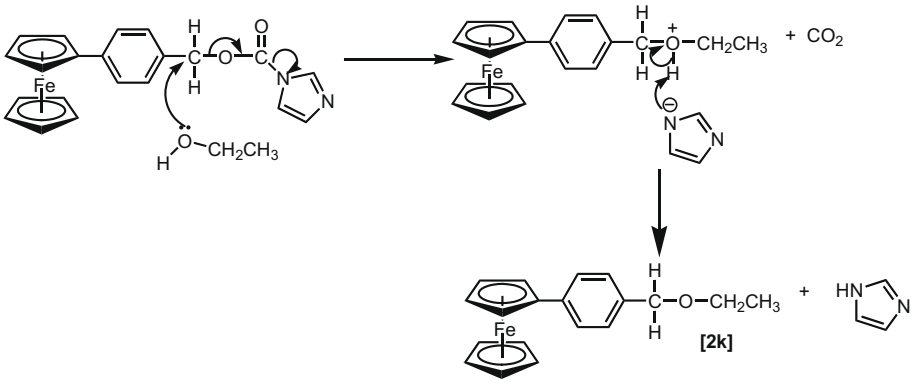
Interestingly, the ether products **2k–2o** were obtained in the absence of a platinum salt by heating 4-ferrocenylbenzyl-1*H*-imidazole-1-carboxylate in a water–alcohol mixture under reflux. A plausible mechanism for the formation of **2k** under these conditions is outlined in Scheme 5. The elevated temperature provides the required energy for bond dissociation and overcomes the energy barrier, hence transforming the reactants to products. This implies that the platinum salt acts as a catalyst by lowering the activation energy; hence the reaction proceeds at room temperature.

2.4. Acid-catalyzed synthesis of ferrocenylbenzyl ethers

Reaction of 4-ferrocenylbenzyl-1*H*-imidazole-1-carboxylate with alcohol in the presence of acid (dilute HCl) at room temperature in the absence of a platinum salt also led to the formation of the ether products **2k–2o**, and a plausible mechanism for this reaction is outlined in Scheme 6. Protonation of the imidazole ring may



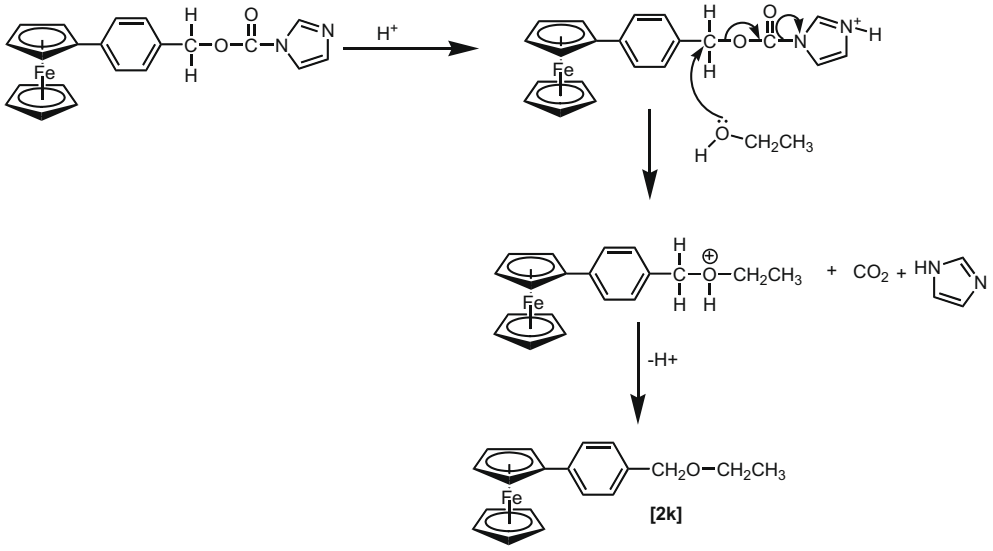
Scheme 4. A plausible mechanism for the synthesis of [4-(ethoxymethyl)phenyl]ferrocene [**2k**].



Scheme 5. Plausible mechanism for the formation of [4-(ethoxymethyl)phenyl]ferrocene.

lead to a lowering of the activation energy, making the reaction possible even at room temperature. The three routes provided the corresponding ethers in modest yields (Table 3). However, from an economic point of view, the platinum catalysed ether synthesis is relatively expensive compared with the other two.

This type of reaction of *N*-carboxybenzyloxyl (Cbz) group with alcohol is unusual but has been reported by Coward and Lock [14]. They reported the unexpected product phenylbenzylether from the reaction of α-(chloromethyl)-*N*-Cbz-pyrrolidine with phenol, and attributed the formation of the product to the intramo-



Scheme 6. Acid-catalyzed synthesis of [4-(ethoxymethyl)phenyl]ferrocene.

Table 3
Yields (%) of ferrocenybenzylethers obtained under different reaction conditions.

Entry	Catalyst-free[a]	Acid-catalyzed[a]	Platinum catalyzed[a]
2k	32	35	48
2l	90	38	67
2m	50	39	41
2n	46	42	40
20	50	46	39

[a] All the yields are based on the starting materials and are isolated ones.

lecular participation by the Cbz group. More recently it was observed that the reaction of alcohols with carbonates favoured the formation of ethers, rather than transesterification [15]. It was argued that alcohols are soft bases while the carbonyl carbon is a hard acid and the adjacent *O*-methyl a soft acid. According to the hard-soft acid–base principle, *O*-methylation is much easier than transesterification. The hard-soft acid–base principle can also be used to explain our observation.

2.5. Synthesis of bis(4-ferrocenylbenzyl)carbonate

The reaction of 4-ferrocenylbenzyl-1*H*-imidazole-1-carboxylate with an aqueous solution of K_2PtCl_4 in the absence of alcohol led to the formation of bis(4-ferrocenylbenzyl)carbonate [**2p**] (Scheme 3). The ether product **2k** and the platinum complex [**A**] (Scheme 3) were not isolated. The product **2p** was not isolated in previous reactions which involved the use of alcohol–water mixture. Reaction of alcohol with **2p** in the absence and in the presence of the platinum salt did not yield the ether product, nor were any new product formed. The carbonate was recovered intact, which led us to conclude that the carbonate **2p** was not an intermediate in the ether formation.

2.6. Synthesis of 4-ferrocenylbenzyl acetate

Another interesting result was obtained when the same reagents and approach in Scheme 3(ii) were used but the solvent system was changed to water–acetone and dichloromethane. Ethyl acetate was introduced as an eluting solvent on the column and upon collection of the fraction, the ethyl acetate solution was left to evaporate slowly to give the red crystalline product 4-ferrocenylbenzylacetate [**2q**]. The ferrocenylimidazolate-platinum complex (**A**) (Scheme 3) was again not isolated.

Acetic acid is postulated to arise from the hydrolysis of ethyl acetate. Acetic acid then possibly reacts with the platinum complexes that form during the reaction, to produce compound **2q**.

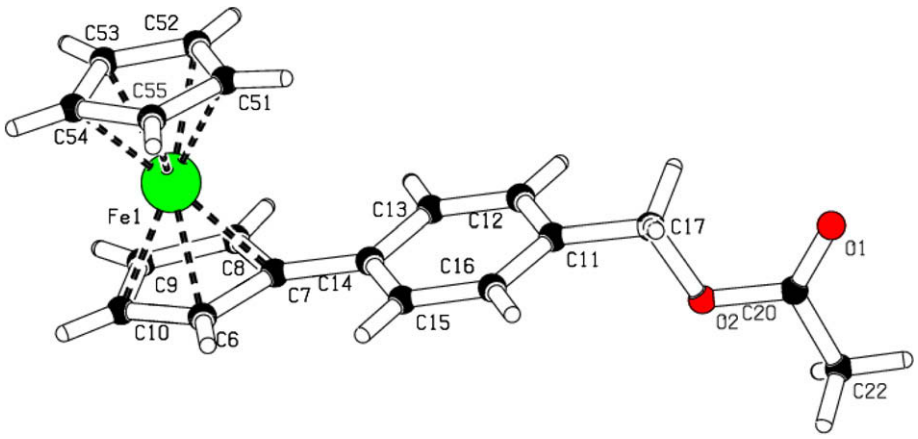


Fig. 2. A perspective view of molecular structure of **2q**.

The crystal structure of compound **2q** is given in Fig. 2 and it was obtained from single crystals grown from a mixture of dichloromethane and hexane. Details of the crystal and structure refinement data are summarized in Table 1. Selected bond lengths and bond angles are listed in Table 2.

The unsubstituted cyclopentadienyl ferrocene ring was disordered over two positions with occupancies of 0.50(2):0.50(2). The disorder was modelled by use of suitable restraints on the cyclopentadienyl rings C7–C10 and C51–C55 during refinement. The methyl protons on C22 were also found to be disordered. The carbon–oxygen double bond (C20–O1) of 1.194(2) Å is the expected bond distance for a typical carbonyl group of an ester. The angles at O1–C20–O2, O1–C20–C22 and O2–C20–C22 are 122.5(2)°, 126.1(2)° and 111.3(2)°, respectively, indicating that carbon C20 is sp^2 hybridized. The torsion angles C10–C9–C8–C7 and C6–C10–C9–C8 are 0.07° and −0.02°, respectively, indicating the planarity of the cyclopentadienyl ferrocene ring.

The dihedral angle between the substituted cyclopentadienyl ferrocene ring and the phenyl ring is 4.53°. The angle between O2–C17–C11 is 107.4(1)°, implying sp3 hybridization for C17. The dihedral angle between the ester functional group plane (O2–C20–O1) and the phenyl plane is 88.59° and indicates that the molecule is kinked at C17. The rest of the structure does not show any unusual characteristics.

3. Conclusion

The synthesis and characterization of ferrocenylimidazolate-palladium(II) and ferrocenylimidazolate-platinum(II) complexes were successful. The use of a biphasic system for their synthesis improved the efficiency of the reactions. However, this approach did not give the expected product for the reaction of 4-ferrocenylbenzyl-1*H*-imidazole-1-carboxylate and K_2PtCl_4, but instead (4-(ethoxymethyl)phenyl)ferrocene [**2k**] was obtained. Similar compounds were synthesized from different alcohols by employing this method. Similar products were also obtained by either heating the reactants under reflux or stirring them in the presence of acid in the absence of the platinum salt. Other products formed by the reaction of 4-ferrocenylbenzyl-1*H*-imidazole-1-carboxylate and K_2PtCl_4 under different reaction conditions were bis(4-ferrocenylbenzyl)carbonate [**2p**] and 4-ferrocenylbenzylacetate [**2q**]. Plausible mechanisms for the formation of **2k, 2p** and **2q** are given. These reactions provide useful synthetic routes for the synthesis of similar compounds.

4. Experimental

Silica gel 50 was used for column chromatography. Melting points were recorded on an Electrothermal IA 900 series digital melting point apparatus and are uncorrected. Infrared spectra were recorded on a DigiLab FTS 3100 Excalibur HE spectrophotometer as KBr disks (for solids) or in chloroform solution. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer as solutions in $CDCl_3$ using TMS as an internal standard. Mass spectra were recorded at the University of the Witwatersrand in Johannesburg. Ferrocene, potassium tetrachloropalladate, potassium tetrachloroplatinate, ferrocene carboxyaldehyde and acetylferrocene were purchased from the Strem Chemical Company USA. *N,N′*-carbonyldiimidazole was purchased from Sigma–Aldrich Chemical Company, Milwaukee, USA. Ferrocenylmethanol and 1-ferrocenylethanol were prepared by the reduction of ferrocene carboxyaldehyde and acetylferrocene with an ethereal solution of lithium aluminium hydride (LAH), while (4-ferrocenylphenyl)methanol was obtained by reduction of 4-ferrocenylbenzoic acid using LAH in dry THF. 4-Ferrocenylbenzoic acid was prepared as described previously [16]. *n*-Bromoalkylferrocenes were synthesized according to the literature [17]. All other common laboratory chemicals were of analytical grade and were used without further purification, unless stated otherwise.

4.1. Synthesis of ligands

4.1.1. General synthetic method for ferrocenylalkylimidazole

A mixture of equimolar amounts of the ferrocenylcarbinol and *N,N′*-carbonyldiimidazole in anhydrous dichloromethane (30 cm^3) was heated under reflux for 1 h. The resulting solution was cooled to room temperature, and diethyl ether (50 cm^3) was added. After stirring for 3 min, the solution was transferred to a separating funnel, where it was washed with phosphoric acid (2 × 50 cm^3). The aqueous phase fractions were then combined and the pH adjusted to 5, using dilute sodium hydroxide. The aqueous solution was then extracted using dichloromethane (3 × 50 cm^3). The dichloromethane extracts were combined, dried over anhydrous sodium sulfate, filtered and the solvent removed under vacuum. The resulting product was subjected to column chromatography on a column of silica gel. Diethyl either was used to elute unreacted starting material and a mixture of ethyl acetate and methanol provided the ferrocenylalkylimidazole.

4.1.1.1. 1-(Ferrocenylmethyl)-1H-imidazole. Ferrocenylmethanol (501 mg, 2.34 mmol), *N,N′*-carbonyldiimidazole (379 mg, 2.34 mmol); Yield: (398 mg, 64%); Yellow crystals; m.p. 66–67 °C, (lit [18] 65 °C); IR (KBr, cm^{-1}): 3095, 1644, 1511, 1463, 1439, 1391, 1336, 1322,1279, 1238, 1221, 1104, 1079, 1040, 1027, 1002, 916, 811, 744, 752, 697, 662, 503, 482; ^1H NMR ($CDCl_3$) 7.50 (1H, s, NCH), 7.06 (1H, s, NCH), 6.94 (1H, s, NCH), 4.88 (2H, s, CH_2), 4.20 (4H, s, C_5H_4); 4.17 (5H, s, C_5H_5); ^{13}C NMR ($CDCl_3$), 137.25, 129.67, 119.36, 83.09, 69.19, 69.16, 68.93, 47.15; *m/z* (EI) 266 (M^+, 100%), 200 (12), 199 (70), 188 (23), 120 (52); (Found: [M^+], 266.050638. $C_{14}H_{14}N_2Fe$ requires [M^+], 266.050668).

4.1.1.2. 1-(1-Ferrocenylethyl)-1H-imidazole. 1-Ferrocenylethanol (500 mg, 2.18 mmol), *N,N′*-carbonyldiimidazole (353 mg, 2.18 mmol); Yield: (415 mg, 68%); Dark oil; IR ($CHCl_3$, cm^{-1}): 3098, 2985, 1634, 1496, 1400, 1221, 1107, 1078, 1001, 938, 819; ^1H NMR ($CDCl_3$): 7.48 (1H, s, NCH), 6.99 (1H, s, NCH), 6.90 (1H, s, NCH), 5.15 (1H, q, *J*, 7.0, CH), 4.19 (2H, t, *J*, 1.8, C_5H_4); 4.14 (5H, s, C_5H_5); 4.07 (2H, t, 1.8, C_5H_4), 1.78 (3H, d, *J*, 7.0 CH_3); ^{13}C NMR ($CDCl_3$): 136.23, 129.29, 117.87, 89.36, 69.28, 68.93, 66.31, 53.22, 22.65; *m/z* (EI) 280 (M^+, 100%), 278 (11), 214 (17), 213 (88), 212 (17), 188 (40), 120 (44); (Found: [M^+], 280.066319. $C_{15}H_{16}N_2Fe$ requires [M^+], 280.066288).

4.1.1.3. 1-(6-Ferrocenylhexyl)-1H-imidazole. Potassium hydroxide powder (128 mg, 2.27 mmol) was added to a solution of imidazole (148 mg, 2.17 mmol) in acetone (2.0 cm^3) and stirring was continued until a homogeneous solution was obtained. The solution was stirred for a further 30 min before 6-bromohexylferrocene (834 mg, 2.39 mmol) in acetone (1.0 cm^3) was introduced dropwise, and stirring was continued for another hour at room temperature. The solution was then filtered and concentrated. The crude product was passed through a column of silica gel. Diethyl ether recovered unreacted 6-bromohexylferrocene (150 mg), while ethyl acetate/methanol (10:1) afforded the product as yellow crystals (591 mg, 81%); m.p. 68–70 °C; IR (KBr, cm^{-1}): 3090, 2932, 2859, 1655, 1508, 1466, 1439, 1234, 1107, 1076, 999, 829, 802, 745, 671, 509, 486; ^1H NMR ($CDCl_3$): 7.47 (1H, s, NCH), 7.07 (1H, s, NCH), 6.91 (1H, s, NCH), 4.09 (5H, s, C_5H_5), 4.04 (4H, m, C_5H_4), 3.91 (2H, t, *J*, 7.1, CH_2), 2.31 (2H, t, *J*, 7.3, CH_2), 1.77 (2H, m, CH_2), 1.48 (2H, m, CH_2), 1.31 (4H, m, 2 × CH_2); ^{13}C NMR ($CDCl_3$): 137.48, 129.76, 119.22, 89.45, 68.87, 68.45, 67.48, 47.42, 31.44,

31.37, 29.89, 29.35, 26.83; *m/z* (EI) 337 (M^++1, 14%), 336 (M^+, 61%), 272 (19), 271 (100), 269 (10), 199 (9), 121 (26). Anal. Calc. for $C_{19}H_{24}N_2Fe$: C, 67.8; H, 7.2; N, 8.3; [M^+], 336.128888. Found: C, 67.5; H, 7.3; N, 8.0; [M^+], 336.128905%.

4.1.1.4. 1-(8-Ferrocenyloctyl)-1H-imidazole. 1-(8-Ferrocenyloctyl)-1*H*-imidazole was synthesized according to the method used in Section 4.1.1.3 Imidazole (148 mg, 2.17 mmol), potassium hydroxide powder (128 mg, 2.27 mmol) and 8-bromooctylferrocene (901 mg, 2.39 mmol) were used. The crude product was obtained and passed through a column of silica gel. Diethyl ether recovered unreacted 8-bromooctylferrocene (57 mg) while ethyl acetate/methanol (10:1) afforded the product as an orange solid (648 mg, 82%); m.p. 27–28 °C; IR ($CHCl_3$, cm^{-1}): 3009, 2932, 2857, 1509, 1466, 1224, 1105, 1078, 1000, 910, 820, 741, 664, 621, 494; ^{1}H NMR ($CDCl_3$): 7.47 (1H, s, NCH), 7.07 (1H, s, NCH), 6.92 (1H, s, NCH), 4.10 (5H, s, C_5H_5), 4.05 (4H, m, C_5H_4), 3.92 (2H, t, *J*, 7.1, CH_2), 2.32 (2H, t, *J*, 7.5, CH_2), 1.79 (2H, m, CH_2), 1.48 (2H, m, CH_2), 1.29 (8H, m, 4 × CH_2); ^{13}C NMR ($CDCl_3$): 137.50, 129.79, 119.17, 89.78, 68.85, 68.44, 67.40, 47,43, 31.48, 29.96, 29.86, 29.71, 29.44, 26.94; *m/z* (EI) 365 (M^++1, 17), 364 (M^+, 65%), 300 (25), 299 (100), 211 (6), 199 (13), 134 (6) 121 (17); (Found: [M^+], 364.160144. $C_{21}H_{28}N_2Fe$ requires M, 364.160188).

4.1.1.5. 1-(11-Ferrocenylundecanyl)-1H-imidazole. 1-(11-Ferrocenylundecanyl)-1*H*-imidazole was synthesized according to the procedure for Section 4.1.1.3. Imidazole (374 mg, 5.49 mmol), potassium hydroxide powder (322 mg, 5.74 mmol) and 11-bromoundecanylferrocene (2.53 g, 6.04 mmol) were used. The crude product obtained was passed through a column of silica gel. Diethyl ether recovered unreacted 11-bromoundecanylferrocene (481 mg) while ethyl acetate/methanol (10:1) afforded the product as a dark brown oil (1.77 g, 77%); IR ($CHCl_3$, cm^{-1}): 3094, 3011, 2929, 2855, 1735, 1509, 1466, 1368, 1283, 1228, 1106, 1077, 1022, 1000, 907, 817, 732, 663, 625, 485; ^{1}H NMR ($CDCl_3$): 7.47 (1H, s, NCH), 7.07 (1H, s, NCH), 6.92 (1H, s, NCH), 4.10 (5H, s, C_5H_5), 4.05 (4H, m, C_5H_4), 3.92 (2H, t, *J*, 7.1, CH_2), 2.32 (2H, t, *J*, 7.5, CH_2), 1.78 (2H, m, CH_2), 1.47 (2H, m, CH_2), 1.28 (14H, m, 7 × CH_2); ^{13}C NMR ($CDCl_3$): 137.47, 129.72, 119.18, 89.94, 69.27, 68.84, 68.43, 67.37, 47.45, 31.51, 31.48, 30.03, 29.97, 29.94, 29.90, 29.82, 29.46, 26.94; *m/z* (EI) 407 (M^++1, 22%), 406 (M^+, 74%), 341 (100), 339 (15), 199 (11), 121 (13). Anal. Calc. for $C_{24}H_{34}N_2Fe$: C, 70.9; H, 8.4; N, 6.9; [M^+], 406.207139. Found: C, 70.8; H, 8.8; N, 6.3; [M^+], 406.207243%.

4.1.1.6. 4-Ferrocenylbenzoylimidazolide. A solution of *N,N′*-carbonyldiimidazole (240 mg, 1.47 mmol) in anhydrous tetrahydrofuran (70 cm^3) was added to a solution of 4-ferrocenylbenzoic acid (450 mg, 1.47 mmol) in anhydrous THF (10 cm^3) and the mixture was stirred for 24 h at room temperature, after which the reaction was stopped and volume was reduced to approximately 10 cm^3 before being passed rapidly through a column of silica gel. Elution with diethyl ether afforded the product as red crystals (412 mg, 92%); m.p. 158–159 °C; IR (KBr, cm^{-1}): 3133, 3094, 2928, 2863, 1682, 1605, 1393, 1285, 1181, 1103, 1065, 1050, 822, 787; ^{1}H NMR ($CDCl_3$): 8.15 (1H, s, NCH), 7.76 (2H, d, *J*, 8.5, ArH), 7.63 (2H, d, *J*, 8.3, ArH), 7.59 (1H, s, NCH), 7.21 (1H, m, NCH), 4.77 (2H, t, *J*, 1.9, C_5H_4), 4.48 (2H, t, *J*, 1.9, C_5H_4), 4.09 (5H, s, C_5H_5); ^{13}C NMR ($CDCl_3$): 166.36, 147.26, 138.59, 131.19, 130.71, 128.92, 126.44, 118.58, 82.80, 70.68, 70.37, 67.47; *m/z* (EI) 357 (M^++1, 25), 356 (M^+, 100%), 262 (11), 261 (49), 168 (15), 145 (10), 140 (29), 139 (47), 120 (16), 56 (14); (Found: [M^+], 356.061224. $C_{20}H_{16}N_2OFe$ requires [M^+], 356.061203).

4.1.1.7. Ferrocenoyl imidazolide. Ferrocenoyl imidazolide was synthesized according to procedure for Section 4.1.1.6. *N,N′*-carbonyldiimidazole (1.50 g, 9.25 mmol) and ferrocenemonocarboxylic acid (2.00 g, 8.70 mmol) afforded the product as red-orange crystals (2.35 g, 95%) m.p. 120 °C (lit [19] 121–122 °C); IR (KBr, cm^{-1}): 3133, 2955, 2864, 1678, 1605, 1393, 1285, 1181, 1103, 1065, 1007, 822, 787, 706, 637; ^{1}H NMR ($CDCl_3$): 8.42 (1H, s, NCH), 7.70 (1H, s, NCH), 7.15 (1H, s, NCH), 4.96 (2H, t, *J*, 1.9, C_5H_4), 4.68 (2H, t, *J*, 1.9, C_5H_4), 4.30 (5H, s, C_5H_5); ^{13}C NMR ($CDCl_3$): 169.43, 137.63, 130.63, 118.04, 73.35, 72.28, 72.06, 71.07; *m/z* (EI) 280 (M^+, 98%), 231 (14), 230 (100), 213 (54), 185 (50), 165 (16), 138 (89), 129 (43), 121 (40). Anal. Calc. for $C_{14}H_{12}N_2OFe$: C, 60.0; H, 4.3; [M^+], 280.029902. Found: C, 59.7; H, 4.3; [M^+], 280.09886%.

4.1.1.8. 4-Ferrocenylbenzyl-1H-imidazole-1-carboxylate. A mixture of 4-ferrocenylbenzyl alcohol (2.00 g, 7.28 mmol) and *N,N′*-carbonyldiimidazole (1.18 g, 7.28 mmol) in anhydrous dichloromethane (50 cm^3) was heated under reflux for about an hour. The mixture was then allowed to cool and then eventually concentrated to about 2 cm^3. The sample was then passed through a column of silica gel using diethyl ether as the eluent. 4-Ferrocenylbenzyl-1*H*-imidazole-1-carboxylate was obtained as orange crystals (2.02 g, 72%); m.p. 125–126 °C; IR (KBr, cm^{-1}) 3140, 2971, 1744, 1530, 1477, 1530, 1477, 1459, 1401, 1323, 1302, 1260, 1168, 1106, 1007, 981, 895, 846, 811, 765, 654, 561, 513, 490; ^{1}H NMR ($CDCl_3$): 8.19 (1H, s, NCH), 7.53 (2H, d, *J*, 8.3, ArH), 7.47 (1H, t, *J*, 1.5, NCH), 7.37 (2H, d, *J*, 8.3, ArH), 7.09 (1H, m, NCH), 5.40 (2H, s, CH_2), 4.67 (2H, t, *J*, 1.9, C_5H_4), 4.36 (2H, t, *J*, 1.9, C_5H_4), 4.07 (5H, s, C_5H_5); ^{13}C NMR ($CDCl_3$): 149.12, 141.19, 137.60, 131.63, 131.08, 129.46, 126.83, 117.60, 84.70, 70.30, 70.07, 69.65, 67.05; *m/z* (EI) 387 (M^++1, 27%), 386 (M^+, 100%), 342 (19), 276 (12), 275 (50), 155 (11), 154 (74), 153 (10), 152 (12), 138 (10), 121 (39). Anal. Calc. for $C_{21}H_{18}N_2O_2Fe$: C, 65.3; H, 4.7; N, 7.2; [M^+], 386.071767. Found: C, 65.2; H, 4.8; N, 7.1; [M^+], 386.071743%.

4.2. Synthesis of Pd and Pt complexes

4.2.1. Ferrocenyl palladium complexes

*4.2.1.1. Dichlorobis[1-(ferrocenylmethyl)-1H-imidazole]palladium [**2a**]: general synthetic procedure.* A solution of $K_2[PdCl_4]$ (100 mg, 0.306 mmol) in a 1:2 ethanol–water (3.0 cm^3) mixture was stirred until a brown homogeneous solution was obtained (~15 min). 1-(Ferrocenymethyl)-1*H*-imidazole (163 mg, 0.61 mmol) in dichloromethane (3.0 cm^3) was then added dropwise. Two layers formed and the top brown aqueous layer, which contained the potassium tetrachloropalladate, lost colour with time. With vigorous stirring a yellow emulsion formed and the reaction was allowed to stir overnight. On completion of the reaction a precipitate was formed, which was filtered off under vacuum. The yellow precipitate was washed once with hexane to give a light yellow powder as the product (199 mg, 92%); m.p. 230–231 °C; IR (KBr, cm^{-1}): 3137, 3091, 2924, 2852, 1646, 1518, 1410, 1274, 1239, 1104, 819, 731, 652, 619, 496, 482, 336, 328, 299; ^{1}H NMR ($CDCl_3$): 8.02 (2H, s, 2 × NCH), 7.37 (2H, s, 2 × NCH), 6.74 (2H, s, 2 × NCH), 4.85 (4H, s, 2 × CH_2), 4.19 (18H, m, 2 × C_5H_5 + 2 × C_5H_4); ^{13}C NMR ($CDCl_3$): 138.68, 130.33, 118.45, 80.99, 69.60, 69.26, 69.20, 48.52; *m/z* (FAB) 708 (M^+, 18%), 307 (16), 289 (14), 266 (15), 199 (18), 179 (6), 153 (100), 136 (86); (Found: [M^+], 707.942927. $C_{28}H_{28}N_4PdCl_2Fe_2$ requires [M^+], 707.942456).

*4.2.1.2. Dichlorobis[1-(1-ferrocenyl)ethyl-1H-imidazole]palladium [**2b**].* Potassium tetrachloropalladate (100 mg, 0.306 mmol) and 1-(1-ferrocenyl)ethyl-1*H*-imidazole (172 mg, 0.613 mmol) provided the product (162 mg, 72%) as yellow crystals; m.p. 100–101 °C; IR (KBr, cm^{-1}): 3146, 2994, 1513, 1412, 1378, 1236, 1110, 1092, 1002, 824, 790, 738, 667, 490; ^{1}H NMR ($CDCl_3$): 8.05 (2H, s, 2 × NCH), 7.35 (2H, s, 2 × NCH), 6.73 (2H, s, 2 × NCH),

5.16 (2H, q, *J*, 6.4, 2 × CH), 4.21 (8H, m, 2 × C_5H_4), 4.18 (10H, s, 2 × C_5H_5), 1.80 (6H, d, *J*, 6.8, 2 × CH_3); ^{13}C NMR ($CDCl_3$): 137.94, 130.07, 117.02, 87.69, 69.39, 68.80, 68.22, 54.83, 22.22; *m*/*z* (FAB) 736 (M^+, 53%), 279 (91), 213 (100), 188 (5), 136 (9), 121 (34). Anal. Calc. for $C_{30}H_{32}N_4PdCl_2Fe_2$: C, 48.9; H, 4.4; N, 7.6; [M^+], 735.973756. Found: C, 48.0; H, 4.3; N, 7.4; [M^+], 735.973891%.

*4.2.1.3. Dichlorobis(4-ferrocenylbenzyl-1H-imidazole-1-carboxylate) palladium [**2c**].* 4-Ferrocenylbenzyl-1*H*-imidazole-1-carboxylate (209 mg, 0.612 mmol) and potassium tetrachloropalladate (100 mg, 0.306 mmol) were used. A light yellow precipitate formed as the reaction proceeded. On completion of the reaction (6 h), a light yellow powder was collected by vacuum filtration as the product (232 mg, 88%); m.p. 150–151 °C; IR (KBr, cm^{-1}): 3161, 3094, 1775, 1613, 1501, 1397, 1242, 1235, 1181, 1077, 1011, 824, 648, 498, 374; ^{1}H NMR ($CDCl_3$) 8.71 (2H, s, 2 × NCH), 7.52 (6H, m, 2 × NCH and 4 × ArH), 7.40 (2H, s, 2 × NCH), 7.35 (4H, d, *J*, 7.9, ArH), 5.42 (4H, s, 2 × CH_2), 4.67 (4H, s, 2 × C_5H_4), 4.36 (4H, s, 2 × C_5H_4), 4.07 (10H, s, 2 × C_5H_5); ^{13}C NMR ($CDCl_3$): 147.43, 141.69, 140.21, 131.37, 130.72, 129.69, 126.92, 117.16, 84.59, 71.62, 70.07, 69.66, 67.07; *m*/*z* (FAB) 949 (M^+, 39%), 446 (5), 385 (30), 319 (20), 274 (40), 154 (100), 136 (89); (Found: [M^+], 948.992448. $C_{42}H_{36}N_4O_4PdCl_2Fe_2$ requires [M^+], 948.992540).

*4.2.1.4. Dichlorobis(4-ferrocenylbenzoyl imidazolide)palladium [**2d**].* 4-Ferrocenylbenzoyl imidazolide (218 mg, 0.613 mmol) and potassium tetrachloropalladate (100 mg, 0.306 mmol) in (1:2) ethanol–water (3.0 cm^3) were used. A precipitate formed after 6 h of stirring under nitrogen. The product was collected *via* vacuum filtration as a red crystalline powder (207 mg, 76%); m.p. 138–140 °C; IR (KBr, cm^{-1}): 3153, 3017, 1718, 1603, 1476, 1420, 1380, 1222, 1204, 1076, 901, 883, 825, 786, 759, 708, 669; ^{1}H NMR ($CDCl_3$): 8.69 (2H, t, *J*, 1.1, 2 × NCH), 7.75 (4H, d, *J*, 8.5, ArH), 7.64 (4H, d, *J*, 8.6, ArH), 7.62 (2H, t, *J*, 0.9, 2 × NCH), 7.54 (2H, t, *J*, 1.7, 2 × NCH), 4.78 (4H, t, *J*, 1.8, 2 × C_5H_4), 4.49 (4H, t, *J*, 1.8, 2 × C_5H_4), 4.10 (10H, s, 2 × C_5H_5); ^{13}C NMR ($CDCl_3$): 164.53, 148.76, 141.11, 131.21, 131.01, 126.89, 126.78, 117.92, 82.41, 70.92, 70.45, 67.62; *m*/*z* (FAB) 889 (M^+, 21%), 356 (19), 307 (13), 289 (11), 260 (10), 154 (100), 136 (88). Anal. Calc. for $C_{40}H_{33}N_4O_2PdCl_2Fe_2$: C, 54.0; H, 3.6; N, 6.3; [M^+], 888.971411. Found: C, 54.6; H, 3.7; N, 5.4; [M^+], 888.971221%.

*4.2.1.5. Dichlorobis(ferrocenoyl imidazolide)palladium [**2e**].* Ferrocenoylimidazolide (172 mg, 0.613 mmol) and potassium tetrachloropalladate (100 mg, 0.306 mmol) were used. A precipitate was observed to form after 6 h of stirring under nitrogen. The product was collected *via* vacuum filtration as an orange powder (162 mg, 72%); m.p. 213–215 °C; IR (KBr, cm^{-1}): 3151, 1692, 1446, 1380, 1291, 1209, 1095, 1080, 824, 757, 650, 503; ^{1}H NMR ($CDCl_3$): 9.20 (2H, s, 2 × NCH), 7.61 (2H, s, 2 × NCH), 7.58 (2H, s, 2 × NCH), 4.97 (4H, s, C_5H_4), 4.77 (4H, s, C_5H_4), 4.42 (10H, s, 2 × C_5H_5); ^{13}C NMR ($CDCl_3$) 168.31, 140.48, 130.57, 117.23, 74.28, 72.27, 71.40, 70.29; *m*/*z* (FAB) 737 (M^+, 10%), 346 (5), 307 (17), 290 (9), 192 (23), 180 (5), 154 (100), 136 (82), 120 (14); (Found: [M^+], 735.901376. $C_{28}H_{24}N_4O_2PdCl_2Fe_2$ requires [M^+], 735.900985.

*4.2.1.6. Dichlorobis[1-(6-ferrocenylhexyl)-1H-imidazole]palladium [**2f**].* A solution of ethanol–water (1:2) (3.0 cm^3) with potassium tetrachloropalladate (100 mg, 0.306 mmol) was introduced into a 25 cm^3 RB flask and allowed to stir. 1-(6-Ferrocenylhexyl)-1*H*-imidazole (206 mg, 0.613 mmol) in dichloromethane (5 cm^3) was added slowly dropwise. The biphasic system was then stirred vigorously for a period of 12 h and then placed in a separating funnel. The organic layer was separated, washed once with water (5.0 cm^3) and dried over anhydrous sodium sulfate. The solution was then filtered and concentrated. The product was precipitated on addition of *n*-pentane (3.0 cm^3) and collected as a light yellow powder by vacuum filtration (221 mg, 85%); m.p. 124–126 °C; IR (KBr, cm^{-1}): 3136, 2930, 2854, 1637, 1578, 1517, 1471, 1436, 1409, 1280, 1238, 1106, 1043, 1024, 1002, 853, 819, 734, 653, 618, 482; ^{1}H NMR ($CDCl_3$): 8.01 (2H, s, 2 × NCH), 7.42 (2H, t, *J*, 1.3, 2 × NCH), 6.79 (2H, t, *J*, 1.5, 2 × NCH), 4.11 (10H, s, 2 × C_5H_5), 4.06 (8H, s, 2 × C_5H_4), 3.89 (4H, t, *J*, 7.2, 2 × CH_2), 2.33 (4H, t, *J*, 7.6, 2 × CH_2), 1.76 (4H, m, 2 × CH_2), 1.50 (4H, m, 2 × CH_2), 1.32 (8H, m, 4 × CH_2); ^{13}C NMR ($CDCl_3$): 139.05, 130.57, 118.71, 89.38, 68.88, 68.48, 67.50, 48.78, 31.30, 30.90, 29.89, 29.25, 26.72; *m*/*z* (FAB) 848 (M^+, 38%), 335 (78), 270 (66), 199 (34), 153 (100), 136 (88), 121 (44). Anal. Calc. for $C_{38}H_{48}N_4PdCl_2Fe_2$: C, 53.7; H, 5.7; N, 6.6; [M^+], 848.098957. Found: C, 53.4; H, 5.6; N, 6.4; [M^+], 848.098847%.

*4.2.1.7. Dichlorobis[1-(8-ferrocenyloctyl)-1H-imidazole]palladium [**2g**].* Dichlorobis[1-(8-ferrocenyloctyl)-1*H*-imidazole]palladium was prepared according to the method used in Section 4.2.1.6. A light yellow powder was obtained as the product when potassium tetrachloropalladate (100 mg, 0.306 mmol) and 1-(8-ferrocenyloctyl)-1*H*-imidazole (223 mg, 0.613 mmol) were used. Yield (217 mg, 78%); m.p. 109–112 °C; IR (KBr, cm^{-1}): 3137, 2926, 2855, 1636, 1516, 1432, 1410, 1274, 1237, 1103, 1047, 1021, 1001, 853, 817, 805, 733, 652, 617, 493; ^{1}H NMR ($CDCl_3$): 8.02 (2H, s, 2 × NCH), 7.43 (2H, s, 2 × NCH), 6.80 (2H, t, *J*, 1.5, 2 × NCH), 4.11 (10H, s, 2 × C_5H_5), 4.06 (8H, m, 2 × C_5H_4), 3.90 (4H, t, *J*, 7.2, 2 × CH_2), 2.33 (4H, t, *J*, 7.7, 2 × CH_2), 1.77 (4H, m, 2 × CH_2), 1.51 (4H, m, 2 × CH_2), 1.31 (16H, m, 8 × CH_2); ^{13}C NMR ($CDCl_3$): 139.06, 130.58, 118.70, 89.81, 68.86, 68.47, 67.41, 48.83, 31.48, 30.94, 29.95, 29.84, 29.62, 29.36, 26.82; *m*/*z* (FAB) 905 (M^+, 36%), 363 (58), 298 (83), 199 (46), 154 (100), 136 (93), 121 (49). Anal. Calc. for $C_{42}H_{56}N_4PdCl_2Fe_2$: C, 55.7; H, 6.2; N, 6.2; [M^+], 905.169382. Found: C, 55.1; H, 6.1; N, 5.8; [M^+], 905.169452%.

*4.2.1.8. Dichlorobis[1-(11-ferrocenylundecanyl)-1H-imidazole]palladium [**2h**].* The complex was prepared according to the method used in Section 4.2.1.6. A light yellow powder was obtained as the product of the reaction of potassium tetrachloropalladate (100 mg, 0.306 mmol) and 1-(11-ferrocenylundecanyl)-1*H*-imidazole (249 mg, 0.613 mmol). Yield (251 mg, 83%); m.p. 91 °C; IR (KBr, cm^{-1}): 3104, 2978, 2933, 1631, 1611, 1518, 1455, 1413, 1381, 1296, 1240, 1105, 1031, 1012, 888, 822, 822, 736, 661, 552, 507, 487; ^{1}H NMR ($CDCl_3$): 8.01 (2H, s, 2 × NCH), 7.42 (2H, s, 2 × NCH), 6.79 (2H, s, 2 × NCH), 4.10 (10H, s, 2 × C_5H_5), 4.06 (8H, m, 2 × C_5H_4), 3.90 (4H, t, *J*, 7.3, 2 × CH_2), 2.32 (4H, t, *J*, 7.7, 2 × CH_2), 1.76 (4H, m, 2 × CH_2), 1.51 (4H, m, 2 × CH_2), 1.29 (28H, m, 14 × CH_2); ^{13}C NMR ($CDCl_3$): 139.04, 130.56, 118.71, 89.99, 68.84, 68.45, 67.37, 48.83, 31.51, 30.96, 30.04, 29.97, 29.93, 29.88, 29.74, 29.39, 26.83; *m*/*z* (FAB) 990 (M^+, 18%), 511 (16), 443 (8), 406 (50), 341 (100), 307 (5), 274 (5), 199 (75), 154 (35), 121 (70); (Found: [M^+], 990.271025. $C_{48}H_{70}N_4PdCl_2Fe_2$ requires [M^+], 990.271108).

4.2.2. Ferrocenyl platinum complexes

*4.2.2.1. Dichlorobis[1-(ferrocenylmethyl)-1H-imidazole]platinum [**2i**].* A solution of 1-(ferrocenylmethyl)-1*H*-imidazole (123 mg, 0.48 mmol) in dichloromethane (3.0 cm^3) was added dropwise to a solution of potassium tetrachloroplatinate (100 mg, 0.24 mmol) in (1:2) ethanol–water (5.0 cm^3). The reaction was stirred at room temperature for 12 h under nitrogen after which an orange precipitate was obtained. The solid was recrystallized from dichloromethane/hexane solution to give yellow crystals (174 mg, 91%); m.p. 70–72 °C; IR (KBr, cm^{-1}): 3105, 2929, 2858, 1648, 1527, 144, 1409, 1391, 1335, 1279, 1239, 1161, 1104, 1079, 1040,

1027, 1001, 926, 812, 741, 696, 663, 622, 504, 482, 313; ^{1}H NMR ($CDCl_3$): 8.47 (2H, s, 2 × NCH), 6.90 (2H, s, 2 × NCH), 6.68 (2H, s, 2 × NCH), 4.93 (4H, s, 2 × CH_2), 4.21 (8H, s, 2 × C_5H_4); 4.18 (10H, s, 2 × C_5H_5); ^{13}C NMR ($CDCl_3$): 138.89, 129.46, 119.32, 81.32, 69.47, 69.36, 48.46; *m*/*z* (FAB) 798 (M^+, 11%), 726 (10), 307 (12), 289 (8), 266 (68), 199 (100), 186 (7), 154 (90), 136 (84), 121 (26); (Found: [M^+], 796.995941. $C_{28}H_{28}N_4Fe_2Cl_2Pt$ requires [M^+], 796.996124).

4.2.2.2. Dichlorobis[1-(1-ferrocenyl)ethyl-1H-imidazole]platinum ***[2j]***. A solution of 1-(1-ferrocenyl)ethyl-1*H*-imidazole (135 mg, 0.48 mmol) in dichloromethane (3.0 cm^3) was added dropwise to a solution of potassium tetrachloroplatinate (100 mg, 0.24 mmol) in (1:2) ethanol–water (5.0 cm^3). The reaction was stirred at room temperature for 24 h under nitrogen. The organic layer was separated, washed once with water (3.0 cm^3), and was dried over anhydrous sodium sulfate, filtered and concentrated. Pentane was used to precipitate out the product as a dark brown solid, which was collected by vacuum filtration. The solid was recrystallized from a dichloromethane/hexane solution to give brown crystals (123 mg, 62%); m.p. 110–111 °C; IR (KBr, cm^{-1}): 3103, 2978, 2929, 1516, 1450, 1411, 1377, 1304, 1239, 1109, 1001, 907, 821, 3737, 652, 506, 486, 332; ^{1}H NMR ($CDCl_3$): 8.36 (2H, s, 2 × NCH), 6.80 (2H, s, 2 × NCH), 6.72 (2H, s, 2 × NCH), 5.32 (2H, q, *J*, 4.3, 2 × CH), 4.21 (4H, m, C_5H_4), 4.17 (10H, s, 2 × C_5H_5), 4.11 (4H, m, C_5H_4), 1.77 (6H, d, *J*, 6.9, 2 × CH_3); ^{13}C NMR ($CDCl_3$): 138.20, 129.30, 117.58, 87.45, 69.50, 68.72, 66.23, 54.85, 22.13; *m*/*z* (FAB) 826 (M^+, 20%), 365 (17), 281 (18), 230 (23) 213 (100), 191 (8), 136 (70), 121 (21); (Found: [M^+], 826.042891. $C_{30}H_{33}N_4Fe_2Cl_2Pt$ requires [M^+], 826.041664).

4.3. Synthesis of ferrocenylbenzylethers

4.3.1. General procedure (method a)

4-Ferrocenylbenzyl-1*H*-imidazole-1-carboxylate (100 mg, 0.29 mmol) and a solution of alcohol–water (1:1) (6 cm^3) were introduced into a 25 cm^3 RB flask and heated under reflux with stirring overnight. The reaction was cooled and extracted with dichloromethane (3 × 10 cm^3). The organic extracts were dried over anhydrous sodium sulfate, concentrated and subjected to column chromatography on silica gel. Elution with hexane/diethyl ether (3:1) and removal of solvent under vacuum afforded the corresponding ether product.

4.3.1.1. (4-(Methoxymethyl)phenyl)ferrocene ***[2l]***. Methanol and 4-ferrocenylbenzyl-1*H*-imidazole-1-carboxylate; yellow solid, yield (80 mg, 90%); m.p. 90–92 °C; IR (KBr, cm^{-1}): 3091, 2922, 2808, 1749, 1528, 1444, 1385, 1280, 1198, 1111, 1029, 1001, 970, 818; ^{1}H NMR($CDCl_3$): 7.44 (2H, d, *J*, 8.0, ArH), 7.27 (2H, d, *J*, 7.4, ArH), 4.68 (2H, s, C_5H_4), 4.46 (2H, s, CH_2), 4.35 (2H, s, C_5H_4), 4.07 (5H, s, C_5H_5), 3.44 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$): 139. 12, 136.17, 128.28, 126.56, 77.63 75.04, 70.28, 69.62, 67.09, 58.57; *m*/*z* (FAB) 306 (M^+ 100%), 275 (30).

4.3.1.2. (4-(Ethoxymethyl)phenyl)ferrocene ***[2k]***. Ethanol and 4-ferrocenylbenzyl-1*H*-imidazole-1-carboxylate; yellow solid, yield (30 mg, 32%); m.p. 58–59 °C; IR (KBr, cm^{-1}): 2971, 2858, 1647, 1530, 1458, 1376, 1278, 1100, 1029, 886, 817; ^{1}H NMR ($CDCl_3$) 7.47 (2H, d, *J*, 8.0, ArH),7.31 (2H, d, *J*, 7.0, ArH), 4.65 (2H, s, C_5H_4), 4.50 (2H,s, CH_2), 4.31 (2H, s, C_5H_4), 4.05 (5H, s, C_5H_5), 3.59 (2H, q, *J*, 7.0, CH_2), 1.29 (3H, t, *J*, 7.0, CH_3); ^{13}C NMR ($CDCl_3$)138.95, 136.52, 128.28, 126.65, 85.66, 73.05, 69.99, 69.27, 66.90, 66.17, 15.68; *m*/*z* (EI) 322 (M^++2, 5%), 321 (M^++1, 36%), 320 (M^+, 100%), 276, (8), 275 (29), 211 (6), 155 (8), 154 (28), 137 (6), 128 (5), 122 (5), 121 (17), 115 (6), 56 (5), 29 (8), 28 (10); (Found: [M^+], 320.086344. $C_{19}H_{20}OFe$ requires [M^+], 320.086355).

4.3.1.3. (4-(Propoxymethyl)phenyl)ferrocene ***[2m]***. Propan-1-ol and 4-ferrocenylbenzyl-1*H*-imidazole-1-carboxylate; yellow solid, yield (48.3 mg, 50%); m.p. 41–42 °C; IR (KBr, cm^{-1}) 2922, 2852, 1528, 1457, 1365, 1277, 1104, 1029, 999, 886, 817; ^{1}H NMR ($CDCl_3$) 7.49 (2H, d, *J*, 8.2, ArH), 7.30 (2H, d, *J*, 8.2, ArH), 4.67 (2H, t, *J*, 1.6, C_5H_4), 4.51(2H, s, CH_2), 4.33 (2H, t, *J*, 1.8, C_5H_4), 3.49 (2H, t, *J*, 6.7, CH_2), 1.69 (2H, m, CH_2), 0.99 (3H, t, *J*, 7.4, CH_3); ^{13}C NMR ($CDCl_3$): 138.89, 136.67, 128.25, 126.52, 85.71, 73.16, 72.59, 70.06, 69.88, 66.91, 23.41, 11.11; *m*/*z* (FAB) 335(M^++1,)335, 334 (M^+ 100%), 275 (40), 262 (15).

4.3.1.4. (4-(Butoxymethyl)phenyl)ferrocene ***[2n]***. Butan-1-ol and 4-ferrocenylbenzyl-1*H*-imidazole-1-carboxylate; yellow oil, yield (48.3 mg, 46%); IR ($CHCl_3$, cm^{-1}): 2922, 2852, 1528, 1457, 1365, 1277, 1104, 1029, 999, 886, 817; ^{1}H NMR ($CDCl_3$): 7.47 (2H, d, *J*, 6.6, ArH), 7.29 (2H, d, *J*, 7.7, ArH), 4.66 (2H, t, *J*, 1.8, C_5H_4), 4.50 (2H, s, CH_2), 4.33(2H, t, *J*, 1.8, C_5H_4), 4.06 (5H, s, C_5H_5), 3.53(2H, t, *J*, 6.7, CH_2), 1.65 (2H, m, CH_2), 1.42(2H, m, CH_2), 0.96(3H, t, *J*, 7.3, CH_3); ^{13}C NMR ($CDCl_3$): 138.88, 136.68, 128.21, 126.50, 85.69, 73.19, 70.00, 69.28, 66.90, 32.29, 19.82,14.39; *m*/*z* (FAB) 348 (M^+, 100%), 275 (50), 262 (10).

4.3.1.5. (4-(4-Ferrocenylbenzyloxymethyl)phenyl)ferrocene ***[2o]***. 4-Ferrocenylbenzylalcohol (100 mg, 0.34 mmol) in THF (3 cm^3) and 4-ferrocenylbenzyl-1*H*-imidazole-1-carboxylate (131.65 mg, 0.34 mmol); (96.7 mg, 50%); m.p. 87–89 °C; IR (KBr, cm^{-1}): 3097, 2925, 1611, 1527, 1423, 1267, 1106, 1083, 1038, 887, 821, 743,670; ^{1}H NMR ($CDCl_3$): 7.49 (4H, d, *J*, 8.2, ArH), 7.28 (4H, d, *J*, 8.2, ArH), 4.66 (4H, t, *J*, 1.8, C_5H_4), 4.61 (4H, s, CH_2), 4.35 (4H, t, *J*, 1.8 C_5H_4), 4.07 (5H, s, C_5H_5); ^{13}C NMR ($CDCl_3$): 140.21, 135.26, 129.12, 126.69, 85.03, 70.07, 69.54, 67.011, 65.74; *m*/*z* (FAB) 566(M^+, 4%), 292 (35), 275 (50).

4.3.2. General procedure (method b)

A solution of alcohol–water (1:1) (3.0 cm^3) with potassium tetrachloroplatinate (100 mg, 0.24 mmol) was introduced into a 25 cm^3 RB flask and the mixture was stirred to give a brown homogenous solution (~15 min). 4-Ferrocenylbenzyl-1*H*-imidazole-1-carboxylate (164 mg, 0.48 mmol) in dichloromethane (3.0 cm^3) was then introduced dropwise. The reaction mixture was stirred overnight. The mixture was extracted with dichloromethane (3 × 5 cm^3) and the extracts were combined, dried over anhydrous sodium sulfate, and filtered, concentrated and subjected to chromatography on silica gel. Elution with hexane/ether (4:1) and removal of solvent under vacuum provided the corresponding ether which was characterized according to Section 4.3.1.

4.3.2.1. (4-(Methoxymethyl)phenyl)ferrocene ***[2l]***. Methanol and 4-ferrocenylbenzyl-1*H*-imidazole-1-carboxylate; yellow solid, yield (60 mg, 67%).

4.3.2.2. (4-(Ethoxymethyl)phenyl)ferrocene ***[2k]***. Ethanol and 4-ferrocenylbenzyl-1*H*-imidazole-1-carboxylate; yellow solid, yield (45 mg, 48%).

4.3.2.3. (4-(Propoxymethyl)phenyl)ferrocene ***[2m]***. Propan-1-ol and 4-ferrocenylbenzyl-1*H*-imidazole-1-carboxylate; yellow solid, yield (40 mg, 41%).

4.3.2.4. (4-(Butoxymethyl)phenyl)ferrocene ***[2n]***. Butan-1-ol and 4-ferrocenylbenzyl-1*H*-imidazole-1-carboxylate; yellow oil, yield (43 mg, 40%).

4.3.2.5. (4-(4-Ferrocenylbenzyloxymethyl)phenyl)ferrocene ***[2o]***. 4-Ferrocenylbenzylalcohol (100 mg, 0.34 mmol) and 4-ferrocenylbenzyl-1*H*-imidazole-1-carboxylate (131.65 mg, 0.34 mmol) gave

(4-(4-ferrocenylbenzyloxymethyl)phenyl)ferrocene as yellow solid (75 mg, 39%). Characterization as in Section 4.3.1.5.

4.3.3. General procedure (c)

4-Ferrocenylbenzyl-1*H*-imidazole-1-carboxylate (100 mg, 0.29 mmol), ethanol (3 cm^3) and 3 M HCl (3 cm^3) were introduced into a 25 cm^3 RB flask and stirred overnight. The reaction mixture was extracted with dichloromethane (3 × 10 cm^3). The extracts were combined and dried over anhydrous sodium sulfate, concentrated and subjected to column chromatography on silica gel. Elution with hexane/diethyl ether (4:1) and removal of solvent under vacuum afforded the corresponding ether, which was characterized according to Section 4.3.1.

*4.3.3.1. (4-(Methoxymethyl)phenyl)ferrocene [**2l**].* 4-Ferrocenylbenzyl-1*H*-imidazole-1-carboxylate, methanol and HCl afforded (4-(methoxymethyl)phenyl)ferrocene (35 mg, 38%).

*4.3.3.2. (4-(Ethoxymethyl)phenyl)ferrocene [**2k**].* 4-Ferrocenylbenzyl-1*H*-imidazole-1-carboxylate, ethanol and HCl afforded (4-(ethoxymethyl)phenyl)ferrocene (33 mg, 35%).

*4.3.3.3. (4-(Propoxymethyl)phenyl)ferrocene [**2m**].* 4-Ferrocenylbenzyl-1*H*-imidazole-1-carboxylate, propan-1-ol and HCl afforded (4-(propoxymethyl)phenyl)ferrocene (40 mg, 39%).

*4.3.3.4. (4-(Butoxymethyl)phenyl)ferrocene [**2n**].* 4-Ferrocenylbenzyl-1*H*-imidazole-1-carboxylate, butan-1-ol and HCl afforded (4-(butoxymethyl)phenyl)ferrocene (39.1 mg, 42%).

*4.3.3.5. (4-(4-Ferrocenylbenzyloxymethyl)phenyl)ferrocene [**2o**].* 4-Ferrocenylbenzylalcohol (100 mg, 0.34 mmol) in THF (3 cm^3), 4-ferrocenylbenzyl-1*H*-imidazole-1-carboxylate (131 mg, 0.34 mmol) and HCl afforded (4-(4-ferrocenylbenzyloxymethyl)-phenyl)ferrocene as a yellow solid (89 mg, 46%).

4.3.4. (4-(Ethoxymethyl)phenyl)ferrocene (method d)

A solution of dichlorobis(4-ferrocenylbenzyl-1*H*-imidazole-1-carboxylate)palladium (90 mg, 0.09 mg) was suspended in an ethanol–water (2 cm^3) (1:1 v/v) mixture and heated under reflux overnight. The resulting yellow solution with some precipitate was filtered and the filtrate extracted with dichloromethane (3 × 5 cm^3). The organic extracts were combined and dried over magnesium sulfate, filtered, concentrated and subjected to chromatography on silica gel. Elution with hexane/ether (4:1) and removal of solvent under vacuum provided the product (4-(ethoxymethyl)phenyl)ferrocene (20 mg, 35%). The compound was characterized as in Section 4.2.1.2.

*4.4. Synthesis and reactions of bis(4-ferrocenylbenzyl)carbonate [**2p**]*

4.4.1. Synthesis of bis(4-ferrocenylbenzyl)carbonate

A solution of 4-ferrocenylbenzyl-1*H*-imidazole-1-carboxylate (100 mg, 0.293 mmol) in dichloromethane (3.0 cm^3) was added to an aqueous solution (3.0 cm^3) of potassium tetrachloroplatinate (53.7 mg, 0.293 mmol), and the mixture was stirred at room temperature for 72 h. The reaction mixture was separated, and the organic layer was washed with water (2 × 5 cm^3), dried over magnesium sulfate, concentrated and subjected to column chromatography on silica gel. Upon elution, two fractions were obtained: the second fraction (eluted with ether) contained 4-ferrocenylbenzyl alcohol (5 mg, 6%), while the first fraction, eluted by hexane/ether (1:1), gave the product bis(4-ferrocenylbenzyl)carbonate as a yellow solid (66.1 mg, 83%); m.p. 158–159 °C; IR (KBr, cm^{-1}): 3096, 2956, 1745, 1614, 1523, 1446, 1391, 1244, 1105, 937, 840, 813; ^{1}H NMR ($CDCl_3$): 7.48 (4H, d, *J*, 8.2, ArH), 7.33 (4H, d, *J*, 8.2, ArH), 5.18 (4H, s, CH_2), 4.66 (4H, t, *J*, 1.7, C_5H_4), 4.34(4H, t, *J*, 1.8, C_5H_4), 4.05(10H, s, C_5H_5); ^{13}C NMR ($CDCl_3$): 5.58, 140.30, 132.94, 129.08, 126.78, 85.13, 70.15, 70.08, 69.52, 67.01; *m*/*z* (FAB) 610 (M^+, 10%), 275 (32).

4.4.2. Reactions of bis(4-ferrocenylbenzyl)carbonate with 4-chlorobenzyl alcohol

(a) Bis(4-ferrocenylbenzyl)carbonate (50 mg, 0.08 mmol) and 4-chlorobenzyl alcohol (23.36 mg 0.16 mmol) were dissolved in dichloromethane (5 cm^3), and the mixture was stirred at room temperature for 48 h. The reaction was monitored on TLC, with no new products being observed. The reaction mixture was concentrated and subjected to column chromatography on silica gel. Two fractions were obtained: fraction one eluted with hexane/ether (1:1) afforded the unreacted bis(4-ferrocenylbenzyl)carbonate, while the second fraction eluted with ether gave the unreacted 4-chlorobenzyl alcohol.

(b) A mixture of bis(4-ferrocenylbenzyl)carbonate (50 mg, 0.08 mmol) and 4-chlorobenzyl alcohol (23.36 mg 0.16 mmol) in dichloromethane (5 cm^3) and a solution of water (3 cm^3) containing potassium tetrachloroplatinate (33.2 mg, 0.08 mmol) were used. The reaction mixture was stirred at room temperature and monitored on TLC. After 48 h, no new products were observed. The reaction mixture was separated and the organic layer washed with water, dried over magnesium sulfate, concentrated and subject to column chromatography on silica gel. Two fractions were obtained: fraction one eluted with hexane/ether (1:1) afforded the unreacted bis(4-ferrocenylbenzyl)carbonate, while the second fraction eluted with ether gave the unreacted 4-chlorobenzylalcohol.

*4.5. Synthesis of 4-ferrocenylbenzylacetate [**2q**]*

Potassium tetrachloroplatinate (100 mg, 0.24 mmol) in a mixture of water–acetone (1:2) (5.0 cm^3) was introduced into a 25 cm^3 RB flask and was allowed to stir for about 15 min. A solution of 4-ferrocenylbenzyl-1*H*-imidazole-1-carboxylate (164 mg, 0.48 mmol) in dichloromethane (3.0 cm^3) was then added dropwise. The reaction mixture was vigorous shaken and then allowed to stir overnight. The organic layer was separated, dried over anhydrous sodium sulfate and filtered. The filtrate was concentrated and subjected to column chromatography on silica gel. An orange band was collected when ethyl acetate was used as the eluting solvent. Upon collection of this band, the ethyl acetate solution was left to evaporate slowly to give a red crystalline solid, identified as 4-ferrocenylbenzylacetate (31 mg, 19%); m.p. 97–98 °C; IR (KBr, cm^{-1}): 3101, 3025, 2954, 2893, 1731, 1616, 1532, 1466, 1358, 1250, 1206, 1117, 1104, 1083, 829, 663, 611, 543, 514, 487, 377; ^{1}H NMR ($CDCl_3$): 7.49 (2H, d, *J*, 8.2, ArH), 7.30 (2H, d, *J*, 8.2, ArH), 5.11 (2H, s, CH_2), 4.67 (2H, t, *J*, 1.8, C_5H_4), 4.35 (2H, t, *J*, 1.8, C_5H_4), 4.07 (5H, s, C_5H_5), 2.15 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$):171.45, 139.96, 133.72, 128.94, 126.68, 85.29, 70.09, 69.51, 67.03, 66.72; *m*/*z* (FAB) 334 (M^+, 100%), 275 (25), 154 (24), 136, (8), 121 (7), 115 (6). Anal. Calc. for $C_{19}H_{18}O_2Fe$: C, 68.3; H, 5.4; [M^+], 334.065619. Found: C, 68.3; H, 5.4; [M^+], 334.0655722%.

4.6. X-ray crystallography

X-ray diffraction data for dichlorobis[1-(1-ferrocenyl)ethyl-1*H*-imidazole]palladium [**2b**] and 4-ferrocenylbenzyl acetate [**2q**] were collected on a Bruker Smart 1K CCD diffractometer with graphite-monochromated Mo Kα radiation. The collection method involved ω-scan of width 0.3°. Data reduction was carried out by

the program SAINT+, Version 6.02 [20]. Multi-scan absorption corrections were made with the program SADABS [21]. The structure was solved by direct methods using SHELXS-97 [22]. Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full-matrix least-squares calculation based on F^2 using SHELXL-97 [22]. Hydrogen atoms were first located in the difference map, then positioned geometrically and allowed to ride on their respective parent atoms. The general purpose crystallographic tool PLATON [23] was used for structure analysis, and ORTEP3 [24] was used for diagram generation.

Supplementary material

CCDC 705391 and 705392 contain the supplementary crystallographic data for **2b** and **2q**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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