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Palladium(II) complexes containing mono-, bi- and tridentate carbene ligands. Synthesis, characterisation and application as catalysts in C–C coupling reactions

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Abstract

Palladium complexes of functionalised heterocyclic carbene complexes have been synthesised. Treatment of imidazolium salts with Ag_2O yields Ag^I(carbene)$_2$ complexes, which act as carbene transfer agents when reacted with palladium salts. In this manner, [Pd(Me)(1-(2-ethylpyridyl)-3-methylimidazolin-2-ylidene)Cl]$_2$ (**4a**) and Pd(Me)(1-benzyl-3-methylimidazolin-2-ylidene)$_2$Cl (**4c**) have been prepared from PdMeCl(cod) (cod = 1,5-cyclooctadiene) and the appropriate silver complex. Similarly, the reaction of a Ag(carbene)$_2$ complex with $PdCl_2(MeCN)_2$ gives Pd(1-benzyl-3-methylimidazolin-2-ylidene)$_2$Cl$_2$ (**4b**). The tridentate carbene complex [Pd(Me)(1,3-di(2-picolyl)imidazolin-2-ylidene)]BF_4 (**6a**) is synthesised via the in situ reaction of the imidazolium salt with Ag_2O, followed by PdMeCl(cod) and $AgBF_4$, whilst [PdCl{1,3-bis(diisopropyl-2-ethylamino)imidazolin-2-ylidene}]BF_4 (**6c**) is synthesised in an identical manner from $PdCl_2(MeCN)_2$. The chelated complexes [1,1′-dimethyl-3,3′-(1,2-xylylene)diimidazolin-2,2′-diylidene]Pd(II) dibromide (**5a**), [1,1′-dimethyl-3,3′-(1,3-xylylene)diimidazolin-2,2′-diylidene]Pd(II) dibromide (**5b**) and Pd(imidazoliophane)Br_2 (**5c**) have been synthesised via the reaction of the appropriate imidazolium salt with $Pd(OAc)_2$. X-ray crystal structures of the imidazolium salt, 1,3-di(2-picolyl)imidazolium chloride (**1f**) and the complex [Pd(Me)(tetramethylimidazolin-2-ylidene)$_2$Cl] (2) are reported. Complex **2** shows square planar coordination with the two carbene ligands *trans* to each other. The carbene ligands are inclined at 65.3° to the coordination plane. Several complexes proved to be highly stable and efficient catalysts for intermolecular Heck and Suzuki coupling reactions, giving turnover numbers of up to 980 000 (Heck) and 177 500 (Suzuki).

Keywords: Palladium(II) complexes; Carbene transfer agents; Heterocyclic carbene complexes

1. Introduction

Transition metal complexes bearing N-heterocyclic carbene (NHC) ligands have been known for many years [1–3], however the true potential of these complexes as catalysts in homogeneous coupling processes has only been realised in the past 5 years [4,5]. This resurgence of interest was stimulated by Arduengo et al., who, in 1991, isolated and characterised the first stable imidazol-2-ylidene [6]. Since that time there has been much interest in free heterocyclic carbenes [7–13], transition metal carbene complexes [14–24], and the application of these complexes in homogeneous catalysis [5,25–27].

Carbene complexes of late transition metals have been applied in many types of homogeneous catalytic reactions, including olefin polymerisation by Ru-based catalysts [28], hydrosilylation by Rh–carbene complexes [29], and the Pd-catalysed copolymerisation of

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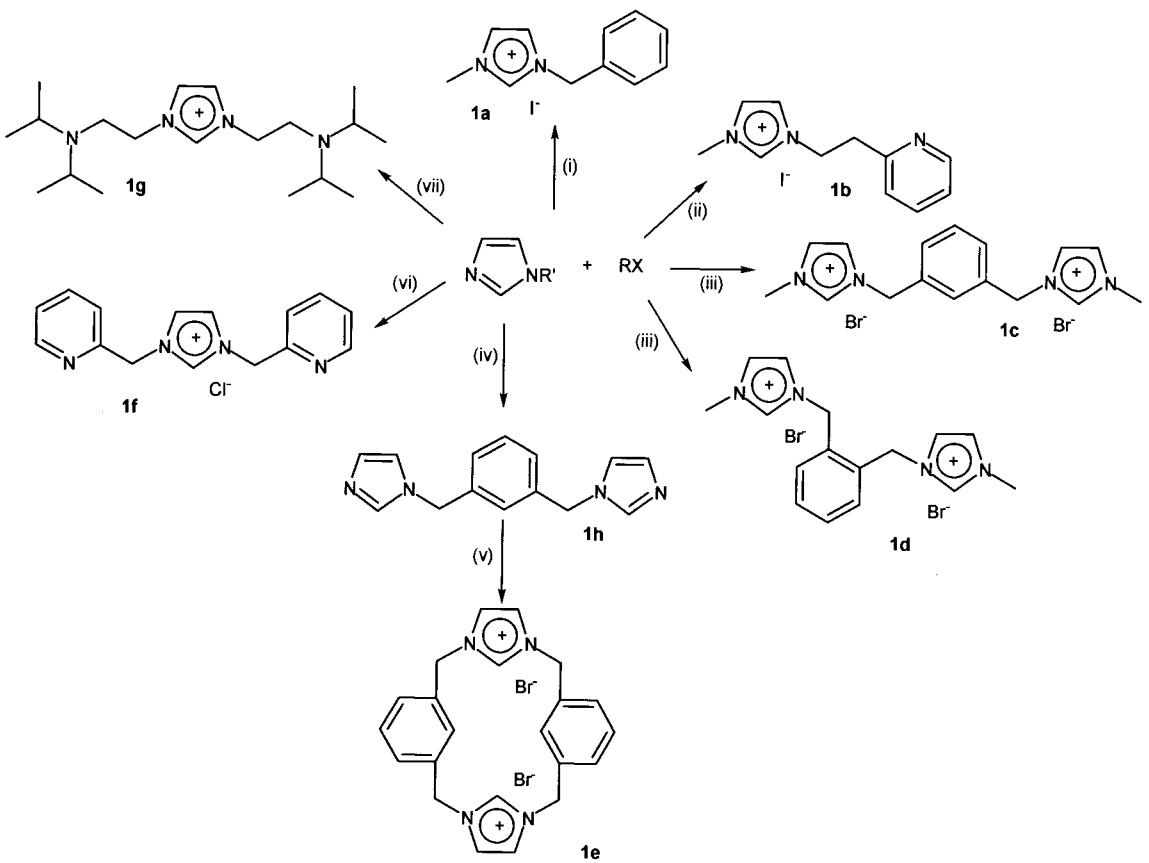
carbon monoxide and ethene [30]. Perhaps the most widespread and successful application of carbene complexes has come in palladium-catalysed carbon–carbon coupling reactions, most notably the Heck and Suzuki type reactions [4,31–34]. Whilst these types of reactions have traditionally been carried out using phosphine based systems [35], complexes of NHCs have been shown to exhibit a number of desirable properties not possessed by the former. The most notable of these include air stability of complexes [36], and the observation that carbene ligands do not readily dissociate from the metal center [4], meaning that an excess of ligand is unnecessary [29] and making immobilisation techniques feasible [18,37].

Following our first reports on the general synthesis and catalytic performance of methylpalladium carbene complexes [19,31], we have recently shown that hemilabile ligands incorporating NHCs as the strong donor group may be applied very successfully in Heck, Suzuki and Sonogashira coupling reactions [38]. These findings have very recently been confirmed by Danopoulos and co-workers [39]. In our original studies we investigated the coordination of the carbene, 3-methyl-1-(2-picolyl)imidazolin-2-ylidene and the complexes formed therefrom as catalysts in coupling processes. As part of our ongoing research in this area we now wish to report the synthesis of a number of new Pd complexes incorporating novel mono-, bi- and tri-dentate carbene ligands. These latest chelating carbene ligands incorporate pyridine and amine donors and also variously linked carbene donors. The complexes have been tested in a number of carbon–carbon coupling reactions, and several have proved to be highly active and very stable catalysts.

2. Results and discussion

2.1. Synthesis of ligand precursors

Functionalised imidazolium salts were prepared via the reaction of an alkyl or benzyl halide with the appropriately substituted imidazole, as outlined in Scheme 1. Whilst compounds analogous to **1e**, and indeed **1e** itself, have previously been reported [40–43], experimental details provided therein are sketchy and the synthesis could not be repeated. Consequently, imidazolium salt **1e** was synthesised via the reaction of potassium imidazolide with α,α′-dibromo-*m*-xylene, to give 1-[3-(1*H*-imidazol-1-ylmethyl)benzyl]-1*H*-imida-



Scheme 1. (i) R′ = Me, NaI, acetone, 18 h; (ii) R′ = Me, NaI, acetone, 50°C, 29 h; (iii) R′ = Me, THF, reflux, 30 min; (iv) R′ = K, THF, 18 h; (v) acetone, reflux, 30 min; (vi) R′ = H, $NaHC0_3$, EtOH, reflux, 2 days; (vii) R′ = H, $NaHC0_3$, MeOH, reflux, 18 h.

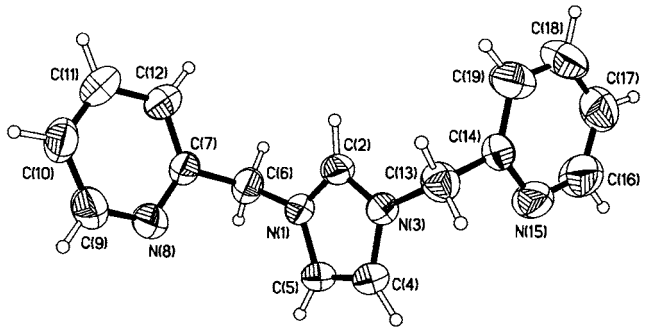


Fig. 1. The molecular structure of the cation in **1f** (70% probability ellipsoids).

Table 1
Selected bond lengths (Å) and bond angles (°) in (**1f**) [a]

Bond lengths			
C(2)–N(l)	1.321(3)	N(3)–C(4)	1.390(3)
C(2)–N(3)	1.320(3)	C(4)–C(5)	1.353(3)
N(l)–C(5)	1.386(3)		
Bond angles			
N(l)–C(2)–N(3)	108.8(2)	C(2)–N(l)–C(6)	125.0(2)
C(2)–N(1,3)–C(5,4)	108.9(2)	C(5)–N(l)–C(6)	126.0(2)
N(l)–C(5)–C(4)	106.8(2)	C(2)–N(3)–C(13)	125.4(2)
N(3)–C(4)–C(5)	106.5(2)	C(4)–N(3)–C(13)	125.6(2)

[a] Estimated S.D.s given in parentheses, see Fig. 1 for atomic numbering.

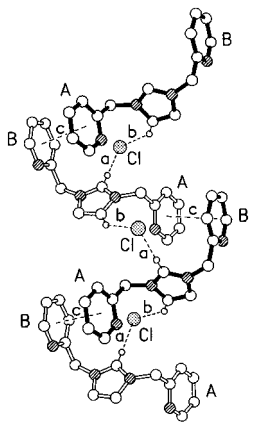


Fig. 2. Part of one of the head-to-tail linked helical chains present in the structure of **1f**. The intrachain hydrogen bonding geometries are [C···Cl], [H···Cl] (Å), [C–H···Cl] (°); (a) 3.39, 2.44, 178; (b) 3.46, 2.66, 142. The centroid···centroid and mean interplanar separations (c) are 3.79 and 3.66 Å, respectively. Adjacent helices are linked by B···A and A···B π-π interactions with centroid···centroid and mean interplanar separations of 3.99 and 3.77 Å, respectively. The interchain C–H···CI geometry is [C···Cl], [H···Cl] 3.45, 2.70 Å and [C–H···Cl] 136°.

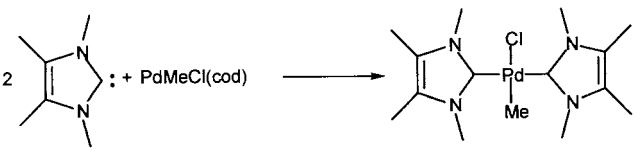
zole (**1h**), followed by further reaction with α,α′-dibromo-*m*-xylene to give the desired ligand.

A single crystal X-ray structure was obtained for the imidazolium salt **1f** and shows the molecule to have non-crystallographic C_2 symmetry about an axis passing through C(2) and bisecting the C(4)–C(5) bond of the imidazolium ring (Fig. 1, Table 1). The torsional twists about the N(1)–C(6), C(6)–C(7) and N(3)–C(13), C(13)–C(14) bonds are ca. 77, 70 and 76, 69°, respectively. The bonding within the imidazolium ring indicates a pattern of delocalisation that extends from N(1) to N(3) through C(2), with N(1)–C(2) [1.321(3) Å] and C(2)–N(3) [1.320(3) Å] being significantly shorter than those between N(1)–C(5) [1.386(3) Å] and N(3)–C(4) [1.390(3) Å]. The nitrogen donors of the picolyl groups are rotated away from the carbon at position 2 in the imidazolium ring, however Fig. 1 shows that the donor arms should be free to rotate such that the nitrogens take up positions suitable for chelation to a metal ligated at C(2). The molecules pack to form helical chains, being linked head-to-tail by pi-pi and C–H···Cl interactions (Fig. 2). Adjacent chains are cross-linked by weaker pi-pi and C–H···Cl interactions to create a three dimensional network containing continuous ···**A**···**B**···**A**···**B**··· stacks.

2.2. Synthesis of palladium(II) carbene complexes

2.2.1. Monodentate ligands

Carbene transition metal complexes are often synthesised via reaction of an imidazolium salt with a basic metal salt (e.g. $Pd(OAc)_2$) to give a complex of the form $Pd(carbene)_2X_2$ [2,4]. We have recently shown, however, that the incorporation of a methyl ligand onto the palladium centre dramatically enhances the catalytic activity of the complex [31]. These types of complexes are not readily accessible through the palladium acetate route, and so the first generalised method for the synthesis of hydrocarbylpalladium carbene complexes from free NHCs was developed [19]. Thus, reacting two equivalents of the free carbene 1,3,4,5-tetramethylimidazolin-2-ylidene (tmiy) with PdMeCl(cod) yielded $PdMeCl(tmiy)_2$ (**2**) in good yield (Reaction (1)). Complex **2** was assigned *trans* geometry based upon its NMR spectra [31].



(1)

The results of a room-temperature single-crystal X-ray structure determination of **2** (Fig. 3), are consistent with the stoichiometry, connectivity and stereochemistry as described above, subject to the caveats of Section 4. The refinement models the complex as presenting in monoclinic space group $P2_1/c$, $Z = 2$, entailing location of the palladium atom on a crystallographic inversion centre, consistent with a *trans* disposition of the tmiy ligands, but incompatible with

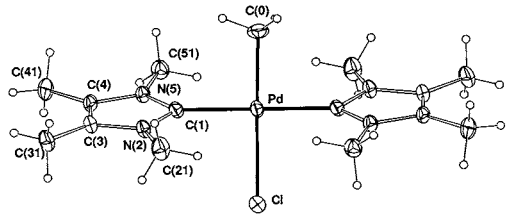


Fig. 3. Projection of **2**, normal to the coordination plane. Thermal ellipsoids with 20% probability are shown for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å.

the *trans* location of chloride versus methyl in the coordination sphere. The latter are modelled as disordered over the two sites, a situation not infrequently found where chloride and methyl entities, very similar in their spatial demands, occupy (pseudo-) symmetrically related sites in a molecule or crystal lattice. While little can be meaningfully said about them and their immediately associated geometries, those associated with the $Pd(tmiy)_2$ array are more readily apprehensible. Pd–$C_{carbene}$, 2.033(4) Å, is typical of such arrays bound to Pd [4,24,31,44], as are the other associated bond lengths and angles (C(carbene)–Pd–Cl, C(methyl) 89.8(1), 91.2(3)°) (Table 2).

Although the present ligand, particularly in its bound form, is not directly comparable with the cation of **1f** described above, the counterpart central ring parameters are of interest: C(carbene)–N are longer than in **1f**, being 1.345(5), 1.347(5), C–N (outer) similar (1.395(5), 1.383(5)), and peripheral C–C, 1.338(6) Å, perhaps shorter. Within the ring the angle at the carbene carbon is diminished to 103.1(3)°, those at the nitrogens increased (112.1(3), 112.6(3)°), and at the outer carbons similar (106.0(3), 106.2(3)°). Exocyclic angles at the nitrogens remain tightly ranged (123.3(3)–124.5(3)°), but those at the peripheral carbon atoms indicate the pair of methyl substituents there to be closed toward each other (angles: 130.7(4), 130.1(4), cf. 123.2(4), 123.7(4)°). The dihedral angle made between the ligand plane and the coordination plane is 65.3(1)°.

The synthesis of free NHCs bearing donor functionalised side arms is problematic given the high acidity of methylene protons in compounds such as **1b** [38], and thus it was necessary to develop a method for the synthesis of donor-functionalised carbene complexes. Hence we have shown that silver-mediated transfer of functionalised carbene ligands onto a palladium precursor, as described by Wang and Lin [45,46] for simple imidazolium salts, is also a suitable method for the preparation of methylpalladium carbene complexes [38]. It has very recently been reported that with the careful selection of deprotonating conditions and with the incorporation of a bulky side group on the second carbene nitrogen free carbene bearing donor functionalised side arms may be generated [39].

When reacted with Ag_2O in dichloromethane (DCM), imidazolium salts **1a**–**b** yield bis(carbene) Ag^I complexes according to Scheme 2. It has previously been noted [38] that complexes of this type incorporating an iodide anion exhibit an unusual stoichiometry, and indeed analysis of complexes **3a**–**b** show that they are of the form $Ag(carbene)_2I{\cdot}x AgI$, where $x = 0.3$–0.4. This unusual stoichiometry probably arises through the substitution of AgI_2^- for I^- in the crystal lattice, although this has not yet been confirmed, as attempts to crystallise complexes **3a** and **3b** have been consistently unsuccessful.

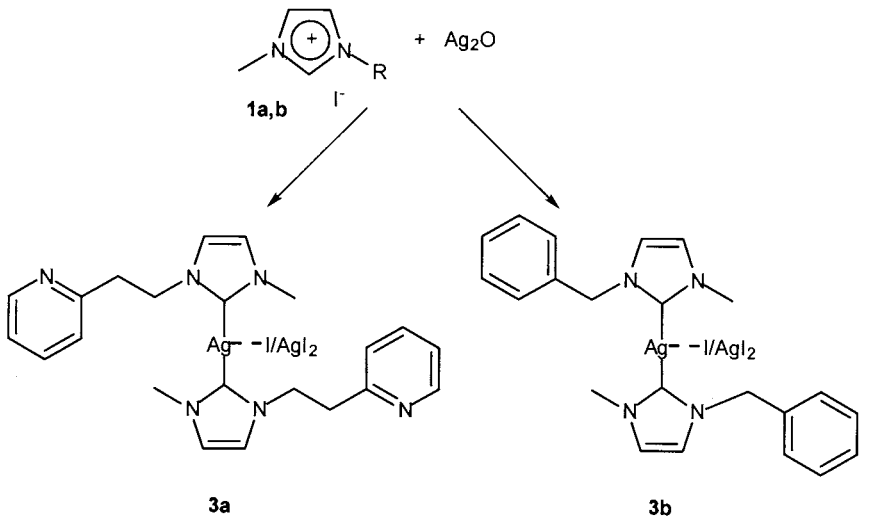
Reaction of complexes **3a** and **3b** with palladium species bearing weakly co-ordinated donor ligands (e.g. 1,5-cyclooctadiene (cod)) yielded a range of disubstituted carbene complexes (Scheme 3).

The reaction of **3a** with two equivalents of the palladium precursor Pd(Me)Cl(cod) yields the dimeric complex **4a**. The mass spectrum of **4a** clearly shows a cluster of peaks corresponding to $[M - Cl]^+$ for the dimeric complex. Within one half of the molecule each methylene proton is unique; the ^{1}H-NMR spectrum shows four individual signals each corresponding to an individual proton. Two protons give rise to doublets of triplets ($J = 12$ Hz, $J_1 = 3$ Hz), whilst the remaining two give rise to broad misshapen doublets. This deformation may arise from the interaction of methylene protons with each other, the neighbouring methylene protons and/or with the palladium methyl protons, for example.

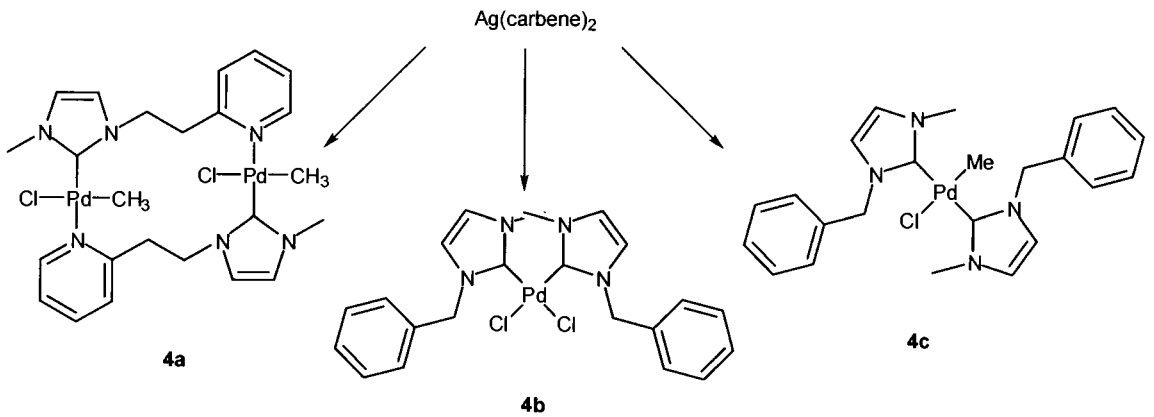
Table 2
Selected bond lengths (Å), bond angles (°), and interplanar dihedral (°) in $PdMeCl(tmiy)_2$; (2) [a]

Bond lengths			
Pd–C(O)	1.98(l)	C(l)–N(2)	1.345(5)
Pd–C(l)	2.033(4)	C(l)–N(5)	1.347(5)
Pd–Cl	2.435(2)	C(3)–C(4)	1.338(6)
Bond angles			
Cl–Pd–C(O)	178.9(3)	N(2)–C(l)–N(5)	103.1(3)
Cl–Pd–C(l)	89.8(l)	Pd–C(l)–N(2)	128.1(3)
Interplanar dihedral			
Pd, C(O), C(l), Cl/C(l), N(2), C(3), C(4), N(5)	65.3(l)		

[a] Esds given in parentheses, see Fig. 3 for atomic numbering.



Scheme 2.



Scheme 3.

The dimeric nature of this complex is in contrast to the complex formed by the related ligand 1-methyl-3-picolylimidazolium bromide. This ligand, which contains only a single methylene spacer between the imidazole ring and the pyridine moiety, has previously been shown to act as a chelating, bidentate ligand upon reaction with Pd(Me)Cl(cod) [38]. Similarly, the carbene 1-mesityl-3-picolylimidazolin-2-ylidene reacts with Pd(Me)Br(cod) to give a monomeric complex in which the ligand exhibits chelating behaviour [39]. Clearly, the second methylene spacer present in **3a** disfavours the formation of a chelated complex.

When **3b** is reacted with an equimolar amount of $PdCl_2(MeCN)_2$ the monomeric bis(carbene) complex **4b** results. The *cis* configuration of the carbene ligands is confirmed by the ^{13}C-NMR, in which the carbenoid signal occurs at 169.3 ppm, a value typical of *cis*-carbene complexes [4,47], and upfield from complexes in which the carbene ligands exhibit a *trans* arrangement [31,38,48]. At ambient temperature, the ^{1}H-NMR (DMSO-d_6) of **4b** indicates that the carbene ligands are non-equivalent. Two broad singlets are noted at 5.73 and 5.60 ppm for each methylene group. The geminal methylene protons do not appear to couple to each other. In addition, each N-methyl substituent also gives rise to a broad singlet (4.07 and 3.93 ppm). As the temperature of the solution is raised (35–50°C), both the methyl and the methylene signals begin to merge, until at 65°C a single signal is noted for each of the methyl and methylene groups (4.02 and 5.69 ppm, respectively). This indicates that there is hindered rotation around the Pd–$C_{carbene}$ bond arising from the bulky phenyl substituent on the carbene ligand.

In a similar manner to that described for **4b**, the reaction between **3b** and Pd(Me)Cl(cod) generates the bis(carbene) complex **4c**. In this case, the complex exhibits *trans* geometry, and the ^{13}C-NMR, which shows the carbenoid signal at 175.7 ppm, again confirms this [31,38,48]. Complex **4c** also shows restricted rotation about the Pd–$C_{carbene}$ bonds at room tempera-

ture. In contrast to **4b**, each methylene proton is found to give rise to a doublet, with a geminal coupling constant of 14 Hz, whilst each methyl group shows a separate singlet. Increasing the temperature of the solution again results in a merging of signals, until at 80°C a single broad signal is noted for the methylene protons (5.61 ppm) and a sharp singlet is seen for both methyl groups (3.94 ppm).

2.2.2. Bidentate ligands

There has been much recent interest in the cyclometallated phosphapalladacycles of Herrmann [49,50]. Complexes of this type have proved to be highly active in carbon–carbon coupling reactions, most notably the Heck reaction [51,52]. It was therefore of interest to prepare several complexes in which there existed the possibility for *ortho*-metallation. There are many examples of cyclometallated complexes incorporating a central *meta*-xylyl functional group [53–57], and we therefore attempted to generate complexes containing this moiety.

The formation of $Ag(carbene)_2$ complexes based on ligands **1c**–**e** was attempted in a manner similar to that described for **3a**,**b**. Unfortunately, the reactions proceeded only in very low yield (ca. 10–15%), and were thus deemed unsuitable for the further generation of palladium complexes. In these cases it was necessary to react the imidazolium salts with $Pd(OAc)_2$ in DMSO at high temperature [32] (Scheme 4) to produce **5a**–**c**.

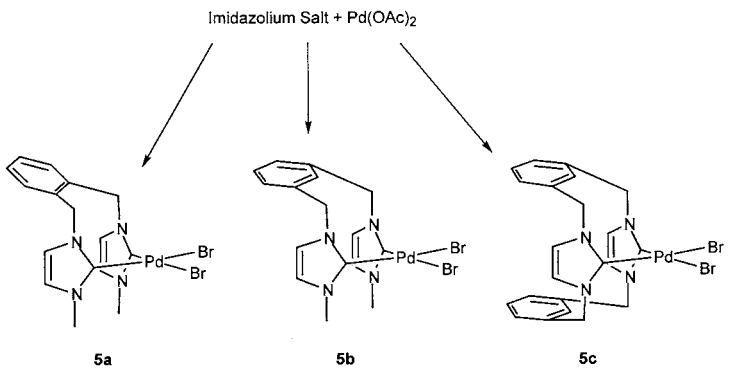
The reaction of $Pd(OAc)_2$ with **1d** yields complex **5a** in good yield. This complex has limited solubility in many common solvents, but exhibits moderate solubility in cold DMSO. At room temperature, the ^{1}H-NMR spectrum shows only one signal for both *N*-methyl groups, indicating a degree of symmetry within the molecule. The methylene protons are non-equivalent, with two doublets (6.49 and 5.12 ppm) exhibiting a geminal coupling constant of 14 Hz. The ^{13}C-NMR shows the carbenoid signal at 160.1 ppm, clearly demonstrating the *cis* geometry of the complex.

Complexes **5b** and **5c** have also been synthesised in good yield from $Pd(OAc)_2$ and the appropriate imidazolium salt (**1c** and **1e**, respectively). Again the complexes have only limited solubility in most common solvents, including cold DMSO. In contrast to **5a**, the ambient temperature ^{1}H-NMR of **5b** and **5c** show only very broad signals. Consequently, it was not possible to obtain ^{13}C-NMR spectra. In an attempt to resolve the peaks each complex was heated to 90°C, but little or no change in the spectra was observed, indicating that broadening does not arise from restricted rotation around bonds within the molecule, but is probably due to either rapid *cis*/*trans* isomerisation, or a dynamic 'ring flip' in which the xylene ring may interchange between a boat and chair type configuration. The low solubility of the complex in NMR solvents prevented any low temperature NMR work from being undertaken, so the reason for this broadening could not be confirmed. Repeated attempts to crystallise **5b** were invariably unsuccessful, and at present the true geometry of the complex remains unknown. It should be noted that the *ortho*-xylene analogue of **5c** has recently been synthesised [58], but no mention is made of structure or NMR properties.

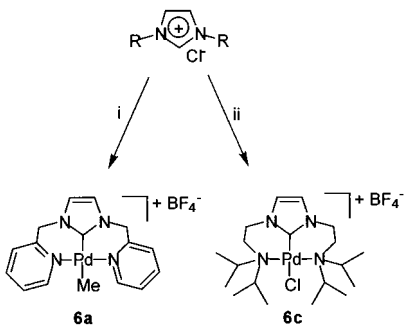
No evidence of cyclometallation was noted for complex **5b** or **5c**, however the former proved to be an excellent Heck catalyst (vide infra). At this time we cannot rule out cyclometallation under Heck conditions, and the synthesis and characterisation of a cyclopalladated carbene complex remains a major goal.

2.2.3. Tridentate ligands

We have previously established that alkyl Pd–carbene complexes are prone to reductive carbene alkyl coupling to give 2-alkyl imidazolium salts and Pd^0, and that this reaction may occur under very mild conditions



Scheme 4.

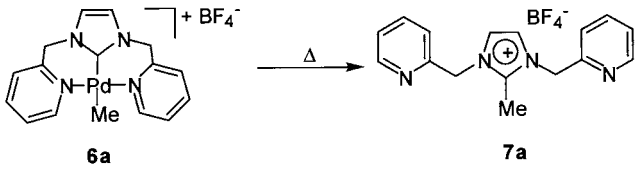


Scheme 5. (i) R = –$CH_2C_5H_4N$-2, Ag_2O, PdMeCl(cod), AgBF4; (ii) R = –$CH_2CH_2N^iPr_2$, Ag_20, $PdCl_2(NCPh)_2$, $AgBF_4$.

in many cases [31,48]. As this represents a possible route to catalyst deactivation we were interested in suppressing this reaction. In order for this reaction to occur we have found that the alkyl group and the carbene must be mutually *cis* to one another [59], thus forcing the alkyl group to sit *trans* to the carbene, through the use of chelating donor groups attached to the carbene, may produce a more stable catalyst. Furthermore, similar tridentate donor–C–donor ligands have recently been shown to give rise to highly active, stable catalysts for Heck couplings [55,60]. Thus we prepared complex **6a** through carbene transfer from an Ag–carbene complex. Attempts to isolate the intermediate Ag–carbene complex led to a product which rapidly darkened and became inactive towards carbene transfer, therefore the Ag–carbene was generated in situ and reacted immediately with PdMeCl(cod) (Scheme 5). This procedure afforded **6a** in a low yield of 12%.

The ^{1}H-NMR spectrum of **6a** contains two Pd methyl peaks at 0.38 and 0.06 ppm in roughly equal proportions. Additionally, the mass spectrum of **6a** contains clusters for both the monomer and the dimeric species. It therefore seems likely that both the chelated tridentate monomer and a bridged dimer, similar to **4a**, occur in solution. The methylene as well as the pyridyl protons appear as broad, overlapping resonances at room temperature, but sharpen as the temperature is increased and the pyridyl protons become resolved. This is most likely due to dynamic conformational flipping of the chelate ring and has been observed previously [38].

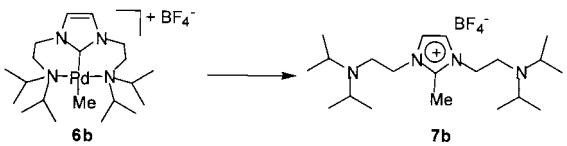
The stability of **6a** was studied by recording changes in the ^{1}H-NMR spectrum (DMSO-d_6) as the temperature was raised. No decomposition is observed until 100°C is reached. At this temperature a Pd^0 deposit begins to form and signals due to 1,3-di(2-picoly)-2-methylimidazolium tetrafluoroborate **7a** slowly rise. After 12 h decomposition is complete with the exclusive product being **7a** (Reaction (2)).



(2)

While **6a** still decomposes via alkyl–carbene coupling, the stability of this complex is much greater than other cationic methyl Pd–NHC complexes, which often decompose (via the same route) at room temperature or below. In order for this decomposition to occur, at least in the case of the monomeric species, a pyridyl arm would first have to dissociate such that the methyl group may take up the requisite *cis* position next to the carbene. Moreover, the complex is probably further destabilised by the strongly coordinating DMSO solvent, which is likely to promote dissociation of the pyridyl arm particularly at high temperatures.

We also attempted to make an analogue of **6a** using imidazolium salt **1g**. After addition of $AgBF_4$ the solution rapidly darkened due to Pd^0 formation. ^{1}H-NMR and MS showed a mixture of the expected complex **6b** along with the decomposition product 1,3-bis(diisopropyl-2-ethylamino)-2-methylimidazolium (**7b**) (Reaction(3)).



(3)

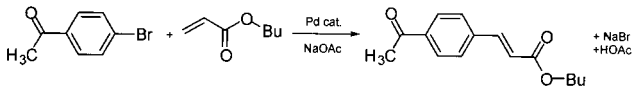
After a short while only the imidazolium salt remains. This result is rationalised in terms of the expected weaker donor ability of the amino group in **6b** relative to the pyridyl group in **6a**. The amino arm in **6b** probably dissociates more easily, allowing the methyl group to occupy a *cis* position to the carbene from which methyl–carbene elimination can occur.

To overcome the decomposition problem we used $PdCl_2(NCPh)_2$ instead of PdMeCl(cod) in the reaction, as halogens are not prone to reductive coupling with NHCs. After addition of $AgBF_4$ this procedure afforded complex **6c**, a stable orange solid, in 80% yield (Scheme 5). Coordination of the ligand results in a downfield shift in the isopropyl C*H* resonance from 2.96 ppm in the imidazolium salt to 3.8 ppm in the complex. Furthermore, the isopropyl CH_3 signal is split into two doublets at 1.74 and 1.10 ppm. Interestingly, there appears to be no tendency towards dimer formation in **6c**.

3. Catalysis

The Heck coupling of 4-bromoacetophenone with *n*-butyl acrylate to form *n*-butyl-(*E*)-4-acetylcinnamate

[(butyl-(*E*)-3-(4-acetylphenyl)-2-propenoate)] (Reaction (4)) was undertaken with complexes **2**, **4a**–**c**, **5a**–**c** and **6a**,**c** (Table 3).



(4)

For the purpose of comparison, initial catalytic testing was undertaken with the simple, non-functionalised carbene complex $Pd(tmiy)_2MeCl$ (**2**). With a catalyst loading of 1.0×10^{-3} mol% a TON of 18 000 resulted after 24 h (run 1). It may be seen from runs 3–5 that, after the same reaction time, functionalised methylpalladium–carbene complexes **4a** and **4c** resulted in higher TONs, while the dichloride **4b** gave a similar conversion to that observed with **2**. Comparison of runs 4 and 5 demonstrates the superiority of methylpalladium–carbene complexes as catalysts when compared to dihalopalladium-carbene complexes in the absence of a reducing agent. This 'methyl effect' has previously been reported by our group [31,38,48]. It is thought that the methyl group promotes catalysis by providing a facile route to the active catalyst, possibly via olefin insertion into the $Pd–CH_3$ bond, followed by β-hydride elimination.

The dibromopalladium complexes **5a**–**b** proved to be moderately good catalysts when tested at the same concentration (1.0×10^{-3} mol%, runs 6–8) in the presence of a reducing agent (such as hydrazine hydrate). The product yield of these complexes, as determined by GC analysis, was generally comparable to the methylpalladium complexes, with the exception of **4c**. It is interesting to note that the *meta*-substituted xylene complex **5b** performed considerably better than the *ortho*-substituted complex **5a**. In contrast, complex **5c** proved to be a poor catalyst when reduced with hydrazine, giving only 7% conversion.

As we had previously shown that functionalised carbene complexes are stable at low concentrations for long periods [38], it was decided to test a number of the complexes at very low concentration. Specifically, complexes **4c**, **5b**, **6a** were tested at a precatalyst concentration of 1.0×10^{-4} mol%. The bis(carbene) complexes **4c** and **5b** both proved to be excellent catalysts at this concentration, giving near quantitative conversion coupled with exceptional TONs (980 000 and 970 000, respectively). It is interesting to note that in both complexes, there exists the possibility of *ortho*-metallation. As noted above, we are as yet unable to rule out cyclometallation under the basic conditions of the Heck reaction.

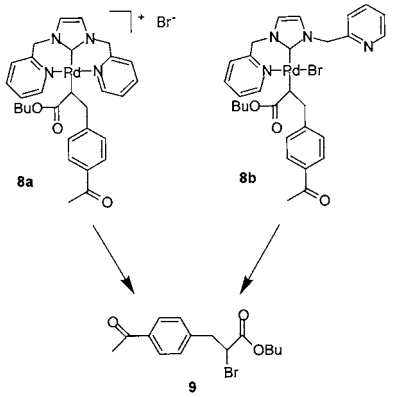
The tridentate complex **6a** also proved to be an efficient catalyst, giving a TON of 660 000 with 66% conversion. Interestingly, this complex led to a product mix that contained 5–10% of the brominated coupling product **9** along with the cinnamate. A possible explanation for this is that the two chelating pyridyl arms of **6a** may hinder β-hydride elimination by blocking coordination sites on Pd. Thus, this catalyst may promote the reductive elimination of **9** from intermediates such as **8a** or **8b** (Scheme 6) in the catalytic cycle.

Complex **6c**, while giving a reasonable TON (44 000, run 10), was not nearly as active as the related complex **6a**. Although synthesis of the chloride **6c** gave a stable complex, it is also expected to reduce the catalytic activity relative to a methyl palladium complex, which

Table 3
Heck coupling of aryl halides with n-butyl acrylate [a]

Run	Catalyst	Amount (mol %)	Aryl halide	Time (h)	Conversion (%) [b]	TON
1	**2**	1.0×10^{-3}	4-Bromoacetophenone	24	18	18 000
2	**5b**	1.0×10^{-3}	4-Bromoacetophenone	24	80	8 000
3	**4a**	1.0×10^{-3}	4-Bromoacetophenone	24	48	48 200
4	**4b** [d]	1.0×10^{-3}	4-Bromoacetophenone	24	25	24 500
5	**4c** [d]	1.0×10^{-3}	4-Bromoacetophenone	24	87	87 000
6	**5a** [c]	1.0×10^{-3}	4-Bromoacetophenone	24	21	20 700
7	**5b** [c]	1.0×10^{-3}	4-Bromoacetophenone	24	57	56 800
8	**5c** [c]	1.0×10^{-3}	4-Bromoacetophenone	24	7	6 600
9	**5c** [d]	1.0×10^{-3}	4-Bromoacetophenone	24	33	33 000
10	**6c** [c]	1.0×10^{-3}	4-Bromoacetophenone	24	44	44 000
11	**4c** [d]	1.0×10^{-4}	4-Bromoacetophenone	92	98	980 000
12	**5b** [c, d]	1.0×10^{-4}	4-Bromoacetophenone	93	97	970 000
13	**6a**	1.0×10^{-4}	4-Bromoacetophenone	72	23	230 000
14	**6a** [e]	1.0×10^{-4}	4-Bromoacetophenone	120	66	660 000
15	**4c** [d]	3.0×10^{-1}	4-Chlorobenzaldehyde	24	11	38

[a] Conditions for catalysis given in Section 4.
[b] Conversions determined by GC.
[c] 10–200 μl hydrazine hydrate added to run.
[d] 5 mmol NPr_4Br added to run.
[e] 10 mmol NPr_4Br added to run.



Scheme 6. Proposed reductive elimination of **9** from intermediate **8a**, **b**.

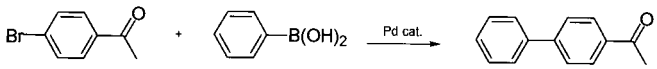
is able to facilitate the generation of the active species. Furthermore, the apparent stability of the precatalyst in this case does not represent the true stability of the active catalyst, which would contain a palladium–aryl and thus would be prone to decomposition via aryl–carbene coupling. Considering the poor stability of the methyl palladium analogue **6b**, it is not surprising that **6c** performs more poorly than **6a**.

Heck olefination with complex **3c** at extremely low catalyst concentration (1.0×10^{-5} mol%, not shown) resulted in very low product yields ($< 10\%$).

In a number of runs (for example runs 5, 12, 14, and 15) tetrapropylammonium bromide was added as a promoter. Salts of this type have long been known to improve the efficiency of Heck coupling [61], either by acting as phase-transfer catalysts, or via the formation of anionic Pd^0 species as the active catalysts [62,63]. Indeed it may be seen that, in the presence of the salt, complex **6a** gave a significantly greater TON (660 000) than in its absence (230 000). Comparison of runs 8 and 9, in which complex **5c** was used as precatalyst also demonstrates the promoting effect of these salts. Additionally, it has been noted that, in the presence of tetrabutylammonium bromide, the induction period commonly observed for dihalopalladium–carbene complexes is absent, suggesting that the ammonium salt acts as a reducing agent [4]. Indeed it may be seen that, while complex **5c** is a poor catalyst when reduced with hydrazine, it is moderately active in the presence of $[N(n\text{-}C_3H_7)_4]Br$. It seems likely that tetraalkylammonium salts are able to function both as reducing agents, and as promoters for Heck catalysis.

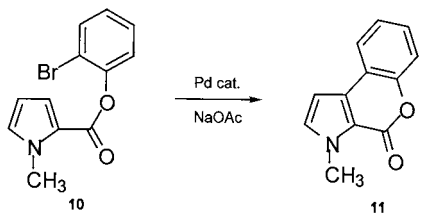
The coupling of 4-chlorobenzaldehyde with butylacrylate as catalysed by **4c** was also tested. It may be seen that the complex proved almost inactive, resulting in only 11% conversion, even in the presence of promoting ammonium salts.

The Suzuki coupling of 4-bromoacetophenone and phenylboronic acid to give 1-(1,1′-biphenyl-4-yl)ethanone (Reaction (5)) was undertaken with complexes **4c** and **6a**, with both complexes proving to be very active. Complex **4c** (4×10^{-4} mol%) gave a conversion of 43% after 48 h, corresponding to a TON of 107 500. Under the same conditions **6a** gave a conversion of 71%, corresponding to a TON of 177 500.



(5)

Complexes **4a**, **4c** and **5b** were also tested in the intramolecular Heck coupling of 2-bromophenyl-1-methyl-1*H*-pyrrole-2-carboxylate (**10**). Successful cyclisation of this substrate would yield the tricyclic product 3-methylchromeno[3,4-*b*]pyrrol-4(3*H*)-one (**11**) (Reaction (6)).



(6)

However, despite several attempts using high catalyst concentrations (3 mol%, 120°C, DMA solvent, NaOAc) and extended reaction times (up to 72 h) no conversion of substrate could be detected by either GC-MS or ^{1}H-NMR analysis. This lack of activity is somewhat surprising, as a similar reaction has previously been shown to be catalysed by traditional phosphine-based systems [64]. The reason for this inactivity is not yet fully understood.

Similarly, the Pd-catalysed reaction of bromobenzene with zirconocene dichloride to produce 1,2,3,4,5-pentaphenylcyclopentadiene [65] was undertaken with complex **4b**. The catalyst again proved inactive, giving biphenyl as the only reaction product in low yield.

4. Experimental

4.1. General comments

Unless otherwise stated all reactions were performed using standard Schlenk line techniques or in a nitrogen glovebox. Solvents were purified by standard methods [66] and distilled under nitrogen immediately prior to use. All other reagents were used as received. The compounds 2-(2-chloroethyl)pyridine hydrochloride [67], Pd(Me)Cl(COD) [68] and $Pd(tmiy)_2MeCl$ [31] were prepared by the established procedures.

4.2. Structure determinations

Imidazolium salt **1f**. The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically using full-matrix least-squares based on F^2 to give $R_1 = 0.030$, $wR_2 = 0.079$ for 1350 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta = 128°$] and 182 parameters. The absolute chirality of **1f** was unambiguously determined by a combination of R-factor tests [$R_1^+ = 0.0304$, $R_1^- = 0.0448$] and by use of the Flack parameter [$x^+ = 0.01(2)$, $x^- = 0.99(2)$].

Crystal data: $C_{15}H_{15}N_4Cl$, $M = 286.8$, orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 9.652(1)$, $b = 9.992(2)$, $c = 15.010(1)$ Å, $V = 1447.7(2)$ Å^3, $Z = 4$, $D_c = 1.316$ g cm^{-3}, $\mu(Cu–K_\alpha) = 22.9$ cm^{-1}, $F(000) = 600$, $T = 183$ K; clear blocky prisms, $0.50 \times 0.23 \times 0.20$ mm, Siemens P4/RA diffractometer, ω-scans, 1398 independent reflections.

PdMeCl(tmiy)$_2$, (**2**): A hemisphere of room-temperature single-counter/'four-circle' diffractometer data was measured ($2\theta/\theta$ scan mode, $2\theta_{max} = 60°$; monochromatic Mo–K_α radiation, $\lambda = 0.7107_3$ Å; T ca. 295 K) yielding 4277 independent reflections, these being merged to 2061 independent ($R_{int} = 0.073$) after gaussian absorption correction, 1697 of these with $I > 2\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement. Anisotropic thermal parameter forms were refined for the non-hydrogen atoms; (x, y, z, U_{iso})$_H$ being constrained at estimated values. As modelled in space group $P2_1/c$, $Z = 2$, the palladium atom is disposed on a crystallographic inversion centre, entailing the not uncommon phenomenon in similar circumstances of the methyl and chloride entities, which have similar steric demands, being disordered over the pair of symmetry-related available sites, independently refinable (caveat: associated geometry). Conventional residuals R, R_w (statistical weights, derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\ \sigma^2(I_{diff})$) on $|F|$ were 0.053, 0.072 at convergence. Neutral atom complex scattering factors were employed within the context of the XTAL 34 program system [69]. Pertinent results are given below and in Fig. 3.

Crystal data: $C_{15}H_{27}ClN_4Pd$, M = 405.3. Monoclinic, space group $P21/c$ (C_{2h}^5, no. 14), $a = 8.293(2)$, $b = 14.220(4)$, $c = 7.814(2)$ Å, $\beta = 104.21(2)°$, $V = 893._3$ Å^3. D_c ($Z = 2$) = 1.50(7) g cm^{-3}. $\mu_{Mo} = 11.9$ cm^{-1}; specimen: $0.24 \times 0.32 \times 0.80$ mm; $A^*_{min,max} = 1.30$, 1.53. $|\Delta\rho_{max}| = 2.3(1)$ e Å^{-3}. CCDC no. 147178.

4.3. Intermolecular heck coupling

In a typical run 4-bromoacetophenone (4.98 g, 25.0 mmol) and anhydrous NaOAc (2.28 g, 27.8 mmol) were placed in a 100 ml flask under N_2. To this was added n-butyl acrylate (5.0 ml, 35 mmol), N,N-dimethylacetamide (25 ml) and a solution of the catalyst in an appropriate solvent (e.g. DCM, DMSO). The reaction vessel was then heated by means of an oil bath (120°C for aryl bromide, 140°C for aryl chlorides). After heating for the desired time, the solution was cooled and analysed by gas chromatography.

4.4. Suzuki coupling

A two-necked 100 ml flask fitted with a reflux condenser and septum was charged with 4-bromoacetophenone (1.99 g, 10 mmol), phenylboronic acid (1.34 g, 11 mmol) and potassium carbonate (2.76 g, 20 mmol) before being put under a nitrogen atmosphere. Toluene (20 ml) was injected and the solution brought to reflux, before a solution of the catalyst in 200 μL DCM was injected. The solution was refluxed for the desired time, after which it was cooled and analysed by GC and ^{1}H-NMR.

4.5. Preparation of compounds

4.5.1. 1-Benzyl-3-methylimidazolium iodide (**1a**)

A solution of benzyl chloride (8.49 g, 67.1 mmol) in acetone (40 ml) was added to a Schlenk flask containing sodium iodide (9.18 g, 61.2 mmol) and 1-methylimidazole (4.66 g, 56.8 mmol). The reaction mixture was stirred overnight, after which time the acetone was removed in vacuo and DCM (40 ml) added. The precipitated sodium chloride was removed by filtration through a pad of celite and the DCM removed in vacuo to yield a pale yellow powder. Yield: 95%. Anal. Calc. for $C_{11}H_{13}N_2I$: C, 44.02; H, 4.37; N, 9.33. Found: C, 43.95; H, 4.52; N, 9.54%. ^{1}H-NMR (200 MHz, DMSO-d_6): δ 9.32 (s, 1H, NC*H*N), 7.85 (m, 1H, imidazole*H*), 7.77 (m, 1H, imidazole*H*), 7.46 (m, 5H, Ar*H*), 5.49 (s, 2H, NCH_2Ph), 3.89 (s, 3H, NCH_3). ^{13}C-NMR (50 MHz, D_2O): δ 136.5 (N*C*N), 134.0 (Ar*C*), 129.9 (Ar*C*), 129.2 (Ar*C*), 124.3 (Ar*C*), 122.8 (H*C* = *C*H), 53.36 (N*C*H$_2$Ar), 36.44 (N*C*H$_3$).

4.5.2. 1-(2-Ethylpyridyl)-3-methylimidazolium iodide (**1b**)

A solution of 2-(2-chloroethyl)pyridine (0.0437 mol, prepared by basifying 7.78 g of 2-(2-chloroethyl)-pyridine hydrochloride), 1-methylimidazole (3.94 g, 0.048 mol) and sodium iodide (6.53 g, 0.0437 mol) was dissolved in acetone (10 ml). These were sealed in a 50 ml reaction bomb and heated to 60°C for 29 h. Following this, the contents of the bomb were poured into DCM (50 ml) and filtered through celite. Ether (20 ml) was then added, which caused an orange oil to separate. This was recrystallised from DCM–ether to yield an orange solid, which was dried in vacuo. Yield: 80%. MS (APCI) m/z: 188 (100%) M$^+$. ^{1}H-NMR (200 MHz, DMSO-d_6): δ 9.12 (s, 1H, NC*H*N), 8.52 (m, 1H,

pyridyl-H_6), 7.67–7.79 (m, 3H, pyridyl-$H_{3,4,5}$), 7.28–7.33 (m, 2H, HC–CH), 4.62 (t, $J = 7$ Hz, 2H, NCH_2), 3.83 (s, 3H, NCH_3), 3.34 (t, $J = 7$ Hz, 2H, CH_2-pyridyl).

4.5.3. 3-methyl-1-{3-[(3-methyl-1H-imidazolium-1-yl)-methyl]benzyl}-1H-imidazolium dibromide (**1c**)

To a solution of α,α′-dibromo-*m*-xylene (3.32 g, 12.6 mmol) in THF (40 ml) was added 1-methylimidazole (2.0 ml, 25.1 mmol). The reaction mixture was then refluxed for 3 h, before the white crystalline product was filtered, washed with ether and dried in vacuo. Yield: 94%. Anal. Calc. for $C_{16}H_{20}N_4Br_2$: C, 44.88; H, 4.71; N, 13.09. Found: C, 44.24; H, 4.77; N, 12.89%. ^{1}H-NMR (200 MHz, DMSO-d_6): δ 9.39 (s, 2H, NCHN), 7.45–7.86 (m, 8H, ArH), 5.49 (s, 4H, NCH_2), 3.90 (s, 6H, NCH_3). ^{13}C (50 MHz, DMSO-d_6): 137.0 (NCN), 135.9 (ArC), 129.9 (ArC), 128.9 (ArC), 124.3 (ArC), 122.6 (HC–CH), 51.68 (NCH_2), 36.24 (NCH_3).

4.5.4. 3-methyl-1-{2-[(3-methyl-1H-imidazolium-1-yl)-methyl]benzyl}-1H-imidazolium dibromide (**1d**)

This compound was prepared in the same manner as **1c** using α,α′-dibromo-*o*-xylene (3.32 g, 12.6 mmol) and 1-methylimidazole (2.0 ml, 25.1 mmol), except that the mixture was refluxed for 30 min. Yield: 94%. Anal. Calc. for $C_{16}H_{20}N_4Br_2$: C, 44.88; H, 4.71; N, 13.09. Found: C, 45.92; H, 4.82; N, 13.04%. ^{1}H-NMR (400 MHz, DMSO-d_6): δ 9.28 (s, 2H, NCHN), 7.79 (m, 4H, ArH), 7.47 (dd, $J = 6$ Hz, $J_1 = 3$ Hz, 2H, imid$H$), 7.33 (dd, $J = 6$ Hz, $J_1 = 3$ Hz, 2H, imid$H$), 5.70 (s, 4H, NCH_2), 3.88 (s, 6H, NCH_3). ^{13}C-NMR (100 MHz, DMSO-d_6): δ 137.6 (NCHN), 133.6 (ArC), 130.3 (ArC), 124.6 (ArC), 123.1 (HC–CH), 49.7 (NCH_2Ar), 36.7 (NCH_3).

4.5.5. 1-[3-(1H-imidazol-1-ylmethyl)benzyl]-1H-imidazole (**1h**)

A solution of α,α′-dibromo-m-xylene in dry THF (20 ml) was added dropwise to potassium imidazolide (1.301 g, 12.1 mmol) suspended in THF (30 ml). After stirring at r.t. for 1 h the solution turned bright yellow. After stirring at ambient temperature overnight, the white suspension was filtered through a pad of celite to remove precipitated KBr, and the solvent removed in vacuo to afford a white powder. Yield: 69%. ^{1}H-NMR (200 MHz, C_6D_6): δ 7.23 (m, 5H, NC(H)N and ArH), 6.87 (t, $J = 7$ Hz, 1H, ArH), 6.85 (d, $J = 7$ Hz, 2H, imidazole$H$), 6.41 (m, 2H, imidazole$H$), 4.15 (s, 4H, ArCH_2N). ^{13}C-NMR (50 MHz, C_6D_6): δ 138.3 (NCN), 138.1 (Ar$C_{1/3}$), 131.0 (imidazoleC_5), 129.8 (ArC), 127.2 (ArC), 126.2 (ArC), 119.5 (imidazoleC_4), 50.12 (ArCH$_2$N).

4.5.6. Imidazoliophane (**1e**)

To a solution of **1h** (0.83 g, 3.48 mmol) in acetone (15 ml) was added dropwise a solution of α,α′-dibromo-m-xylene (0.92 g, 3.49 mmol), also in acetone (10 ml). Following complete addition, the solution was stirred at ambient temperature for 15 min before being refluxed for half an hour. The resultant white precipitate was isolated by filtration and dried in vacuo. Yield: 72%. Anal. Calc. for $C_{16}H_{20}N_4Br_2$: C, 52.61; H, 4.42; N, 11.16. Found: C, 52.27; H, 4.54; N, 11.08%. ^{1}H-NMR (200 MHz, DMSO-d_6): δ 9.57 (s, 2H, NCHN), 7.23–7.97 (m, 12H, ArH and imidazole$H$), 5.48 (s, 8H, ArCH_2N).

4.5.7. 1,3-di(2-picolyl)imidazolium chloride (**1f**)

Picolylchloride hydrochloride (11.861 g, 72.3 mmol), imidazole (2.461 g, 36.1 mmol) and $NaHCO_3$ (9.11 g, 112 mmol) were taken up in ethanol (100 ml) and refluxed for 2 days. The solvent was removed in vacuo, the residue taken up in DCM and dried over $CaSO_4$, and the solution filtered. Removal of the DCM in vacuo gave an oil that was triturated with 40 ml THF to give a powder. This was further washed with THF (2×20 ml) and dried in vacuo. Yield: 7.46 g (72%). Anal. Calc. for $C_{15}H_{15}N_4Cl$: C, 62.82; H, 5.27; N, 19.54. Found: C, 62.76; H, 5.34; N, 19.38%. MS (FAB): m/z 251 $[M]^+$. ^{1}H-NMR (250 MHz, $CDCl_3$): δ 10.90 (s, 1H, NC(H)N), 8.52 (m, 2H, pyridylH_6), 7.73 (m, 4H, pyridylH_4, $HCCH$), 7.63 (m, 2H, pyridylH_3), 7.29 (m, 2H, pyridylH_5), 5.71 (s, 4H, NCH_2). ^{13}C-NMR (63 MHz, $CDCl_3$): δ 152.4 (pyridylC_2), 149.8 (pyridylC_6), 138.0 (NCN), 137.7 (pyridylC_4), 124.0, 123.9, 122.3 (pyridylC_3, pyridylC_5, NCCN), 54.1 (NCH_2).

4.5.8. 1,3-bis(diisopropyl-2-ethylamino)imidazolium chloride (**1g**)

2-(diisopropylamino)ethyl chloride hydrochloride (9.432 g, 47.12 mmol) and imidazole (3.217 g, 47.25 mmol) were taken up in MeOH (70 ml) and refluxed for 18 h, after which $NaHCO_3$ (3.969 g, 47.24 mmol) followed by more of the amine HCl (9.457 g, 47.25 mmol) was added and refluxing continued. After a further 48 h the MeOH was removed in vacuo, the remaining oil taken up in water, and treated with $NaHCO_3$ (7.939 g, 94.50 mmol). The solution was stirred at 70°C until the evolution of CO_2 had ceased, then the product was extracted into DCM, dried over $MgSO_4$, filtered and the DCM removed in vacuo. Recrystallisation from DCM–pentane at −78°C afforded white platelets that were collected by filtration and dried in vacuo. Yield: 10.93 g (65%). Anal. Calc. for $C_{19}H_{39}N_4Cl$: C, 63.57; H, 10.95; N, 15.61. Found: C, 63.55; H, 10.87; N, 15.50%. MS (FAB): m/z 323 $[M]^+$. ^{1}H-NMR (250 MHz, $CDCl_3$): δ 10.47 (s, 1H, NC(H)N), 7.42 (s, 2H, $HCCH$), 4.28 (t, $J = 5$ Hz, 4H, N_{Im}–CH_2), 2.96 (m, $J = 7$ Hz, 4H, NCH), 2.82 (t, $J = 5$ Hz, 4H, N_{Im}–CH_2CH_2), 0.88 (d, $J = 5$ Hz, 24H, NC(CH_3)$_2$). ^{13}C-NMR (63 MHz, $CDCl_3$): δ 137.6 (NCN), 122.2 (HCCH), 49.4 (N_{Im}–CH_2), 47.9 (NC(CH_3)$_2$), 45.3 (N_{Im}–CH_2CH_2), 20.6 (NC(CH_3)$_2$).

4.5.9. [Ag(1-(2-ethylpyridyl)-3-methylimidazolin-2-ylidene)$_2$I·0.3AgI] (**3a**)

A mixture of **1b** (2.74 g, 8.69 mmol) and silver(I) oxide (0.99 g, 4.27 mmol) in DCM (100 ml) was stirred at ambient temperature for 4 h. The reaction mixture was then filtered through Celite, and the solvent removed in vacuo. The residual product was repeatedly recrystallised from DCM–Ether (4:10 ml) to give a pale yellow–brown powder, which was dried in vacuo. Yield: 34%. Anal. Calc. for $C_{22}H_{26}N_6Ag_{1.3}I_{1.3}$: C, 38.88; H, 3.86; N, 12.36. Found: C, 39.19; H, 4.08; N, 12.12%. ^{1}H-NMR (400 MHz, DMSO-d_6): δ 8.44 (d, $J = 5$ Hz, 2H, Ar*H*), 7.65 (dt, $J = 8$ Hz, $J_1 = 2$ Hz, 2H, Ar*H*), 7.47 (ds, $J = 2$ Hz, 2H, Ar*H*), 7.40 (ds, $J = 2$ Hz, 2H, Ar*H*), 7.19 (t, $J = 8$ Hz, 4H, Ar*H*), 4.56 (t, $J = 7$ Hz, 4H, pyCH_2), 3.76 (s, 6H, NCH_3), 3.26 (t, $J = 7$ Hz, 4H, NCH_2). ^{13}C-NMR (50 MHz, DMSO-d_6): δ 180.9 (*C*-Ag), 157.7 (Ar*C*), 149.5 (Ar*C*), 136.9 (Ar*C*), 123.8 (H*C*=*C*H), 123.2 (Ar*C*), 122.2 (Ar*C*), 122.0 (Ar*C*), 50.46 (py*C*H$_2$), 38.27 (N*C*H$_2$). The signal from N*C*H$_3$ is superimposed upon the DMSO-d_6 solvent peaks.

4.5.10. [Ag(1-benzyl-3-methylimidazolin-2-ylidene)$_2$I·0.35AgI] (**3b**)

Complex **3b** was prepared from **1a** and Ag_2O as described for **3a** except that the residual product was recrystallised from DCM–Ether (4:15 ml) to yield a white powder. Yield: 41%. Anal. Calc. for $C_{22}H_{24}N_4Ag_{1.35}I_{1.35}$: C, 39.95; H, 3.66; N, 8.47. Found: C, 40.29; H, 2.97; N, 8.24%. ^{1}H-NMR (200 MHz, DMSO-d_6): δ 7.56 (d, $J = 2$ Hz, 1H, imid*H*), 7.47 (d, $J = 2$ Hz, 1H, imid*H*), 7.32 (m, 5H, Ar*H*), 5.35 (s, 2H, NCH_2Ph), 3.79 (s, 3H, NCH_3). ^{13}C-NMR (100 MHz, DMSO-d_6): δ 181.9 (*C*Ag), 138.1 (Ar*C*), 129.7 (Ar*C*), 129.0 (Ar*C*), 128.7 (Ar*C*), 128.0 (Ar*C*), 124.2 (Ar*C*), 123.5 (Ar*C*), 54.55 (N*C*H$_2$Ph), 38.93 (N*C*H$_3$).

4.5.11. [Pd(Me)(1-(2-ethylpyridyl)-3-methylimidazolin-2-ylidene)Cl]$_2$ (**4a**)

A mixture of **3a** (0.38 g, 0.56 mmol) and Pd(Me)Cl(COD) (0.30 g, 1.13 mmol) was dissolved in DCM (30 ml) and stirred for 4.5 h. After this time, the reaction mixture was filtered through a pad of celite to remove precipitated AgI. The DCM was removed in vacuo to leave a yellow solid, which was recrystallised repeatedly from DCM–Ether (3:10 ml), and finally dried at reduced pressure to give a pale yellow powder. Yield: 34%. Anal. Calc. for $C_{24}H_{32}N_6Pd_2Cl_2·0.3CH_2Cl_2$: C 40.89, H 4.60, N 11.77. Found: C, 41.45; H, 4.45; N, 11.22%; (DCM indicated by ^{1}H-NMR). HRMS (LSIMS): Calc. for $C_{24}H_{32}N_6Pd_2Cl$: 647.04601. Found: 647.04657. MS (LSIMS) m/z: 653 (53) $[M - Cl]^+$; 202 (100%) $[\text{ylidene} + CH_3]^+$. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.06 (d, $J = 5$ Hz, 1H, *o*-py*H*), 7.46–7.49 (m, 2H, py*H*), 7.18–7.23 (m, 1H, py*H*), 6.79 (d, $J = 2$ Hz, 1H, imid*H*), 6.50 (d, $J = 2$ Hz, 1H, imid*H*), 6.18 (dt, $J = 12$ Hz, $J_1 = 3$ Hz, 1H, C*H*2), 5.19 (d, br, $J = 12$ Hz, 1H, CH_2), 4.71 (dt, $J = 12$ Hz, $J_1 = 4$ Hz, 1H, CH_2), 4.20 (d, br, $J = 12$ Hz, 1H, CH_2), 4.12 (s, 3H, NCH_3), 0.106 (s, 3H, PdCH_3). ^{13}C-NMR (50 MHz, CDCl3): δ 173.5 (N*C*N), 158.8 (Ar*C*), 151.7 (Ar*C*), 137.6 (Ar*C*), 128.5 (Ar*C*), 123.9 (Ar*C*), 123.1 (Ar*C*), 120.5 (Ar*C*), 50.06 (*C*H$_2$), 40.75 and 38.81 (*C*H$_2$ and N*C*H$_3$), -10.23 (Pd*C*H$_3$).

4.5.12. [Pd(1-benzyl-3-methylimidazolin-2-ylidene)$_2$Cl$_2$] (**4b**)

A mixture of **3b** (0.45 g, 0.68 mmol) and $PdCl_2(MeCN)_2$ (0.17 g, 0.65 mmol) was dissolved in DCM (30 ml) and stirred at ambient temperature for 1 h. The solution was filtered through celite to remove precipitated AgI, before the solvent was reduced in vacuo to a volume of ca. 5 ml. To this was added 20 ml PET ether (40–60°) to precipitate the product. The solvent was decanted, and the residue was recrystallised from DCM–PET ether (4:12 ml), washed twice with PET ether (5 ml) and dried in vacuo to afford a pale yellow powder. Yield: 76%. Anal. Calc. for $C_{22}H_{24}N_4PdCl_2·0.2CH_2Cl_2$: C, 49.49; H, 4.56; N, 10.39. Found: C, 48.93; H, 4.77; N, 10.39%. MS(LSIMS) m/z: 657 (16%) $[M - Cl + \text{ylidene}]^+$; 521 (8%) $[M + H]^+$; 487 (100%) $[M + H - Cl]^+$; 449 (22%) $[M - H - 2Cl]^+$. ^{1}H-NMR (200 Hz, DMSO-d_6): δ 7.64 (s, br, 2H, HCC*H*), 7.52 (s, br, 2H, HCC*H*), 7.39–7.18 (m, 10H, Ar*H*), 5.73 (s, br, 1H, NCH_2), 5.61 (s, br, 1H, NCH_2), 4.07 (s, 3H, NCH_3), 3.93 (s, 3H, NCH_3). ^{1}H-NMR (200 MHz, 65°C, DMSO-d_6): δ 7.58 (s, br, 2H, HCC*H*), 7.12–7.36 (m, 5H, Ar*H*), 5.69 (s, 4H, NCH_2), 4.02 (s, 6H, NCH_3). ^{13}C-NMR (60 MHz, DMSO-d_6): δ 169.3 (N*C*N), 137.4 (Ar*C*), 128.7 (Ar*C*), 128.6 (Ar*C*), 128.5 (Ar*C*), 128.0 (Ar*C*), 127.9 (Ar*C*), 123.4 (Ar*C*), 121.2 (Ar*C*), 52.99 (N*C*H$_2$), 37.2 (N*C*H$_3$).

4.5.13. [Pd(Me)(1-benzyl-3-methylimidazolin-2-ylidene)$_2$Cl] (**4c**)

A mixture of **3b** (0.72 g, 1.11 mmol) and Pd(Me)Cl(COD) (0.28 g, 1.06 mmol) was taken up in DCM and stirred overnight. The reaction mixture was filtered through a pad of celite, before the solvent was removed in vacuo to yield a white residue. This was recrystallised from DCM–ether (4:15 ml), and dried in vacuo to afford a pure white powder. Yield: 72%. Anal. Calc. for $C_{23}H_{27}N_4PdCl·0.5CH_2Cl_2$: C, 51.90; H, 5.19; N, 10.30. Found: C, 51.42; H, 5.51; N, 10.06%. MS (LSIMS) m/z: 485 (3%) $[M - CH_3]^+$, 450 (7%) $[M - CH_3 - Cl]^+$, 369 (33%) $[M - C_{10}H_{11}]^+$, 278 (17%) $[M - CH_3 - Cl - \text{ylidene}]^+$, 187 (100%) $[\text{ylidene} + CH_3]^+$. ^{1}H-NMR (400 MHz, DMSO-d_6): δ 7.23–7.50 (m, 14H, Ar*H*/imid*H*), 5.73 (d, $J = 14$ Hz, 1H, NCH_2), 5.65 (d, $J = 14$ Hz, 1H, NCH_2), 5.34 (d, $J = 14$ Hz, 1H, NCH_2), 5.39 (d, $J = 14$ Hz, 1H, NCH_2), 3.94 (s, 3H, NCH_3), 3.83 (s, 3H, NCH_3), -0.24 (d, $J = 7$ Hz, 3H,

PdCH_3). ^{13}C-NMR (100 MHz, DMSO-d_6): δ 175.7 (NCN), 135.3 (ArC), 129.1 (ArC), 129.0 (ArC), 128.7 (ArC), 128.5 (ArC), 128.3 (ArC), 128.2 (ArC), 123.3 (ArC), 53.73 (CH_2), 37.85 (NCH_3), −4.32 (PdCH_3).

4.5.14. [1,1′-dimethyl-3,3′-(1,2-xylylene)-diimidazolin-2,2′-diylidene]Pd(II) dibromide (**5a**)

To a solution of $Pd(OAc)_2$ (0.10 g, 0.45 mmol) in DMSO (10 ml) was added 1 d (0.20 g, 0.47 mmol) dissolved in DMSO (15 ml). The red-brown solution was stirred for 90 min before being heated to 135°C for 60 min, causing the colour to change to olive green. The DMSO was removed by heating in vacuo to give a yellow–green foam. This was triturated with methanol, washed with two further portions of methanol (10 ml) and dried in vacuo to give a pale yellow powder. Yield: 66%. Anal. Calc. for $C_{16}H_{18}N_4PdBr_2$: C, 36.08; H, 3.41; N, 10.52. Found: C, 35.99; H, 3.48; N, 10.34%. MS (LSIMS) m/z: 532 (15%) $[M]^+$; 453 (100%) $[M-Br]^+$; 371 (15%) $[M-HBr_2]^+$. ^{1}H-NMR (200 MHz, DMSO-d_6): δ 7.86–7.90 (m, 1H, ArH), δ 7.64 (d, $J=2$ Hz, 1H, imidH), δ 7.40–7.45 (m, 1H, ArH), δ 7.31 (d, $J=2$ Hz, 1H, imidH), δ 6.49 (d, $J=14$ Hz, 1H, NCH_2Ar), δ 5.12 (d, $J=14$ Hz, 1H, NCH_2Ar), δ 3.93 (s, 3H, NCH_3). ^{13}C-NMR (60 MHz, DMSO-d_6): δ 160.1 (NCN), δ 135.8 (ArC), δ 131.9 (ArC), δ 131.9 (ArC), δ 124.4 (ArC/imidC), δ 121.7 (ArC/imidC), δ 50.51 (NCH_2Ar), δ 38.12 (NCH_3).

4.5.15. [1,1′-dimethyl-3,3′-(1,3-xylylene)-diimidazolin-2,2′-diylidene]Pd(II) dibromide (**5b**)

Prepared in an analogous fashion to **5a** from $Pd(OAc)_2$ (0.15 g, 0.67 mmol) and **1c** (0.30 g, 0.70 mmol). Yield: 64%. Anal. Calc. for $C_{16}H_{18}N_4PdBr_2 \cdot 0.4(CH_3)_2SO$: C, 35.79; H, 3.65; N, 9.94. Found: C, 35.40; H, 3.25; N, 9.68%. MS (LSIMS) m/z: 533 (17%) $[M+H]^+$; 454 (17%) $[MH-Br]^+$; 453 (15%) $[MH-HBr]^+$; 372 (61%) $[M-Br_2]^+$; 371 (100%) $[M-HBr_2]^+$. ^{1}H-NMR (400 MHz, DMSO-d_6): δ 6.84–7.86 (m, br, 8H, xylylH/imidH), 5.15–5.71 (m, br, 4H, 2 × CH_2), 3.75–4.00 (m, br, 6H, NCH_3).

4.5.16. Pd(imidazoliophane)Br_2 (**5c**)

Prepared in an identical manner to **5a** from palladium acetate (0.08 g, 0.36 mmol) and **1e** in DMSO (20 ml). Yield: 62%. Anal. Calc. for $C_{22}H_{20}N_4Br_2Pd \cdot 0.75(CH_3)_2SO$: C, 42.42; H, 3.71; N, 8.42; S, 3.61. Found: C, 41.10; H, 3.87; N, 8.64; S, 3.51%. MS (LSIMS) m/z: 445 $[M-2Br-H]^+$.

4.5.17. [Pd(Me)(1,3-di(2-picolyl)imidazolin-2-ylidene)]BF_4 (**6a**)

Imidazolium **1f** (0.178 g, 0.621 mmol) and Ag_2O (0.14 g, 0.60 mmol) were taken up in ethanol–DCM (15:15 ml) and stirred for 1.5 h with exclusion of light, after which time PdMeCl(cod) (0.144 g, 0.543 mmol) was added and the solution stirred for a further 30 min. $AgBF_4$ (0.113 g, 0.580 mmol) was added and after 15 min the solvent removed in vacuo. The residue was taken up in DCM (10 ml), filtered through celite and the filter cake washed twice with DCM (3 ml). The solvent was then removed until ca. 1 ml remained and 5 ml of ether added to precipitate the product. Washing with ether (2 × 10 ml) and drying in vacuo afforded a pale orange powder. Yield 31 mg (12%). Anal. Calc. for $C_{16}H_{17}N_4PdBF_4$: C, 41.91; H, 3.74; N, 12.22. Found: C, 41.88; H, 3.48; N, 12.42%. MS (LSIMS): m/z 743 $[M]^+$ (dimer, 1%), 621 $[M+\text{carbene}]^+$ (monomer, 20%), 371 $[M]^+$ (monomer, 15%), 356 $[M-Me]^+$ (monomer, 35%), 256 [2-methyl-1,3-di(2-picolyl)imidazolium]$^+$ (100%), 250 [carbene]$^+$ (40%). ^{1}H-NMR (200 MHz, DMSO-d_6, 60°C): δ 8.32–8.20 (m, 2H, pyridylH$_6$), 7.90, 7.71 (2 × m, 2H, pyridylH$_4$), 7.5–7.1 (m, pyridylH$_5$, pyridylH$_3$, HCCH), 5.54 (s, 4H, NCH_2), 0.38 (s, 3H, PdCH_3, dimer), 0.06 (s, 3H, PdCH_3, monomer). ^{13}C-NMR (100 MHz, DMSO-d_6, 60°C): δ 149, 137, 135, 124, 123 (br, pyridylC), 122 (br, HCCH), 54.4 (NCH_2).

Heating a DMSO-d_6 solution of the complex at 100°C for 12 h resulted in decomposition (Pd^0 deposit) and the exclusive formation of 1,3-di(2-picolyl)-2-methylimidazolium tetrafluoroborate. MS (LSIMS): m/z 265 $[M]^+$. ^{1}H-NMR (400 MHz, DMSO-d_6, 60°C): δ 8.52 (d, $J=5$ Hz, 2H, pyridylH$_6$), 7.87 (m, 2H, pyridylH$_4$), 7.71 (s, 2H, HCCH), 7.44 (d, $J=8$ Hz, 2H, pyridylH$_3$), 7.37 (m, 2H, pyridylH$_5$), 5.57 (s, 4H, NCH_2), 2.62 (s, 3H, CCH_3). ^{13}C-NMR (100 MHz, DMSO-d_6, 60°C): δ 153.1 (pyridylC$_2$), 149.4 (pyridylC$_6$), 137.2 (NCN, pyridylC$_4$), 123.2, 122.1, 122.0 (pyridylC$_3$, pyridylC$_5$, NCCN), 51.9 (NCH_2), 9.7 (CCH_3).

4.5.18. Attempted preparation of [PdMe{1,3-bis(diisopropyl-2-ethylamino)imidazolin-2-ylidene}]BF_4 (**6b**)

The procedure followed was the same as that for **5a** to yield a very dark solid composed of **6b** and 1,3-bis-(diisopropyl-2-ethylamino)-2-methylimidazolium tetrafluoroborate **7b**. ^{1}H-NMR of the complex (200 MHz, DMSO-d_6): δ 7.49 (s, 2H, HCCH), 4.15 (m, br, 4H, N_{Im}–CH_2), 3.1 (m, br, 4H, NCH), 2.7–2.9 (m, br, 4H, N_{Im}–CH_2CH_2), 1.04 (d, 24H, NC(CH_3)$_2$), 0.41 (s, 3H, PdCH_3). MS (LSIMS): m/z 443 $[M]^+$ (0.5%), 427 $[M-CH_4]^+$ (1%), 337 [7b]$^+$ (70%), 128 [^{i}Pr$_2$NCH$_2$CH$_2$]$^+$ (100%). The completely decomposed sample gave the following spectra for **7b**: ^{1}H-NMR (200 MHz, DMSO-d_6, 100°C): δ 7.68 (s, 2H, HCCH), 4.21 (br, t, $J=6$ Hz, 4H, N_{Im}–CH_2), 3.20 (br, m, $J=8$ Hz, 4H, NCH), 2.95 (br, t, $J=6$ Hz, 4H, N_{Im}–CH$_2$CH_2), 2.72 (s, 3H, NCCH_3), 1.02 (d, $J=8$ Hz, 24H, NC(CH_3)$_2$). ^{13}C-NMR (100 MHz, DMSO-d_6, 100°C): δ 143.7 (NCN), 121.3 (HCCH), 48.8 (br, CH$_2$), 46.5 (NC(CH$_3$)$_2$), 44.0 (CH$_2$), 19.4 (NC(CH$_3$)$_2$), 9.2 (NCCH$_3$).

4.5.19. [PdCl{1,3-bis(diisopropyl-2-ethylamino)-imidazolin-2-ylidene}]BF_4 (**6c**)

This complex was prepared in the same manner as **6a** using imidazolium **1g** (0.159 g, 0.443 mmol), Ag_2O (0.07 g, 0.3 mmol), $PdCl_2(NCPh)_2$ (0.160 g, 0.417 mmol) and $AgBF_4$ (0.087 g, 0.447 mmol) to give an off-orange powder. Yield: 0.183 g (80%). Anal. Calc. for $C_{19}H_{38}N_4ClPdBF_4$: C, 41.40; H, 6.95; N, 10.16. Found: C, 41.42; H, 7.16; N, 10.25%. MS (LSIMS): m/z 463 $[M]^+$ (30%); 427 $[M-HCl]^+$ (25%); 323 [carbeneH]$^+$ (100%); 128 $[^iPr_2NCH_2CH_2]^+$ (100%). ^{1}H-NMR (200 MHz, $CDCl_3$): δ 7.32 (s, 2H, *H*CC*H*), 4.36 (br, t, 4H, N_{Im}–CH_2), 3.8 (br, 4H, NC*H*), 2.79 (br, 4H, N_{Im}–CH_2CH_2), 1.74 (d, $J=6$ Hz, 12H, NC(CH_3)$_2$), 1.10 (d, $J=6$ Hz, 12H, NC(CH_3)$_2$). ^{13}C-NMR (50 MHz, CD_2Cl_2): δ 122.4 (H*C*C*H*), 62.3 (N_{Im}–*C*H_2), 51.5 (N*C*(CH$_3$)$_2$), 50.9 ($N_{Im}CH_2C$*H*$_2$), 24.0, 20.2 (NC(*C*H$_3$)$_2$).

4.5.20. 2-bromophenyl-1-methyl-1H-pyrrole-2-carboxylate (**10**)

Oxalyl chloride (1.0 ml, 11.5 mmol) was added to a stirred solution of 1-methyl-2-pyrrolecarboxylic acid (1.35 g, 10.8 mmol) in DCM (50 ml) containing DMF (5 drops). The resultant deep red solution was stirred for 90 min, during which time the colour changed to dark brown. To this was added *o*-bromophenol (1.2 ml, 10.3 mmol) and triethylamine (3.3 ml, 23.7 mmol) dissolved in DCM (50 ml). Following cessation of HCl evolution, the mixture was stirred for 60 min before being concentrated onto silica gel (20 g). The residue was chromatographed (silica gel, 3:1 hexane–ether elution) and the appropriate fractions ($R_f=0.35$) concentrated in vacuo to give a cream powder. Yield: 65%. Anal. Calc. for $C_{12}H_{10}NO_2Br$: C, 51.45; H, 3.60; N, 5.00. Found: C, 51.38; H, 3.69; N, 4.98%. MS (EI) m/z: 281 (15%), 279 (15%) $[M]^+$; 109 (8%) $[M-C_6H_3BrO]^+$; 108 (100%) $[M-C_6H_4BrO]^+$; 80 (9%) $[M-C_7H_4BrO_2]^+$; 53 (9%) $[M-C_9H_7BrO_2]^+$. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 7.64 (d, $J=8$ Hz, 1H, pyrrole*H*), δ 7.12–7.39 (m, 4H, ArH/pyrrole*H*), δ 6.92 (s, 1H, ArH), δ 6.23 (t, $J=4$ Hz, 1H, pyrrole*H*), δ 3.98 (s, 3H, NCH_3). ^{13}C-NMR (50 MHz, $CDCl_3$): δ 227.0 (*C*–O), δ 158.9 (Ar*C*), δ 148.6 (Ar*C*), δ 133.8 (pyrrole*C*), δ 131.5 (Ar*C*), δ 128.9 (Ar*C*), δ 127.6 (pyrrole*C*), δ 124.8 (Ar*C*), δ 120.4 (Ar*C*), δ 117.2 (pyrrole*C*), δ 109.0 (pyrrole*C*), δ 37.41 (N*C*H$_3$).

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