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Chelating and 'pincer' dicarbene complexes of palladium; synthesis and structural studies †

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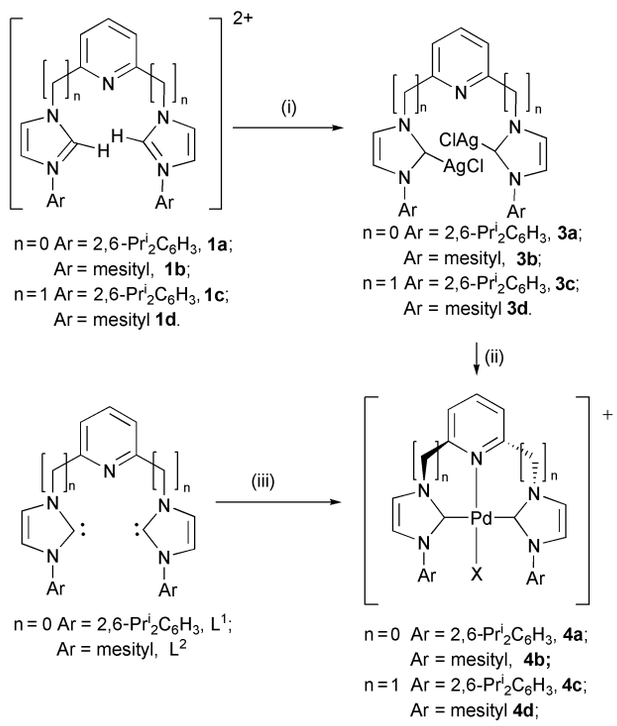
A series of 'pincer' 2,6-pyridyl dicarbene complexes of the type $[(C–N–C)PdX]^+$, **4a**, **4b**, 2,6-lutidinyl dicarbene complexes of the type $[(C\hat{}N\hat{}C)PdX]^+$, **4c**, **4d**, 1,3-xylyl dicarbene complexes of the type $[(C\hat{}C\hat{}C)PdX]$, **5a**,**5b**,**5c** and 1,2-xylyl dicarbene complexes $[(CC)PdX_2]$, **8**, where carbene is 3-arylimidazol-2-ylidene, aryl = mesityl, 2,6-$Pr^i_2C_6H_3$, X = Br or Cl, have been prepared by (i) transmetallation from the corresponding silver complexes, *i.e.* $[(C–N–C)\text{-}Ag_2Cl_2]$, $[(C\hat{}N\hat{}C)Ag_2Cl_2]$ and $[(CC)Ag_2Cl_2]$ to palladium, (ii) substitution of cod in $(cod)PdX_2$ by the 'pincer' (C–N–C) (iii) palladation of bis-imidazolium salts $[C(H)\hat{}C(H)\hat{}C(H)]$ in the presence of base. The crystal structures show that the ligands act as chelates in **4**–**5**, while in **8** as both chelate and bridging.

Introduction

The research interest in metal N-heterocyclic carbene (NHC) complexes is now expanding to the study of new versatile ligand topologies, which have shown promising spectator characteristics with 'classical' functional groups.[1] One of these is the 'pincer' architecture, which provides a preorganised backbone capable of blocking meridional or *pseudo*-meridional coordination sites of the metal, leaving the remaining available for catalysis.[2] 'Pincer' phosphine, amine, amide, imine, thioether and oxazoline complexes have been extensively studied and show interesting properties,[3] for example, unusually high thermal and air stability, stabilisation of uncommon oxidation states, stabilisation of unstable fragments on the metal, helical chirality and catalytic activity. In this paper we give full details of our efforts towards the synthesis and structural studies of various 'pincer' bis-NHC and 1,2-xylyl bis-NHC complexes. Part of this work has already been communicated.[4] Analogous complexes with methyl substituted bis-NHC functional groups have been only recently reported by Crabtree and Cavell.[5] Comparative catalytic studies of the complexes described here and the heteroatom functionalised chelating NHC complexes reported in a previous paper[6] will appear shortly. The compounds described in this paper are shown in Schemes 1, 2 and 3. The structures of compounds shown in the schemes in bold have been determined crystallographically.



Scheme 1 Reagents and conditions: (i) Ag_2O, 1,2-dichloroethane, 4Å molecular sieves, reflux; (ii) $Pd(cod)X_2$, CH_2Cl_2, RT; (iii) $Pd(cod)X_2$, THF, RT.

Results and discussion

The 2,6-pyridine- and α,α′-2,6-lutidine-bis-NHC 'pincer' complexes **4a**–**d** were prepared as shown in Scheme 1. The most general route takes advantage of the easy transmetallation of NHCs from silver to palladium firstly reported by Lin and coworkers.[7] The complexes **3a**–**d** were in turn easily accessible from bis-imidazolium salts **1a**–**d** and Ag_2O.[8] By analogy to published work on similar compounds[8] and based on ^{1}H-NMR spectroscopy we propose the structures given in Scheme 1 for **3a**–**d**; ionic isomers comprising bis-NHC silver cations and $(AgCl_2)^-$ anions are also plausible. The transmetallation reactions are usually slower than analogous with monodentate NHCs.[6] A drawback of the transmetallation method appears to be the dependence on reaction conditions (reaction time, solvent, temperature) of the composition (halide/$AgCl_2^-$) of the counter anion accompanying the cationic species (C–N–C)-PdX^+ and $(C\hat{}N\hat{}C)PdX^+$. When necessary, the residual $AgCl_2^-$ can be removed by exchange with halide or other anions or repeated recrystallisations (as has been established by ES/MS). A more convenient method applicable to (C–N–C) complexes involves the interaction of a palladium precursor with the free 'pincer' carbene ligand[9] in inert solvents. In this case quantitative yields of pure products are obtained. The palladium precursor used critically determines the nature of the complex isolated. The precursor leading to **4a**,**b** is $(cod)PdX_2$, X = Br, Cl. The products isolated from $Pd(tmed)(CH_3)_2$ and free (C–N–C) will be reported in a forthcoming paper. The complexes **4a**–**d** were characterised by analytical and spectroscopic methods, which supported the proposed stoichiometry. Of particular interest were the ^{1}H NMR data,[4] which gave a useful insight

† Electronic supplementary information (ESI) available: crystallographic data and ORTEP plot for compound **5c**. See http://www.rsc.org/suppdata/dt/b2/b209739g/

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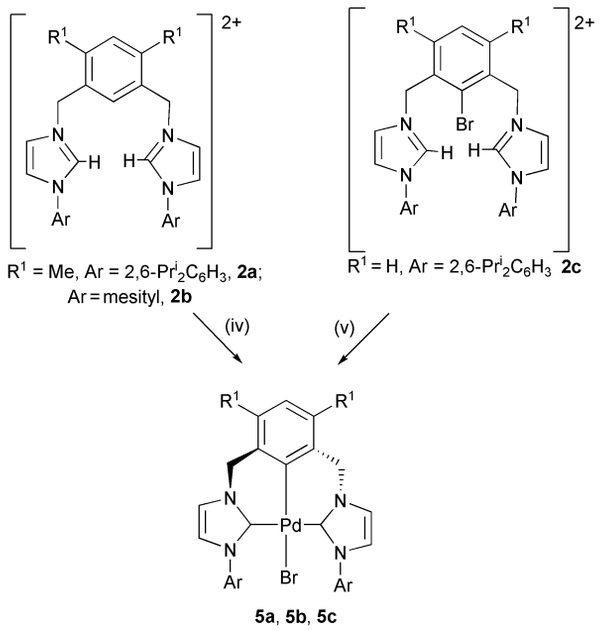
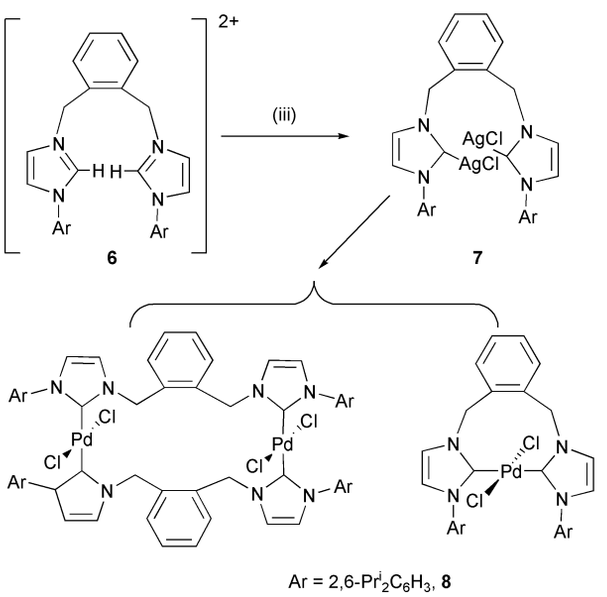


Scheme 2 Reagents and conditions: (iv) $Pd(OAc)_2$, DMAc, NaOAc, 160 °C, 24 h; (v) $Pd_2(DBA)_3$, DMAc, 160 °C, 24 h.



Scheme 3

into the symmetry of the solution structure. In this respect, the methyls of the 2,6-diisopropyl and *o*-methyls of the mesityl groups in **4a** and **4b** appear as two doublets and one singlet, respectively, indicating the presence of a symmetry plane in the molecule. The crystal structure of **4a** has already been reported[4] and **4b** is certainly isostructural based on NMR data. Compounds **4c** and **4d** were prepared in good yields following general method 1 (see Experimental section). The ^{1}H NMR data of these complexes are noteworthy. The methyls of the 2,6-diisopropyl and *o*-methyls of mesityl groups appear as four doublets and two singlets, respectively, indicating a desymmetrisation process rendering these groups diastereotopic.

An additional feature of high diagnostic value is the appearance of the CH_2 linker peaks, as an AB pattern at room temperature. These features support a non-planar dissymmetric structure in solution, which can be easily rationalised by the increased bite angles of the two fused six-membered chelate rings after the formal incorporation of the methylene linker, resulting in a non-planar helical conformation. The structure of **4c** in the solid state has already been communicated.[4] In order to study the effect (if any) of the size of the NHC aryl

Table 1 Selected bond lengths (Å) and angles (°) for **4d**

Pd(1)–N(1)	2.071(4)	N(1)–Pd(1)–Cl(1)	179.82(15)
Pd(1)–Cl(1)	2.2880(15)	C(7)–Pd(1)–C(20)	174.5(2)
Pd(1)–C(7)	1.999(6)	C(7)–Pd(1)–N(1)	87.1(2)
Pd(1)–C(20)	2.021(6)	C(20)–Pd(1)–N(1)	87.76(19)

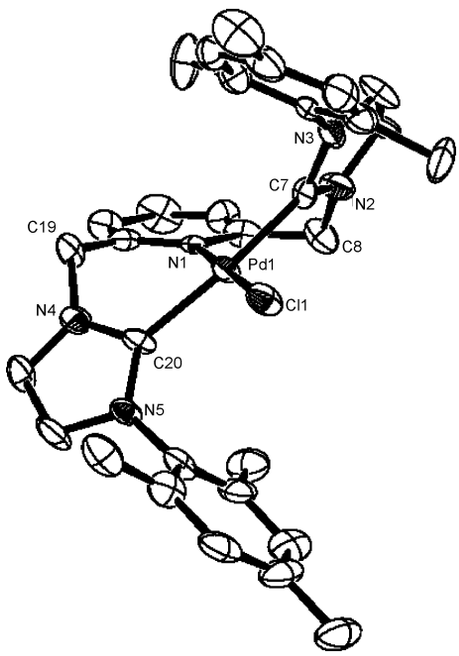


Fig. 1 Crystal structure of **4d**. Hydrogen atoms and counter ion are omitted for clarity, ellipsoids shown at 50%.

substituent on the conformation of the complex we determined the structure of **4d** in the solid state by X-ray diffraction. A diagram of the molecule is shown in Fig. 1; important bond lengths and angles are in Table 1.

The structure is based on a square-planar palladium centre and the observed conformation shows a C_2 idealised symmetry identical to the one observed for **4c**. The corresponding bond lengths in the two structures are virtually identical. Both fused six-membered rings of the 'pincer' exist in the boat conformation. The deviation from planarity of the structure **4d** can be quantified by the degree of puckering of the two chelate rings. For example, referring to Fig. 1, the distance of C(19) from the plane of C(20)–N(4)–N(1)–C(1) lies within 0.6373–0.6098 Å and the corresponding Pd from C(20)–N(4)–N(1)–C(1) is 0.8012 and 0.8051 Å. The corresponding range for **4c** is 0.5853–0.6370 and 0.8171–0.8494 Å, respectively. Therefore, it can be concluded that the degree of puckering is independent of the size of the aryl group of the NHC functionality and possibly dependent on the length of the linker and the size of the other coligands.

Formal replacement of the central pyridine nitrogen atom in **4a**–**d** with the isoelectronic C^- gives rise to cyclometallated 'pincer' backbones. It is expected that these would show higher conformational rigidity due to the stability and inertness of the aromatic carbon-metal σ-bond. Toward this end we tried to prepare the cyclometallated analogues of **4c** and **4d** by two different synthetic methods as shown in Scheme 2.

The first route involved oxidative addition of the aryl-Br of **2c** to $Pd_2(dba)_3$ leading to **5c** in good yields. The same approach has been used recently by Crabtree and coworkers[5a,b] to prepare analogues of **4c** and **4d** in which the NHC is substituted by methyls. The second method involves cyclometallation of **2a** and **2b** with $Pd(OAc)_2$ in DMAC at 160 °C. In contrast to recent reports by other researchers,[5] this reaction gave good yields of the cyclometallated analogues of **4c** and **4d** as the only spectroscopically detected and isolated products. One reason, which

Table 2 Selected bond lengths (Å) and angles (°) for **5a**

Pd(1)–C(1)	2.033(3)	C(24)–Pd(1)–C(7)	172.86(12)
Pd(1)–C(7)	2.030(3)	C(1)–Pd(1)–Br(1)	174.59(9)
Pd(1)–C(24)	2.015(3)	C(24)–Pd(1)–C(1)	86.64(13)
Pd(1)–Br(1)	2.5057(4)	C(7)–Pd(1)–C(1)	86.75(13)

could account for the observed difference is the nature of the substituents of the central aromatic ring in **2a**,**5a**, **2b** and **5b**. The presence of the methyl groups *ortho* to the imidazolium-methyl substituents could promote cyclometallation of the 2-position by blocking competing reaction at the 4- and 6-position and by increasing the electron density of the aromatic ring, favouring electrophilic attack by the palladium centre.[10] Compounds **5a**, **5b** and **5c** were characterised by spectroscopic and analytical methods. The ^{1}H NMR spectra od **5a** and **5c** are very similar, the only difference between them being the presence of the methyls of the aromatic ring at 2.3 ppm in the spectrum of **5c**. More interestingly, the symmetry of the spectra of all three species is identical with that observed for **4c** and **4d**, *i.e*. four doublets or singlets assignable to the diastereotopic methyls of the isopropyl and methyl groups of the aromatic rings, respectively, and a doublet of doublets due to the diastereotopic protons of the methylene linkers. The appearance of the ^{1}H-NMR spectrum remains unchanged up to 110 °C (toluene-d^{8}), indicating conformational rigidity. Of high diagnostic value is also the ^{13}C{^{1}H} NMR spectra in which the metallated aromatic carbons and the NHC carbons appear at *ca.* 155 and 180 ppm, respectively.

The structures of **5a** and **5c** have been determined by X-ray diffraction methods. A diagram of **5a** is given in Fig. 2; important bond lengths and angles are in Table 2. The relevant structural data for the closely related **5c** including lists of bond lengths and angles have been deposited as electronic supplementary information. The molecule adopts a C_2 symmetric structure, in which the extended system of the five linked aromatic rings of the 'pincer' ligand wraps around the square-planar palladium centre. The fused six-membered chelate rings adopt a boat conformations similar to that observed in **4c** and **4d**. The Pd–C bond lengths are Pd(1)–C(24) 2.015(3) Å, Pd(1)–C(7) 2.030(3) Å and Pd(1)–C(1) 2.033(3) Å. Attempts to synthesise the cyclometallated analogues of **4a** and **4b** are in progress.

The mechanism of formation of **5a** and **5c** is not clear, especially the nature of the species that undergoes metallation

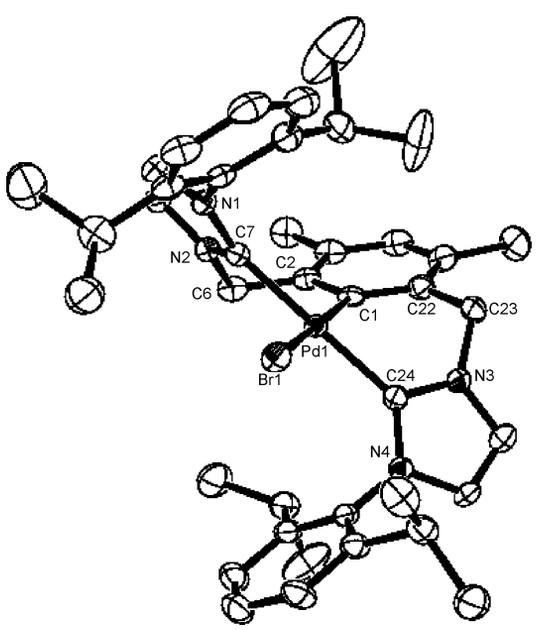


Fig. 2 Crystal structure of **5a**. Hydrogen atoms are omitted for clarity, ellipsoids shown at 50%.

Table 3 Selected bond lengths (Å) and angles (°) for **8**

Chelate complex			
Pd(2)–C(13)	1.976(17)	Cl(1)–Pd(2)–Cl(2)	176.85(16)
Pd(2)–C(24)	2.043(17)	C(13)–Pd(2)–C(24)	163.6(7)
Pd(2)–Cl(1)	2.286(4)	C(13)–Pd(2)–Cl(1)	90.1(4)
Pd(2)–Cl(2)	2.352(4)	C(13)–Pd(2)–Cl(2)	90.6(4)
Bridging complex			
Pd(1)–Cl(3)	2.310(4)	Cl(4)–Pd(1)–Cl(3)	177.61(16)
Pd(1)–Cl(4)	2.309(4)	C(51)–Pd(1)–C(89)	171.2(7)
Pd(1)–C(51)	1.969(15)	C(51)–Pd(1)–Cl(4)	88.8(4)
Pd(1)–C(89)	1.996(15)	C(51)–Pd(1)–Cl(3)	91.2(4)

of the imidazolium and the aromatic C–H carbons. The ease of formation of NHC complexes of palladium under the reaction conditions employed, points to a mono- or *trans* bis-NHC complex as being initially formed, which could further undergo cyclometallation.

Interaction of the disilver complex **7**[6] with Pd(cod)Cl$_2$ gave after recrystallisation **8** (Scheme 3). MS (ES) data for **8** indicate the association of one or two bis-NHC ligands with one or two palladium centres, respectively. The ^{1}H NMR spectrum proved to be unassignable because of the large number, and broadness, of the peaks. The ^{1}H NMR spectrum of the reaction mixture appeared to contain peaks for a number of other oligomers. The ^{13}C NMR spectrum was also unassignable due to the large numbers of similar peaks. In order to establish the identity of **8** the solid state structure was determined by X-ray diffraction. There are two molecules in the asymmetric unit; one cyclic dimeric species and one monomeric species. They are shown schematically in Fig. 3 and Fig. 4, respectively. Important bond lengths and angles are in Table 3. The dimeric species comprises two square-planar palladium centres bridged by the bidentate NHCs, which are disposed *trans* to each other. In the monomer the *trans*-disposition of the carbene function is maintained. It is interesting that the same ligand backbone with methyl substituted imidazol-2-ylidenes has been used as ligand of palladium.[11] Based on ^{13}C{^{1}-H} NMR data the authors have assigned *cis* geometry to the isolated complexes. Our difficulty in obtaining simple NMR spectra does not allow direct comparison of **8** with the compound reported in the literature.

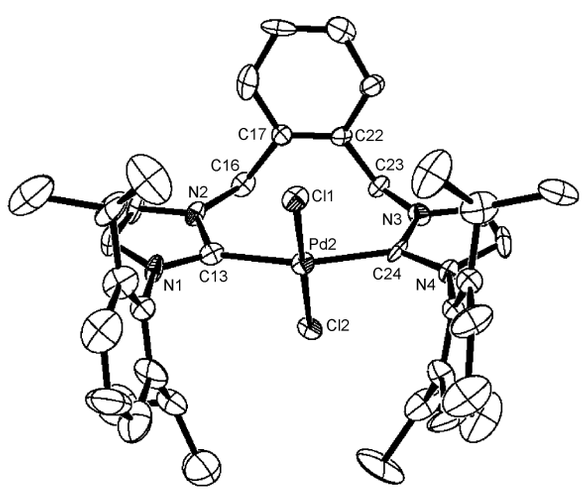


Fig. 3 Crystal structure of chelating component of **8**. Hydrogen atoms are omitted for clarity, ellipsoids shown at 50%

Experimental

Elemental analyses were carried out by the University College London Microanalytical Laboratory. NMR data were recorded on Bruker AMX-300 and DX-400 spectrometers, operating at 300 and 400 MHz (^{1}H), respectively. The spectra were

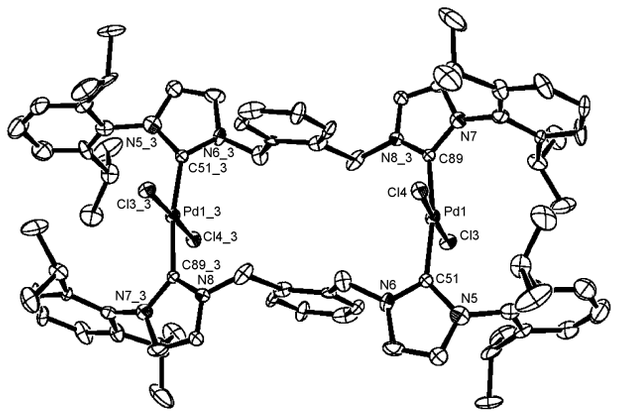


Fig. 4 Crystal structure of bridging component of **8**. Hydrogen atoms are omitted for clarity, ellipsoids shown at 50%.

referenced internally using the signal from the residual protio-solvent (^{1}H) or the signals of the solvent (^{13}C). Mass spectra (electrospray ionisation) were obtained from acetonitrile solutions on a VG Biotec platform. The calculated isotopic envelopes agree well with the experimentally observed patterns. Commercial chemicals were from Acros, Aldrich and Avocado; the light petroleum had bp 40–60 °C. The following starting materials were synthesised according to the established methods: 1,3-bis(bromomethyl)-4,6-dimethylbenzene,[10a] Pd(cod)X_2 and, Pd(cod)(CH_3)X, X = Br or Cl[12a,b] and Pd_2(dba)$_3$.[12c] The 1,2-xylyl imidazolium salts **6** and their silver carbene complexes **7** were prepared as reported previously.[8] α,α′-bis-[3-(2,6-diisopropylphenyl)imidazolium]-2-bromo-1,3-xylene **3c** was prepared following a modification of the method reported by Crabtree and coworkers.[5b] Details of the synthesis and isolation of free functionalised NHC ligands from the corresponding imidazolium salts will be described in a forthcoming paper.

2,6-Bis[3-(2,6-diisopropylphenyl)imidazolium]pyridine dibromide 1a

In a sealed glass ampoule, completely immersed in an oil bath, containing a mixture of 1-(2,6-diisopropylphenyl)imidazole (4.7 g, 21.1 mmol) and 2,6-dibromopyridine (2.0 g, 8.4 mmol) was heated at 140 °C for 4 days. After cooling to room temperature, the ampoule was opened, the brown residue was washed three times with diethyl ether and the insoluble solid was isolated by filtration. The product was obtained as a white solid. Yield: 95%. Mp: > 250 °C. MS (ES): *m*/*z* 267 (1/2M$^+$). δ_H ($CDCl_3$): 1.1, 1.2 [2 × 12H, d, CH(C*H*$_3$)$_2$], 2.4 [4H, septet, C*H*(CH$_3$)$_2$], 7.3 (4H, d, Pr$^i_2$C$_6$*H*$_2$H), 7.3 (1H, s, 5-imidazolium *H*), 7.5 (2H, t, Pr$^i_2$C$_6$H$_2$*H*), 8.1 (1H, t, 4-pyridyl *H*), 9.1 (1H, d, 3,5-pyridyl *H*), 9.9 (1H, s, 4-imidazolium *H*), 12.0 (1H, s, 2-imidazolium *H*) (Found: C, 60.99; H, 6.37; N, 9.68. Calc. for $C_{29}H_{31}Br_2N_5$: C, 60.61; H, 6.25; N, 10.10%).

2,6-Bis[3-(mesityl)imidazolium]pyridine dibromide 1b

This was prepared as **1a** from 2,6-dibromopyridine (2.0 g, 8.4 mmol) and 1-(mesityl)imidazole (3.9 g, 21.1 mmol). Yield: 95%. Mp: > 250 °C. MS (ES): *m*/*z* 225 (1/2(M + 1)$^+$). δ_H (D_2O): 2.08 (12H, s, *o*-C*H*$_3$), 2.36 (6H, s, *p*-C*H*$_3$), 7.15 (4H, s, C$_6$*H*$_2$Me$_3$), 7.85 (2H, s, 5-imidazol-2-ylidene *H*), 8.10 and 8.50 (2H, d and 1H, t, pyridine ring protons), 7.85 (2H, s, 4-imidazol-2-ylidene *H*) (Found: C, 57.00; H, 5.10; N, 11.42. Calc. for $C_{37}H_{47}Br_2N_5$: C, 57.16; H, 5.13; N, 11.49%).

α,α′-Bis-[3-(2,6-diisopropylphenyl)imidazolium]lutidine dibromide 1c

A biphasic system consisting of an aqueous solution of 2,6-di(bromomethyl)pyridine hydrogen bromide (3.0 g, 8.6 mmol), covered with diethyl ether, was neutralised at 0 °C by dropwise addition of aqueous sodium carbonate solution. The liberated free pyridine was extracted into additional diethyl ether (3 × 50 cm^3). Care is needed since the free pyridine is a persistent lachrymator. The combined diethyl ether extracts were dried with magnesium sulfate and filtered. To this rapidly stirred diethyl ether solution of 2,6-di(bromomethyl)pyridine was added 1-(2,6-diisopropylphenyl)imidazole (4.0 g, 17.5 mmol) dissolved in methanol (100 cm^3); removal of the diethyl ether under reduced pressure, eventually left the reaction mixture in methanol. This was stirred at room temperature for 12 h and at reflux for 3 h. The completion of the reaction was ensured by recording the ^{1}H NMR spectrum of aliquots. After filtering the volatiles were removed under vacuum, and the resulting solid was washed with three portions of diethyl ether giving the product as a white solid. Yield: 75%. Mp: > 250 °C. MS (ES): *m*/*z* 281 (1/2M$^+$). δ_H ($CDCl_3$): 1.05, 1.12 [2 × 12H, d, CH(C*H*$_3$)$_2$], 2.24 [4H, septet, C*H*(CH$_3$)$_2$], 6.03 (2H, s, C*H*$_2$), 7.21 (4H, d, Pr$^i_2$C$_6$*H*$_2$H), 7.28 (1H, d, 3,5-picolyl *H*), 7.32 (1H, s, 5-imidazolium *H*), 7.52 (2H, t, Pr$^i_2$C$_6$H$_2$*H*), 7.73 (1H, t, 4-picolyl *H*), 8.62 (1H, s, 4-imidazolium *H*), 10.52 (1H, s, 2-imidazolium *H*). δ_C ($CDCl_3$): 24.5, 24.8 [CH(*C*H$_3$)$_2$], 28.6 [*C*H(CH$_3$)$_2$], 54.1 (*C*H$_2$), 122.1, 124.2, 125.1, 129.5, 130.4, 132.3, 138.8, 139.7, 145.8, 153.9 (aromatics + imidazolium *C*) (Found: C, 61.40; H, 6.18; N, 9.43. Calc. for $C_{37}H_{47}Br_2N_5$: C, 61.58; H, 6.56; N, 9.71%).

α,α′-Bis[3-(mesityl)imidazolium]lutidine dibromide 1d

This was prepared as **1c** from 2,6-di(bromomethyl)pyridine hydrogen bromide (3.0 g, 8.6 mmol) and 1-(mesityl)imidazole (3.3 g, 17.6 mmol). Yield: 80%. Mp: > 250 °C. MS (ES): *m*/*z* 239 (1/2(M + 1)$^+$). δ_H ($CDCl_3$): 1.95 (12H, s, *o*-C*H*$_3$), 2.28 (6H, s, *p*-C*H*$_3$), 5.52 (4H, s, C*H*$_2$), 7.10 (4H, s, C$_6$*H*$_2$Me$_3$), 7.58 (2H, s, 5-imidazol-2-ylidene *H*), 7.60 and 8.15 (2H, d and 1H, t, pyridine ring protons), 7.78 (2H, s, 4-imidazol-2-ylidene *H*) (Found: C, 58.50; H, 5.72; N, 10.55. Calc. for $C_{31}H_{35}Br_2N_5$: C, 58.41; H, 5.53; N, 10.99%).

1,3-[Bis{3-(2,6-diisopropylphenyl)imidazolium)methyl}-4,6-dimethylbenzene dibromide 2a

1,3-Bis(bromomethyl)-4,6-dimethylbenzene (2.5 g, 8.65 mmol) and 1-(2,6-diisopropylphenyl)imidazole (2.17 g, 9.5 mmol) in dioxane (100 cm^3) was heated at 90 °C for 8 h, resulting in a white suspension. After cooling to room temperature, removal of the volatiles under reduced pressure, and washing of the white residue with diethyl ether (3 × 50 cm^3) gave the product as a white powder which was dried under vacuum. Yield: 5.3 g, 82%. MS (ES): *m*/*z* 294 (1/2M$^+$). δ_H ($CDCl_3$): 1.15, 1.20 [2 × 12H, d, CH(C*H*$_3$)$_2$], 2.3 [4H, septet, C*H*(CH$_3$)$_2$], 2.45 (6H, s, aromatic methyls), 5.95 (4H, s, C*H*$_2$, bridge), 6.95 and 7.95 (each 1H, s, aromatic *H*), 7.12 and 8.88 (each 2H, s, 4- and 5-imidazolium *H*), 7.33 (4H, d, Pr$^i_2$C$_6$*H*$_2$H), 7.50 (2H, t, Pr$^i_2$C$_6$H$_2$*H*), 10.7 (2H, s, 2-imidazolium *H*) (Found: C, 64.00 H, 6.85; N, 7.42. Calc. for $C_{40}H_{51}Br_2N_4$: C, 64.17; H, 7.00; N, 7.48%).

1,3-[Bis{3-(mesityl)imidazolium)methyl}-4,6-dimethylbenzene dibromide 2b

This was prepared by a method analogous to **2a** from 1,3-bis-(bromomethyl)-4,6-dimethylbenzene (0.81 g, 2.78 mmol) and 1-(mesityl)imidazole (1.15 g, 6.13 mmol). Yield: 1.60 g, 87%. MS (ES): *m*/*z* 252 (1/2M$^+$). δ_H ($CDCl_3$): 2.0 (12H, s, mesityl *o*-C*H*$_3$), 2.3 (2 × 6H, s, mesityl *p*-C*H*$_3$ and phenyl *m*-C*H*$_3$), 5.8 (4H, s, C*H*$_2$), 6.9 (4H, s, mesityl *H*), 7.0 and 7.8 (2 × 1H, s, phenyl *H*), 7.1 and 8.4 (2 × 2H, s, 4- and 5-imidazolium *H*), 10.3 (1H, s, 2-imidazolium *H*). δ_C ($CDCl_3$): 17.5, 19.1, 20.9 (aromatic *C*H$_3$), 66.9 (*C*H$_2$), 123.1, 124.6 (4- and 5-imidazolium *C*), 129.5, 129.7, 130.6, 133.8, 134.0, 137.3, 137.4, 138.9, 141.0 (aromatic and 2-imidazolium *C*) (Found: C, 61.52; H, 6.15; N, 8.45. Calc. for $C_{40}H_{52}Br_2N_4$: C, 61.45; H, 6.07; N, 8.43%).

[2,6-Bis{3-(2,6-diisopropylphenyl)imidazol-2-ylidene]pyridine disilver dichloride 3a

A mixture of **1a** (2.6 g, 4 mmol), Ag_2O (1.8 g, 8 mmol) and 4Å molecular sieves was refluxed in 1,2-dichloroethane (30 cm^3) for 16 h. After removal of the volatiles under reduced pressure, the remaining solids were extracted with dichlomethane (3 × 30 cm^3) and filtered through Celite. Evaporation of the dichloromethane under reduced pressure gave the crude product as a light brown solid, which was purified by trituration with chloroform to give a white product. Yield: 2.2 g, 75%. δ_H ($CDCl_3$): 1.17, 1.28 [2 × 12H, d, $CH(CH_3)_2$], 2.51 [4H, septet, $CH(CH_3)_2$], 7.23 (2H, s, 5-imidazol-2-ylidene *H*), 7.53 (2H, s), 7.31 (4H, d, $Pr^i_2C_6H_3$), 7.53 (2H, t, $Pr^i_2C_6H_3$), 8.20 (3H, m, pyridyl *H*), 8.35 [2H, br s, 4-imidazol-2-ylidene *H*]. δ_C ($CDCl_3$): 24.5, 24.7 [$CH(CH_3)$], 28.5 [$CH(CH_3)$], 116.2, 121.2 (4-,5-imidazol-2-ylidene *C*), 124.6, 125.4, 131.0, 134.8, 143.1, 145.6, 150.3 (aromatic *C*), 174.5 (2-imidazol-2-ylidene *C*).

[2,6-Bis{3-(mesityl)imidazol-2-ylidene]pyridine disilver dichloride 3b

This was prepared by a method analogous to **3a** starting from **1b** and Ag_2O. The light brown solid was purified by dissolving in the minimum amount of acetone and reprecipitating by addition of light petroleum. The white product was separated by filtration and was dried *in vacuo*. Yield: 72%. ^{1}H NMR ($CDCl_3$): δ_H 2.00 (12H, s, *o*-CH_3), 2.32 (6H, s, *p*-CH_3), 7.05 (4H, s, $C_6H_2Me_3$), 7.8–8.6 (three very broad singlets, aromatic and imidazol-2-ylidene protons). δ_C ($CDCl_3$): 18.5, 21.7 (mesityl-CH_3), 116.4, 121.9, 124.6, 130.2, 135.0, 136.0, 140.4, 143.5, (aromatic + 4-,5-imidazol-2-ylidene *C*) 150.8 (2-imidazol-2-ylidene *C*).

[2,6-Bis{3-(2,6-diisopropylphenyl)imidazol-2-ylidene]lutidine disilver dichloride 3c

A mixture of **1c** (0.5 g, 0.7 mmol), Ag_2O (0.32 g, 1.4 mmol) and 4Å molecular sieves was refluxed in 1,2-dichloroethane (30 cm^3) for 16 h. After removal of the volatiles under reduced pressure, the remaining solids were extracted with dichlomethane (3 × 30 cm^3) and the suspension was filtered through Celite. Evaporation of the dichloromethane under reduced pressure gave the crude product as a light brown solid. This was purified by dissolving in the minimum amount of acetone and reprecipitating by addition of light petroleum. The white solid was separated by filtration and was dried *in vacuo*. Yield: 0.50 g, 85%. δ_H ($CDCl_3$): 1.15, 1.20 [d, 24H, s, $CH(CH_3)_2$], 2.3 [4H, septet, $CH(CH_3)_2$], 5.53 (4H, s, CH_2), 6.95 and 7.95 (each 1H, s, aromatic *H*), 7.12 and 8.88 (each 2H, s, 4- and 5-imidazolium *H*), 7.33 (4H, d, $Pr^i_2C_6H_2H$), 7.50 (2H, t, $Pr^i_2C_6H_2H$).

[2,6-Bis{3-(mesityl)imidazol-2-ylidene}]lutidine disilver dichloride 3d

This was prepared by a method analogous to **3a** starting from **1d** (3.2 g, 5 mmol) and Ag_2O (5.8 g, 25 mmol). Yield: 2.6 g (60%). δ_H ($CDCl_3$): 1.96 (12H, s, *o*-CH_3), 2.34 (6H, s, *p*-CH_3), 5.53 (4H, s, CH_2), 6.95 (4H, s, $C_6H_2Me_3$), 6.98 (2H, s, 5-imidazol-2-ylidene), 7.19 and 7.73 (2H, d and 1H, t, pyridine ring protons), 7.54 (2H, s, 4-imidazol-2-ylidene *H*).

Preparation of palladium complexes

General method 1

A dichloromethane solution of the corresponding silver carbene complex **3a**–**d** was added dropwise to a solution of (cod)PdX_2 and stirred at room temperature for 12–24 h. After completion of the reaction, the mixture was filtered, the volatiles were removed under vacuum, and the resulting solid was washed with diethyl ether. Drying under vacuum gave the products as pale yellow solids. Purification was carried out by recrystallisation from a saturated solution of dichloromethane and diethyl ether or by extraction into hot toluene and precipitation by cooling or slow evaporation.

General method 2

A THF solution of the free 'pincer bis-NHC was added dropwise to a cold (−50 °C) solution of an equimolecular amount of Pd(cod)Cl_2 in the same solvent. After warming to room temperature and stirring for 6 h the volatiles were evaporated under reduced pressure, the product was washed with petroleum and dried under vacuum. Crystallisation can be carried out as above.

{{2,6-Bis[3-(2,6-diisopropylphenyl)imidazol-2-ylidene]pyridine}-(chloro)palladium} chloride/(silver dichloride) salt 4a

This was prepared following the general method 1 from {2,6-bis[3-(2,6-diisopropylphenyl)imidazol-2-ylidene]pyridine}-disilver dichloride **3a** (0.5 g, 0.61 mmol) and (cod)$PdCl_2$ (0.17 g, 0.61 mmol) in dichloromethane (150 cm^3) by stirring at room temperature for 24 h. The product was obtained in quantitative yields as a yellow solid. X-Ray diffraction quality crystals were obtained by layering a saturated dichloromethane solution with light petroleum. MS (ES): *m*/*z* 674.1, $[Pd(ligand)Cl]^+$. δ_H ($CDCl_3$): 1.1, 1.2 (24H, 2 × d, isopropyl CH_3), 2.5 (4H, septet, isopropyl *CH*), 7.0 (2H, d, 5-imidazol-2-ylidene *H*), 7.2 (4H, d, $Pr^i_2C_6H_2H$), 7.4 (2H, t, $Pr^i_2C_6H_2H$), 8.5 (1H, t, 4-pyridyl *H*), 9.0 (2H, d, 3,5-lutidyl *H*), 9.3 (2H, d, 4-imidazol-2-ylidene *H*). δ_C ($CDCl_3$): 23, 24 [$CH(CH_3)$], 28 [$CH(CH_3)$], 111 (5-imidazol-2-ylidene *C*), 120 ($Pr^i_2C_6H_3$ *C*), 124 (3,5-pyridyl *C*), 126, 132, 135 ($Pr^i_2C_6H_3$ *C*), 145 (4-midazol-2-ylidene *C*), 151 (4-pyridyl *C*), 170 (2,6-pyridyl *C*), 174 (2-imidazol-2-ylidene *C*) [Found: C, 53.22; H, 5.60; N, 8.61. Calc. for $(C_{35}H_{41}Cl_2N_5Pd)_5$-$(AgCl)_3$: C, 52.87; H, 5.20; N, 8.81%].

The same compound was obtained by following the general method 2 from the 'pincer' dicarbene L^1 (0.3 g, 0.62 mmol) and (cod)$PdCl_2$ (0.17 g, 0.61 mmol) in thf. Yield quantitative. The isolated product is identical (by ^{1}H NMR) to that prepared by method 1.

{{2,6-Bis[3-(mesityl)imidazol-2-ylidene]pyridine}(chloro)-palladium} chloride/(silver dichloride) salt 4b

This was prepared following the general method 1 from {2,6-bis[3-(mesityl)imidazol-2-ylidene]pyridine}disilver dichloride (0.2 g, 0.27 mmol) and (cod)$PdCl_2$ (0.08 g, 0.27 mmol) in dichloromethane (100 cm^3) by stirring at room temperature for 24 h. The product was obtained in quantitative yield as a yellow solid. MS (ES): *m*/*z* 589.7, $[Pd(ligand)Cl]^+$. δ_H ($CDCl_3$), 2.0 (12H, s, mesityl CH_3), 2.2 (6H, s, mesityl CH_3), 6.9 (4H, s, mesityl *H*), 6.9 (2H, d, 5-imidazol-2-ylidene *H*), 8.5 (1H, d, 4-picolyl *H*), 9.0 (2H, d, 3,5-picolyl *H*), 9.3 (2H, d, 4-imidazol-2-ylidene *H*). δ_C ($CDCl_3$): 18, 21 (CH_3), 111 (5-imidazol-2-ylidene *C*), 121 (mesityl *C*), 125 (3,5-pyridyl *C*), 129, 133, 134 (mesityl *C*), 140 (4-imidazol-2-ylidene *C*), 151 (4-pyridyl *C*), 169 (2,6-pyridyl *C*), 175 (2-imidazol-2-ylidene *C*) {Found: C, 49.64; H, 6.12; N, 7.01. calc. for $[C_{29}H_{29}Cl_2N_5Pd(C_4H_{10}O)_3]$-AgCl: C, 49.71; H, 6.00; N, 7.07%}.

The same compound was obtained by following the general method 2 from the 'pincer' dicarbene L^2 (0.28 g, 0.62 mmol) and (cod)$PdCl_2$ (0.17 g, 0.61 mmol) in thf. Yield quantitative. The isolated product is identical (by ^{1}H NMR) to that prepared by method 1.

{{α,α′-Bis[3-(2,6-diisopropylphenyl)imidazol-2-ylidene]lutidine}-(chloro)palladium} chloride/(silver dichloride) salt 4c

This was prepared following the general method 1 from {α,α′-bis[3-(2,6-diisopropylphenyl)imidazol-2-ylidene]lutidine}-disilver dichloride **3c** (0.5 g, 0.59 mmol) and (cod)$PdCl_2$ (0.17 g, 0.59 mmol) in dichloromethane (150 cm^3) by stirring at room

temperature for 24 h. The product was obtained in quantitative yield as a yellow solid. X-Ray diffraction quality crystals were obtained by layering a saturated dichloromethane solution with light petroleum. MS (ES): *m*/*z* 702.2, $[Pd(ligand)Cl]^+$. δ_H ($CDCl_3$): 0.9, 1.0, 1.2, 1.3 (24H, 4 × d, isopropyl C*H*$_3$), 1.9, 2.6 (4H, 2 × septet, isopropyl C*H*), 5.4, 6.5 (4H, 2 × d, C*H*$_2$), 6.7 (2H, d, 5-imidazol-2-ylidene *H*), 7.1, 7.2 (4H, 2 × d, $Pr^i_2C_6H_2H$), 7.3 (2H, t, $Pr^i_2C_6H_2H$), 8.0 (1H, t, 4-lutidyl *H*), 8.0 (2H, d, 4-imidazol-2-ylidene *H*), 8.4 (2H, d, 3,5-lutidyl *H*). δ_C ($CDCl_3$): 23, 24, 25, 26 [CH(*C*H$_3$)], 28, 29 [*C*H(CH$_3$)], 55 (C*H*$_2$), 122 (5-imidazol-2-ylidene *C*), 123 ($Pr^i_2C_6H_3$ *C*), 124 (3,5-pyridyl *C*), 125, 127, 130, 135 ($Pr^i_2C_6H_3$ *C*), 142 (4-pyridyl *C*), 145 (4-imidazol-2-ylidene *C*), 147 ($Pr^i_2C_6H_3$ *C*), 155 (2,6-pyridyl *C*), 168 (2-imidazol-2-ylidene *C*) [Found: C, 54.39; H, 5.95; N, 8.22. Calc. for $(C_{37}H_{45}Cl_2N_5Pd)_5(AgCl)_3$: C, 53.99; H, 5.57; N, 8.51%].

{α,α′-Bis[3-(mesityl)imidazol-2-ylidene]lutidine}(chloro)-palladium} chloride/(silver dichloride) salt 4d

This was prepared following the general method 1 from {α,α′-bis[3-(mesityl)imidazol-2-ylidene]lutidine} disilver dichloride **3d** (0.2 g, 0.26 mmol) and (cod)$PdCl_2$ (0.08 g, 0.26 mmol) in dichloromethane (100 cm^3) by stirring at room temperature for 24 h. The product was obtained in quantitative yields as a yellow solid. X-Ray quality crystals were obtained by layering a saturated dichloromethane solution with light petroleum. MS (ES): *m*/*z* 618.0, $[Pd(ligand)Cl]^+$. δ_H ($CDCl_3$): 1.9 (6H, s, C*H*$_3$), 2.1 (6H, s, C*H*$_3$), 2.3 (6H, s, C*H*$_3$), 6.3, 5.5 (4H, 2 × d, C*H*$_2$), 6.7 (1H, d, 4-imidazol-2-ylidene *H*), 6.9 (2H, s, mesityl *H*), 6.9 (2H, s, mesityl *H*), 7.9 (1H, d, 5-imidazol-2-ylidene *H*), 8.1 (1H, t, 4-lutidyl *H*), 8.4 (1H, d, 3,5-lutidyl *H*). δ_C($CDCl_3$): 19, 19 21, (mesityl *C*H$_3$), 55 (C*H*$_2$), 122 (5-imidazol-2-ylidene *C*), 123 (mesityl *C*), 127 (3,5-lutidyl *C*), 129, 129 134, 135, 136, (mesityl *C*), 139 (4-imidazol-2-ylidene *C*), 141 (4-lutidyl *C*), 155 (2,6-lutidyl *C*), 168 (2-imidazol-2-ylidene *C*) (Found: C, 50.27; H, 4.81; N, 8.71. Calc. for $(C_{31}H_{33}Cl_2N_5Pd)_3(AgCl)_2$: C, 49.74; H, 4.44; N, 9.36%).

Bromo{1,3-[bis{3-(2,6-diisopropylphenyl)imidazol-2-ylidene)-methyl}-4,6-dimethylbenzene}palladium 5a

A mixture of $Pd(OAc)_2$ (0.07 g, 0.31 mmol), **2a** (0.23 g, 0.31 mmol), $NaOOCCH_3$ (0.26 g, 3.5 mmol) and *N*,*N*′-dimethylacetamide (20 cm^3) was heated in a sealed rotaflo ampoule at 160 °C for 24 h, giving a dark-red–purple mixture. After removal of the volatiles under reduced pressure at 70–80 °C, the residue was extracted into diethyl ether (3 × 30 cm^3), the extracts were passed through a short alumina pad deactivated with thf, and concentated to *ca.* 5 cm^3, to give the product as a white crystalline material. X-Ray quality crystals were obtained from diethyl ether solutions by slow evaporation. Yield: 0.12 g, 52%. MS (ES): *m*/*z* 732.0, $[Pd(ligand)(MeCN)]^+$. δ_H ($CDCl_3$): 0.6, 1.0, 1.2, 1.3 (24H, 4 × d, isopropyl C*H*$_3$), 2.2, 2.8 (4H, 2 × septet, isopropyl C*H*), 2.3 (6H, s, *o*-C*H*$_3$), 4.9, 5.2 (4H, 2 × d, C*H*$_2$, AB pattern), 6.4 (1H, s, aromatic *H*), 6.5 (2H, d, 5-imidazol-2-ylidene *H*), 6.9 (2H, d, 4-imidazol-2-ylidene *H*), 7.0, 7.1 (4H, 2 × d, $Pr^i_2C_6H_2H$), 7.3 (2H, t, $Pr^i_2C_6H_2H$). δ_C ($CDCl_3$): 18.9 (*C*H$_3$-phenyl), 22.2, 22.6, 23.4, 23.7 [CH(*C*H$_3$)], 26.9, 27.6 [*C*H(CH$_3$)], 52.9 (*C*H$_2$), 117.9, 121.9 (4- and 5-imidazol-2-ylidene *C*), 122.6, 122.7, 125.6, 127.9, 129.4, 135.3, 136.1, 144.2, 145.3, 155.5 (*C-ipso*), 180.9 (imidazol-2-ylidene *C*) (Found: C, 62.06; H, 6.45; N, 6.91. Calc. for $C_{40}H_{49}N_4BrPd$: C, 62.22; H, 6.40; N, 7.26%).

Bromo{1,3-[Bis{3-(mesityl)imidazol-2-ylidene)methyl}-4,6-dimethylbenzene}palladium 5b

A mixture of $Pd(OAc)_2$ (0.07 g, 0.31 mmol), **2a** (0.21 g, 0.31 mmol), $NaOOCCH_3$ (0.303 g, 3.7 mmol) and *N*,*N*′-dimethylacetamide (20 cm^3) was heated in a sealed rotaflo ampoule at 160 °C for 24 h, giving a dark-red–purple mixture. After removal of the volatiles under reduced pressure at 70–80 °C, the residue was extracted into diethyl ether (3 × 30 cm^3), the extracts were passed through a short alumina pad deactivated with thf, and concentated to *ca.* 5 cm^3, to give the product as a white crystalline material. X-Ray quality crystals were obtained from diethyl ether solutions by slow evaporation. Yield: 0.12 g, 60%. *m*/*z* 650.0, $[Pd(ligand)(MeCN)]^+$. δ_H ($CDCl_3$): 1.8 (6H, s, phenyl C*H*$_3$) 2.2, 2.3 (2 × 6H, s, mesityl C*H*$_3$), 2.4 (6H, s, mesityl C*H*$_3$), 5.1, 5.3 (2 × 2H, d, C*H*$_2$, AB pattern), 6.6 (3H, br s, 5-imidazol-2-ylidene *H* and *p*-phenyl *H*), 6.9 (4H, s, mesityl *H*), 7.1 (2H, s, 4-imidazol-2-ylidene *H*). δ_C ($CDCl_3$): 18.6, 19.3, 19.9, 21.0 (*C*H$_3$), 53.7 (*C*H$_2$), 119.4, 121.5 (4- and 5-imidazol-2-ylidene *C*), 127.0, 128.5, 128.7, 130.7, 134.6, 136.0, 136.4, 136.9, 137.6, 156.2 (*C-ipso*), 180.9 (2-imidazol-2-ylidene *C*) (Found: C, 58.55 H, 5.65; N, 8.05. Calc. for $C_{34}H_{37}N_4BrPd$: C, 59.36; H, 5.42; N, 8.14%).

Bromo{1,3-[bis{3-(2,6-diisopropylphenyl)imidazol-2-ylidene)-methyl}benzene}palladium 5c

A mixture of $Pd_2(dba)_3$ (0.080 g, *ca.* 0.1 mmol), **2a** (0.16 g, 0.2 mmol), $NaOOCCH_3$ (0.25 g, excess) and *N*,*N*′-dimethylacetamide (20 cm^3) was heated in a sealed rotaflo ampoule at 160 °C for 24 h, giving a dark-red–brown mixture. After removal of the volatiles under reduced pressure at 70–80 °C, the residue was extracted into diethyl ether (3 × 30 cm^3), the extracts were passed through a short alumina pad deactivated with thf, and concentated to *ca.* 5 cm^3, to give the product. Crystals were grown by slowly evaporating ether solutions. The compound is soluble in hot toluene and chlorinated solvents. Yield: 0.1 g, *ca.* 65%. δ_H ($CDCl_3$): 0.6, 1.1, 1.3, 1.4 (24H, 4 × d, isopropyl C*H*$_3$), 2.2, 2.9 (4H, 2 × septet, isopropyl C*H*), 3.0 (6H, s, *o*-C*H*$_3$), 4.7, 5.5 (4H, 2 × d, C*H*$_2$), 6.7 (2H, d, 5-imidazol-2-ylidene *H*), 7.1, 7.2 (4H, 2 × d, $Pr^i_2C_6H_2H$), 7.3 (2H, t, $Pr^i_2C_6H_2H$), 8.0 (2H, d, 4-imidazol-2-ylidene *H*), 7.5 (2H, d, aromatic *H*), 7.7(1H, t, aromatic *H*).

Dichloro{α,α′-bis[3-(2,6-diisopropylphenyl)imidazol-2-ylidene]-*o*-xylene}palladium 8

This was prepared following general method 1 from {α,α′-bis-[3-(2,6-diisopropylphenyl)imidazol-2-ylidene]-*o*-xylene} disilver dichloride (0.2 g, 0.24 mmol) and (cod)$PdCl_2$ (0.07 g, 0.24 mmol) in dichloromethane (100 cm^3) by stirring at room temperature for 24 h. The crude product was obtained in quantitative yields as a yellow solid. X-Ray diffraction quality crystals were obtained by layering a saturated dichloromethane solution with light petroleum. MS (ES): *m*/*z* 617.2, $[Pd(ligand)Cl]^+$, 656.3, $[Pd(ligand)Cl + MeCN]^+$, 694.2, $[Pd(ligand)Cl_2 + MeCN]^+$, 1302.1, $[Pd_2(ligand)_2Cl_4 - 1]^+$.

δ_H ($CDCl_3$): very broad spectrum (see Discussion) (Found: C, 62.64; H, 6.74; N, 6.92. Calc. for $C_{38}H_{46}Cl_2N_4Pd$: C, 62.00; H, 6.30; N, 7.60%).

Crystallography

A summary of the crystal data, data collection and refinement parameters for compounds **4d**, **5a** and **8** are given in Table 4. Data for compound **5c** are provided as supplementary data to the main paper and CIF files are available. All data sets were collected on a Enraf Nonius KappaCCD area detector diffractometer with rotating anode FR591 and an Oxford Cryosystems low-temperature device operating in omega scanning mode with phi and omega scans to fill the Ewald sphere. The programs used for control and integration were Collect, Scalepack and Denzo.[13] The crystals were mounted on a glass fibre with silicon grease, from Flombin vacuum oil. All solutions and refinements were performed using the WinGX package[14] and all software packages within. The unit cell of compound **4d** contains the palladium pincer complex and a

Table 4 Crystallographic summary for compounds **4d**, **5a** and **8**

	4d	**5a**	**8**
Chemical formula	$C_{31}H_{33}Cl_2N_5Pd$	$C_{42}H_{49}BrN_4OPd$	$C_{76}H_{92}Cl_4N_8Pd_2$
Formula weight	652.92	812.16	1472.18
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
a/Å	10.823(2)	12.0839(2)	16.948(3)
b/Å	20.571(4)	15.3863(3)	33.444(7)
c/Å	19.286(4)	20.9393(5)	16.958(3)
α/°	90	90	90
β/°	90.86(3)	90.3890(10)	98.70(3)
γ/°	90	90	90
V/Å^3	4293.5(15)	3893.08(14)	9501(3)
Z	4	4	4
T/K	150	150	150
μ/mm^{-1}	0.577	1.540	0.527
No. data collected	30684	24463	33683
No. unique data	9674	8755	12810
R_{int}	0.0863	0.0534	0.2468
Final $R(\|F\|)$ for $F_o > 2\sigma(F_o)$	0.0860	0.0444	0.0982
Final $R(F^2)$ for all data	0.2511	0.1158	0.3377

chloride counter ion, the chloride being disordered over multiple sites in the unit cell. This is believed to be caused by the C_2 symmetry of the cation creating possible locations that a chloride ion can occupy. As an ion pair they exist quite tight to one another creating two non-superimposable ion pairs that the crystal packing is unable to discriminate. From modelling the density based on the weightings from the FVAR command it is calculated from the data that the two general locations total a 50 : 50 split of the electron density for one chloride ion, confirming the possibility of the two locations. The unit cell of **5a** contains a disordered unit of diethyl ether which was the solvent of crystallistion, residual high electron density peaks are associated with this disorded unit and do not represent another species in the unit cell. The unit cell of **5c** contains three units of the palladium complex and one unit of diethyl ether, the data for this is supplied as a supplementary CIF file. The crystals of **8** were of a poor quality and associated errors are due to this, as many discordant reflections were omitted from the final refinements of the structure. The cell contains two independent molecules, a chelating palladium complex and a cyclic bridged species which have co-crystallised. On close examination there was no detectable independent crystals of a single product from the sample.

CCDC reference numbers 194842–194845.

See http://www.rsc.org/suppdata/dt/b2/b209739g/ for crystallographic data in CIF or other electronic format.

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