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Functionalised and chelate heterocyclic carbene complexes of palladium; synthesis and structural studies †

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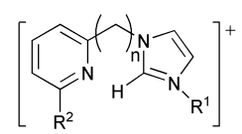
Received 20th September 2002, Accepted 17th December 2002
First published as an Advance Article on the web 24th January 2003

A series of picolyl-functionalised, [(C^N)PdXY], **1a**, **2a**, **3a** and **4**, pyridyl-functionalised, [(C–N)PdXY], **5a**, **6**, **7** and **8**, methoxymethyl-functionalised, $[(C^O)Pd(\mu\text{-}X)X]_2$, **10**, and *trans*-$[(C^O)_2PdX_2]$, **11**, and diethylcarbamoylmethyl-functionalised, *trans*-$[(C^amide)_2PdX_2]$, **12**, N-heterocyclic carbene (NHC) complexes of palladium(II), (C^N) = (3-R^1)-[1-(α-picolyl)imidazol-2-ylidene, (C–N) = (3-R^1)[1-(2-pyridyl)imidazol-2-ylidene, R^1 = Bu^t, mesityl, 2,6-$Pr^i_2C_6H_3$, (C^O) = (3-R^1)(1-methoxymethyl)imidazol-2-ylidene, R^1 = 2,6-$Pr^i_2C_6H_3$, (C^amide) = (3-R^1)(1-diethylcarbamoyl-methyl)imidazol-2-ylidene, R^1 = 2,6-$Pr^i_2C_6H_3$, Y = Me, X = Br or Cl, have been synthesised by interaction of (1,5-cod)-PdXY or (1,5-cod)PdX_2 with the corresponding silver NHC complexes, or (in certain cases) with the free functionalised NHC ligands. Derivatives of **1a**, **2a**, **3a** and **5a** were prepared by substitution of the halide X by weakly coordinating anions. The majority of the complexes described here were characterised by spectroscopic and diffraction methods and show that the (C–N) and (C^N) ligands act as chelates, while the methoxymethyl- and diethylcarbamoylmethyl-functions in **10**, **11** and **12**, respectively, are dangling. Derivatives of **5a** in which the pyridine ring is substituted with electron withdrawing or bulky substituents show only minor variation of the pyridine–palladium distances.

Introduction

The use of N-functionalised nucleophilic heterocyclic carbene (NHC) ligands is a recent development in successful ligand designs incorporating NHCs.[1] The rationale for their synthesis originated from the desire to tailor the coordination sphere of a metal by chelating ligands incorporating a strongly bound, robust functional group, (NHC), with additional tethers carrying labile donors.[2] The latter can temporarily dissociate during catalytic reactions creating electronic and coordinative unsaturation, which is important for catalysis. Towards this end we have synthesised NHC precursors functionalised with substituted pyridine rings (Scheme 1).[3] Related ligand designs, where R^1 = Me, n = 1, have been simultaneously[4a] or lately[4b] reported by others.



R^1 = Bu^t, mesityl, 2,6-$Pr^i_2C_6H_3$

Scheme 1

Herein, we give full details on the synthesis, structures and the substitution chemistry of palladium complexes with pyridine-, picoline-, methoxymethyl- and diethylcarbamoylmethyl-functionalised imidazol-2-ylidenes. In a forthcoming paper comparative catalytic studies of the palladium complexes in C–C coupling reactions will be reported. A preliminary communication of this work has already appeared.[5]

Results and discussion

Ligand designs

The σ-donating pyridine rings tethered to the NHCs are believed to add versatility to the ligand designs for the following reasons: (i) the pyridine function is expected to bind weakly to lower, softer oxidation states of the metal. (ii) This, in combination with adjustment of the chelate ring size by using variable length linkers, can promote ligand hemilability with possible implications on the catalytic activity. (iii) The electronic asymmetry of the chelating N-functionalised NHC ligand renders the corresponding *trans*-sites electronically inequivalent, due to large difference in the *trans* effect of the chelating ends. (iv) The donor and steric characteristics of the pyridine and NHC functional groups are easily tunable by a variety of substituents. In order to test these hypotheses and gain a better understanding of the effect of the functional group on the structure and reactivity of the palladium complexes we synthesised the compounds shown in Scheme 2.

Synthesis and characterisation of the palladium complexes

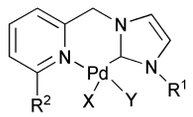
The palladium complexes can be easily prepared by one of the following synthetic methods (Scheme 3): (1) Interaction of a palladium precursor complex, usually Pd(cod)(CH_3)Br or Pd(cod)Cl_2, with silver carbene reagents, resulting in mild and quantitative transmetallation. (2) Interaction of the palladium precursor complex with the free functionalised carbene in an inert solvent. (3) Reaction of the palladium precursor complex with the functionalised carbene generated *in situ* from the corresponding imidazolium salt and lithium or potassium amide bases in thf.

The method of choice depends on the nature of the ligand to be introduced. In general, method 2 is best suited to pyridine (not picoline) functionalised ligands and can easily be scaled up. However, the limited stability of picoline functionalised carbenes presents a serious limitation to the wider applicability of method 2. In this case, transmetallation from silver carbenes can successfully be carried out. Finally, reaction of the *in situ* generated carbene with the palladium precursors is also widely applicable even though product mixtures that are difficult to purify are sometimes obtained.

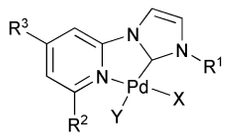
All palladium complexes described in this paper were obtained as white or yellow air-stable solids and characterised

† Electronic supplementary information (ESI) available: crystallographic data and ORTEP plots for complexes **4**, **7**, **8** and **13**. See http://www.rsc.org/suppdata/dt/b2/b209231j/

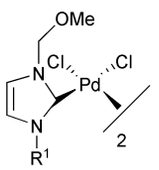
DOI: 10.1039/b209231j



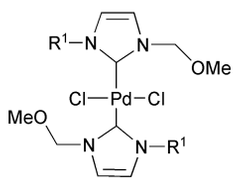
R^2= H, R^1 = Bu^t, Y=CH_3 X=Br, 1a; X=OTs, 1b; X=OTf, 1c; X=$OOCCF_3$, **1d**.[5]
R^2=H, R^1 = 2,4,6-$Me_3C_6H_2$, Y=CH_3 , X=Br, **2a**;[5] X=OTs, 2b; X=OTf, 2c; X=$OOCCF_3$, 2d.
R^2=H, R^1 = 2,6-$Pr^i_2C_6H_3$, Y=CH_3, X=Br, **3a**; X=OTs, 3b;
R^2 = CH_3, R^1 = 2,6-$Pr^i_2C_6H_3$, Y=CH_3, X=Br, **4**.



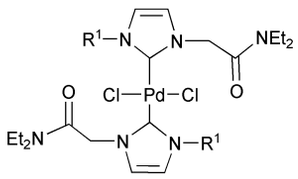
R^2, R^3 = H, R^1 = 2,6-$Pr^i_2C_6H_3$, Y=CH_3, X=Br **5a**; X=OTs, **5b**.
R^2=$SiMe_3$, R^3=H, R^1 = 2,6-$Pr^i_2C_6H_3$, X=Br, Y=CH_3 6
R^2 =H, R^3 =$SiMe_3$, R^1 = 2,6-$Pr^i_2C_6H_3$, X=Br, Y=CH_3 **7**
R^2 =H, R^3 =CF_3, R^1 = 2,6-$Pr^i_2C_6H_3$, X=Br, Y=CH_3 **8**



R^1 = 2,6-$Pr^i_2C_6H_3$, **10**

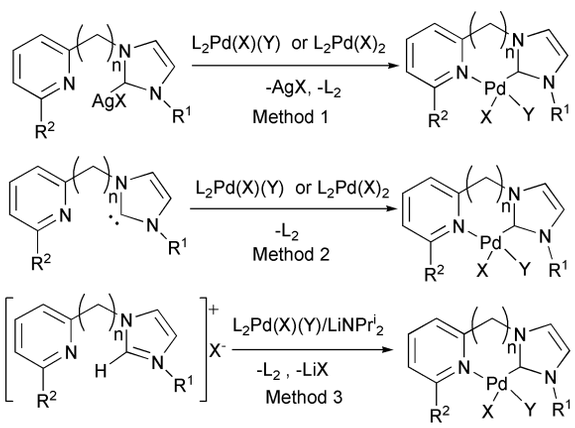


R^1 = 2,6-$Pr^i_2C_6H_3$, **11**



R^1 = 2,4,6-$Me_3C_6H_2$, **12**

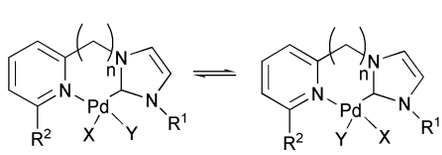
Scheme 2 Palladium complexes described in this paper. Compounds given in bold have been structurally characterised.



Scheme 3

by spectroscopic and analytical methods. Of particular diagnostic value were the ES mass spectra, which showed the association of the ligand system with the Pd(CH_3CN)(Me) or Pd(CH_3CN)X fragments, and the ^{1}H and $^{13}C\{^1H\}$ NMR spectra. The majority of the ^{1}H NMR spectra reported here show sharp peaks at room temperature, with the exception of the peaks assignable to the CH_2 linker of the C^N ligands, which can be broad at room temperature. Fluxional behaviour was observed at elevated temperatures (*vide infra*). The features used to identify the formation of the palladium complexes were: a weak peak between 163 and 185 ppm in the $^{13}C\{^1H\}$ NMR spectra assignable to the carbene carbon; a broad singlet or pair of doublets observed between 5.2 and 6.5 ppm in the ^{1}H NMR and a peak observed between 55 and 59 ppm in the ^{13}C NMR spectra, assigned to the protons and the carbons, on the methylene bridge of the picolyl complexes **2** and **3** and the methoxy- and diethylcarbamoyl-methyl complexes **10**, **11** and **12**, respectively; a low field doublet or a doublet of doublets between 9.0 and 9.6 ppm and a triplet of doublets between 7.5 and 8.0 ppm in the ^{1}H NMR spectra for the C^N and C–N complexes assigned to the protons in the 6- and 4-positions of the pyridine rings, respectively; ‡ two doublets, between 6.7 and 7.1 ppm, and 7.2 and 8.0 ppm in the ^{1}H NMR spectra, assigned to the protons in the 5- and 4- position of the imidazol-2-ylidene ring, when the ligand is acting as a chelate. When the R^1 group is *tert*-butyl a singlet is observed at around 2.0 ppm; when R^1 is mesityl, the methyls appear as singlets at around 2.1 and 2.3 ppm; when R^1 is 2,6-diisopropylphenyl the isopropyl groups give rise to two doublets between 0.8 and 1.5 ppm and one septet between 2.0 and 2.7 ppm, respectively.

Variable temperature ^{1}H NMR spectroscopy revealed that the diastereotopic protons of the methylene bridge in **1a**, **2a** and **3a**, **3b** exchanged at room temperature. The rate of the dynamic process is affected by the size of the R^1 group, with the larger ones (*i.e.* 2,6-diisopropylphenyl) slowing it down the most. Thus, the broad singlet or pair of doublets observed between 5.2 and 6.5 ppm is split to a pair of doublets or coalesces to a singlet by cooling or warming the sample, respectively. This behaviour is thought to originate from chelate ring flipping, which renders the coordination plane as the symmetry plane of the molecule on the NMR time scale. The same process is thought to be responsible for the temperature dependence of the isopropyl region of the spectrum of **3a**. In this case the diastereotopic methyls of the isopropyl groups appear as two doublets at room temperature and the methine proton as a septet. At *ca.* −20 °C each of the doublets splits further into two doublets and, simultaneously, the methine septet splits into two, giving rise to the spectrum corresponding to the static structure. With the more rigid five-membered chelate ring in **5**–**8** there is no ring flipping observed. Another interesting feature of the ^{1}H NMR spectra of **1a**–**5a**, is the apparent duplication of all peaks of the spectrum. The intensity ratio of the associated resonances varies between 6 : 1 and 4 : 1. This is possibly arising from the presence of two isomers as shown in Scheme 4 and supported by 2D NOESY and C–H correlation NMR experiments.



Scheme 4

Further insight into the identity of the compounds **3a**, **4** and **5a** was gained by X-ray diffraction studies. The molecules **3a** and **5a** are shown in Figs. 1 and 2, respectively; important bond lengths and angles are in Tables 1 and 2. In both molecules the metal is square planar with the carbene moiety *trans* to the bromide and the pyridine *trans* to the methyl. The bite angle of the chelating ligand in **3a** is 85.2° and in **5a** is 79.1°.

The Pd–C(carbene) bond lengths are identical (within the esds) in both compounds [1.969(4) and 1.970(4) Å], slightly shorter than the predicted value (2.08 Å), where pure Pd–C σ-bonding is considered; the Pd–methyl bond lengths are not unusual (*i.e.* 2.05–2.15 Å). In **3a** the ligand adopts a puckered

‡ For the numbering of the ligand systems adopted in this paper see Scheme 6.

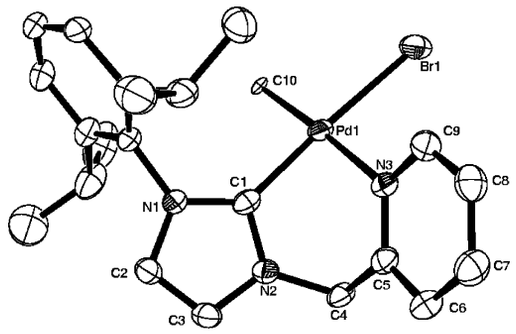


Fig. 1 ORTEP representation of the structure of **3a** (50% probability of thermal ellipsoids). Hydrogen atoms are omitted for clarity.

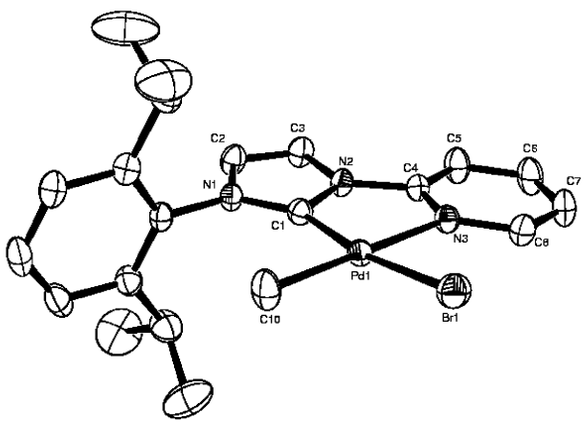


Fig. 2 ORTEP representation of the structure of **5a** (50% probability of thermal ellipsoids). Hydrogen atoms are omitted for clarity.

Table 1 Bond lengths [Å] and angles [°] for **3a**

Pd1–C10	2.126(3)	Pd1–N3	2.168(3)
Pd1–Br1	2.4890(5)	C1–N1	1.356(4)
Pd1–C1	1.969(4)	C1–N2	1.349(4)
C1–Pd1–Br1	176.89(10)	C10–Pd1–Br1	90.01(8)
C10–Pd1–N3	176.58(11)	N3–Pd1–Br1	93.37(8)
C1–Pd1–N3	85.22(13)	C1–Pd1–C10	91.44(12)

Table 2 Bond lengths [Å] and angles [°] for **5a** and **5b**

5a		**5b**	
Pd1–C10	2.034(4)	Pd1–C21	2.017(4)
Pd1–Br1	2.4528(5)	Pd1–O3	2.124(2)
Pd1–C1	1.970(4)	Pd1–C1	1.947(3)
Pd1–N3	2.166(3)	Pd1–N1	2.124(3)
C1–N1	1.348(5)	C1–N3	1.358(4)
C1–N2	1.369(5)	C1–N2	1.368(4)
C1–Pd1–Br1	171.53(11)	C1–Pd1–O3	173.08(11)
C10–Pd1–N3	175.17(17)	C21–Pd1–N1	176.44(17)
C1–Pd1–N3	79.15(3)	C1–Pd1–N1	79.49(11)
C10–Pd1–Br1	88.07(13)	C21–Pd1–O3	88.04(14)
N3–Pd1–Br1	96.18(8)	N1–Pd1–O3	94.24(9)
C1–Pd1–C10	96.91(17)	C1–Pd1–C21	98.36(15)

conformation in order to minimise conformational strain. The torsion angles around the chelate ring fall into the expected ranges, and the 2,6-$Pr^i_2C_6H_3$ ring is orientated at right angles to the ring of the imidazol-2-ylidene. Complex **4** adopts similar geometry and conformation, however, the Pd–C(methyl) are slightly shorter and the Pd–N(pyridine) distances are longer than **3a**, possibly due to increased steric interactions. Structural data for **4** are included as electronic supplementary information.

Table 3 Bond lengths [Å] and angles [°] for **9**

Pd1–Cl4	2.371(2)	Pd1–N1	2.048(7)
Pd1–Cl5	2.331(2)	C9–N2	1.330(12)
Pd1–Cl6	2.3968(19)	C9–N3	1.328(13)
Cl4–Pd1–N1	87.1(2)	Cl5–Pd1–N1	176.3(2)
Cl4–Pd1–Cl6	175.63(6)	N2–C9–N3	109.0(9)

It is interesting that the reaction of the imidazolium picoline salts with $PdCl_2(CH_3CN)_2$ in the absence of base results in the formation of imidazolium substituted pyridine complexes of palladium(II).

One example obtained by interaction of 1-(2,6-diisopropylphenyl)-3-(2-α-picolyl)imidazolium bromide was characterised by X-ray crystallography. The structure of **9** is shown in Fig. 3,

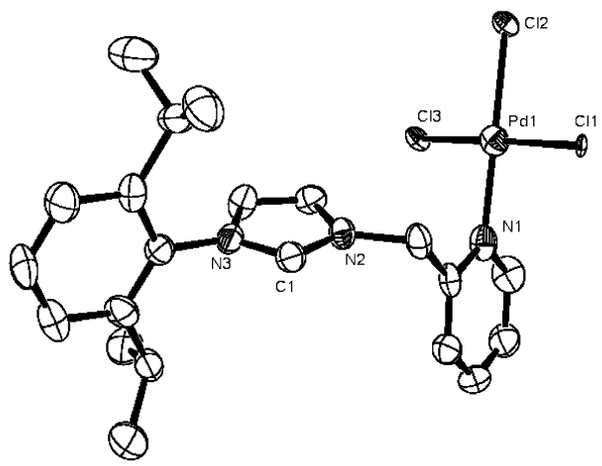


Fig. 3 ORTEP representation of the structure of **9** (50% probability of thermal ellipsoids). Hydrogen atoms are omitted for clarity.

important bond lengths and angles are given in Table 3. The coordination sphere of the square-planar metal comprises halide (chloride/bromide) ligands and one substituted pyridine group. There is no interaction of the dangling imidazolium with any other atom in the unit cell.

In order to establish a possible dependence of the metrical data of the observed structures upon the nature of the pyridine ring substituents and, subsequently, correlate catalytic activity with bond elongation and hemilabile behaviour, we prepared the complexes **6**, **7** and **8**. They are analogous to **5a**, bearing 6-trimethylsilyl-2-pyridyl- ($C–N^{TMS-6}$), 5-trimethylsilyl-2-pyridyl- ($C–N^{TMS-5}$) and 5-trifluoromethyl-2-pyridylimidazol-2-ylidene, ($C–N^{CF3}$) ligands, respectively. They were synthesised from (cod)Pd(CH_3)Br following the general method 1 and found to be isostructural with **5a**, featuring bidentate chelating (C–N) ligands. The relevant structural data and the lists of bond lengths and angles have been deposited as electronic supplementary information (ESI). Generally, there is only slight variation of the Pd–N(pyridine) and Pd–C(carbene) bond lengths. Minor differences are observed, *i.e.* for **5a**, Pd–C 1.970(4), Pd–N 2.166(3) Å; for **7**, Pd–C 1.965(4), Pd–N 2.149(4) Å; and for **8**, Pd–C 1.988(4), Pd–N 2.155(4) Å. Comparative catalytic studies in Heck reactions for **3a**, **5a** and **6**–**8** will be reported in a forthcoming paper.

Attempts to prepare bis-carbene complexes by interaction of (cod)PdXY with an excess of silver NHC transfer reagent or imidazolium salts and base gave only mixtures of products, the mass spectra of which supported the presence of complexes with metal : ligand ratios of 1 : 1, 1 : 2 and 1 : 3. The ^{1}H NMR spectra of these mixtures were complicated and separation of the components proved impossible. The reactions of the Pd(0) precursor complexes with isolated free functionalised NHCs will be reported in a forthcoming paper.

Interaction of (cod)$PdCl_2$ with two equivalents of (3-R^1)-(1-methoxymethyl)imidazol-2-ylidene silver chloride, R^1 = 2,6-$Pr^i_2C_6H_3$, prepared following a method described previously,[3a] gave rise to a mixture of mono- or di-carbene complexes of palladium **10** and **11**, respectively. It was impossible to obtain **10** or **11** separately by adjusting the ratio of the reactants. However, **10** was isolated as analytically pure solid by crystallisation from concentrated dichloromethane/ether solutions (see Experimental section). A few crystals of the less soluble **11** were hand picked and used for structural determination only.

The structures of **10** and **11** have been determined by X-ray diffraction and are shown in Figs. 4 and 5, respectively. Important bond lengths and angles are in Table 4. Complex **10** is a chloride bridged dimer. The functionalised NHC is monodentate and the methoxy functional group is dangling. The coordination sphere of palladium is completed with one terminal chloride. The palladium–carbene bond length is within the expected range and the imidazol-2-ylidene plane is perpendicular to the coordination plane. Complex **10** is therefore related to the non-functionalised monocarbene complexes reported previously.[6]

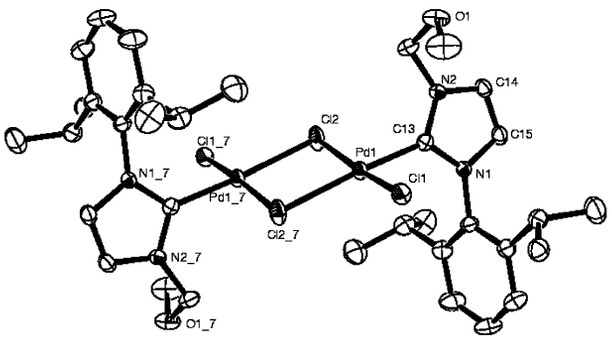


Fig. 4 ORTEP representation of the structure of **10** (50% probability of thermal ellipsoids). Hydrogen atoms are removed for clarity.

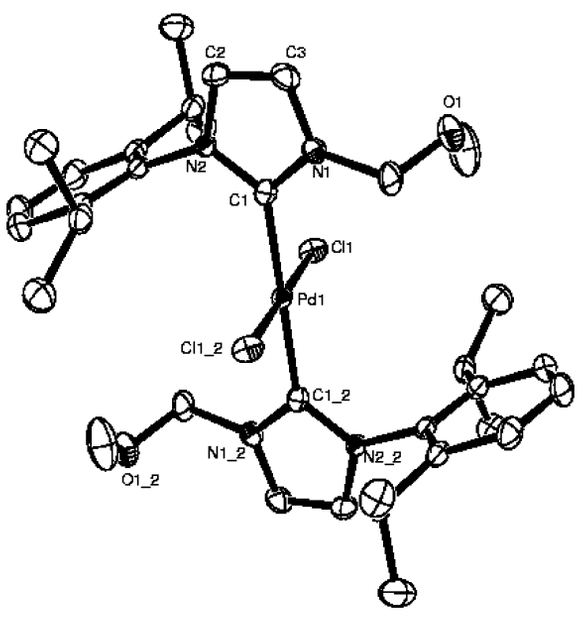


Fig. 5 ORTEP representation of the structure of **11** (50% probability of thermal ellipsoids). Hydrogen atoms are omitted for clarity.

In the centrosymmetric **11** the metal is coordinated to two carbene and two chloride ligands in a *trans* geometry. Here too, the ether functional groups are not coordinated to the metal centre. The NHC ring is perpendicular to the coordination plane. All bond lengths are similar to those observed for **10**.

Table 4 Selected bond lengths [Å] and angles [°] for **10**, **11** and **12**

10			
Pd(1)–Cl(1)	2.2727(6)	C(13)–Pd(1)–Cl(1)	89.78(7)
Pd(1)–Cl(2)	2.3398(6)	C(13)–Pd(1)–Cl(2)	91.38(7)
Pd(1)–C(13)	1.943(2)	C(13)–Pd(1)–Cl(2)_1	174.14(7)
Pd(1)–Cl(2)_7	2.3981(6)	Cl(1)–Pd(1)–Cl(2)	172.07(2)
11			
Pd(1)–Cl(1)	2.3037(6)	C(1)–Pd(1)–Cl(1)	91.09(7)
Pd(1)–C(1)	2.022(2)	C(1)–Pd(1)–Cl(1)_2	88.91(7)
12			
Pd(1)–Cl(2)	2.3164(6)	C(1)–Pd(1)–Cl(2)	87.91(7)
Pd(1)–C(1)	2.015(2)	C(1)–Pd(1)–Cl(2)_1	92.09(7)

Complex **12** was prepared by transmetallation from silver complexes following general method 1. The structure of the product was determined by single crystal X-ray diffraction study and is shown in Fig. 6. Important bond lengths and angles are in Table 4. The molecule is analogous to **11** with a square-planar metal and *trans* carbenes. There is no interaction of the carbamoyl functional group with any other atom in the unit cell. Attempts to impose coordination of the functional groups by halogen abstraction from the metal using silver salts with non-coordinating anions gave only intractable mixtures of products.

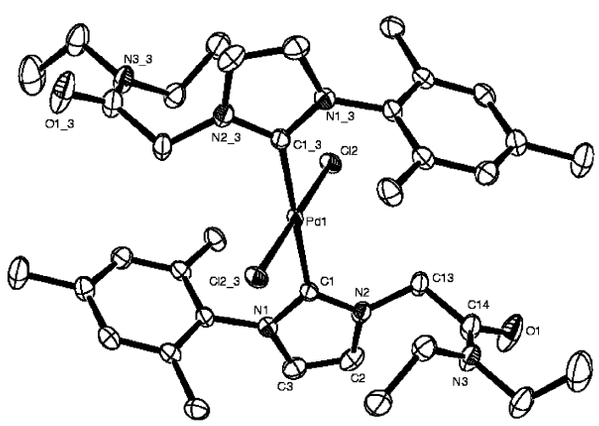


Fig. 6 ORTEP representation of the structure of **12** (50% probability of thermal ellipsoids). Hydrogen atoms are omitted for clarity.

Halide substitution reactions

The anionic coligands X or Y are known to play an important role in catalytic reactions involving palladium(II).[7,8] Well documented is the change of reactivity and enantioselectivity in the Heck reactions by replacing halides with weakly coordinating triflates, trifluoroacetates tosylates *etc*. (neutral *vs*. cationic pathway, respectively),[9] leading to increased (co)polymerisation activity *etc*.

For this reason we synthesised halide substitution derivatives of some representative complexes shown in Scheme 3. The substitutions are easily carried out by reaction with silver salts in noncoordinated solvents. All products were characterised by analytical and spectroscopic methods and, where possible, crystallographically. The crystal structure of **5b**, obtained by substitution of the bromide by tosylate in **5a** is shown in Fig. 7; important bond lengths and angles are in Table 2. In solution this structure is maintained as supported by the ^{1}H NMR spectrum which is comparable to that of **5a**.

Interestingly, substitution of the halide by trifluoroacetate in **1a** does not give the expected simple monomeric product. Instead a tetrameric 'metallamacrocycle' **1d** was isolated and structurally characterised.[5] The observed structure features a

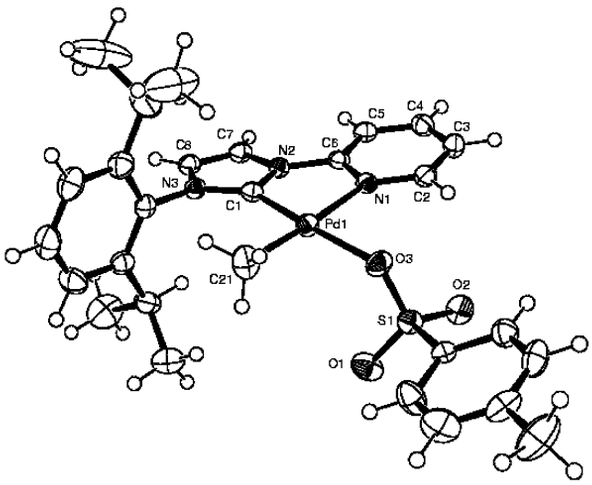


Fig. 7 ORTEP representation of the structure of **5b** (50% probability of thermal ellipsoids).

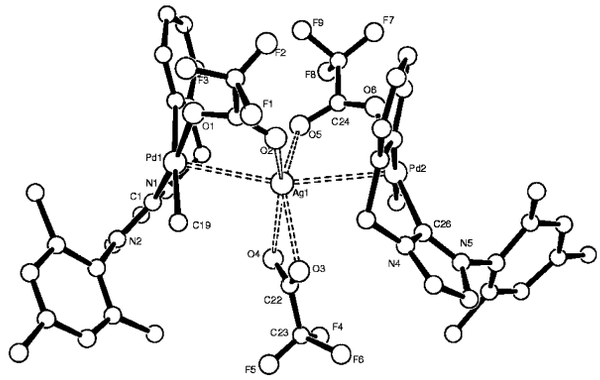


Fig. 8 Structural representation of **13**. Due to the quality of the data this picture shows connectivity only.

rare example of bridging pyridine functionalised NHC ligand [3b] with the pyridine and the carbene functionalities occupying mutually *trans* positions.It is noteworthy that in the ^{1}H NMR spectrum of **1d** the peaks assigned to the protons in the 5- and 4-position of the imidazol-2-ylidene ring appear at considerably higher field (6.4 and 7.0 ppm) than in similar complexes with chelating ligands. The chemical shifts of the protons of the methylene linker in bridging and chelating ligands are found in the same spectral region, albeit they are observed as a very broad singlet at room temperature or just below in the bridging ligands and as a pair of doublets (*vide supra*) in chelating geometries. Using these observations as qualitative spectroscopic probes for the geometries adopted in solution we propose chelating structures for **1a**, **1b**, **1c**, **2b–d**, **3b** and **5b**.

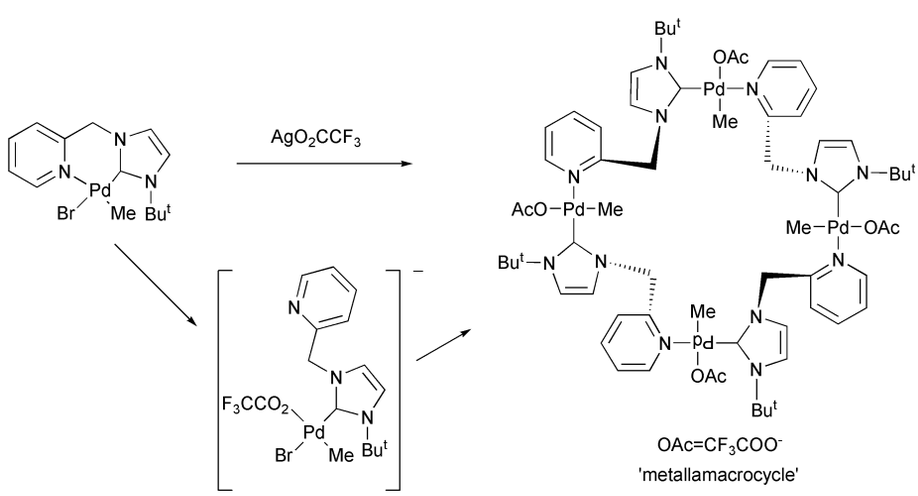
An additional point related to the formation of the 'metallamacrocycle' **1d** is the *trans* arrangement of the pyridine and NHC ligands. Bearing in mind that the ligand in **1a** is believed to act as chelate, it is reasonable to assume that halide exchange is accompanied by partial dissociation of the chelate. We consider this as an indirect evidence of the hemilabile nature of the C^N ligands (see Scheme 5). Based on accepted metal–NHC and –pyridine bond strengths it is reasonable to assume that the pyridine end is the most labile.

Finally, although the substitution of bromide by trifluoroacetate in **2a** resulted in the formation of **2d**, which could be obtained as analytically pure after repeated recrystallisations, in the presence of excess of $AgOOCCF_3$ we were able to crystallise a new compound **13** (Fig. 8). Attempts to determine the crystal structure of **13** were of limited success due to the small size of the crystals. The data sets obtained were of poor quality, however, they were adequate to derive a reasonable model and establish the coarse features of the structure. The molecule comprises two square-planar palladium atoms and one silver centre situated between them. The palladium atom is ligated by the chelating C^N ligands. The remaining coordination sites are occupied by the methyl and the trifluoroacetate groups, the latter bridging the palladium and the unique silver atoms. We have been unable to obtain **13** free from excess $AgOOCCF_3$.

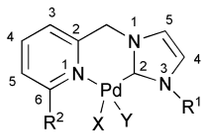
Experimental

Elemental analyses were carried out by the University College London Microanalytical Laboratory. NMR data were recorded on Bruker AMX-300 and DPX-400 spectrometers, operating at 300 and 400 MHz (^{1}H), respectively. The spectra were 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 used had bp 40–60 °C. The starting materials were synthesised according to the established methods: $Pd(cod)X_2$, $Pd(cod)(CH_3)X$, X = Br, Cl.[10] All silver NHC complexes were prepared as described previously.[3,11] The synthesis and isolation of free functionalised NHC ligands from the corresponding imidazolium salts will be described in a forthcoming paper.

The names of the complexes described in this paper were derived using the numbering system given in Scheme 6.



Scheme 5



Scheme 6

Synthesis of palladium halide complexes

General method 1. A dichloromethane solution of the corresponding silver carbene complex was added dropwise to a solution of (cod)Pd(CH_3)Br/Cl or (cod)$PdCl_2$, or (cod)$PdBr_2$ and stirred at room temperature for 12–24 h. After completion, the precipitated silver halide was removed by filtration, and the filtrate was evaporated to dryness. The remaining solid residue was washed with diethyl ether and dried under vacuum. The products were obtained as pale yellow solids, which in most cases were spectroscopically and analytically pure. If necessary, further purification was carried out by recrystallisation from a saturated solution of dichloromethane and diethyl ether or by extraction into hot toluene.

General method 2. To a solution of (cod)PdX_2 or (cod)Pd(CH_3)X in toluene under nitrogen was added dropwise by cannula a solution of carbene in the same solvent. The precipitated product was isolated by filtration, washed with light petroleum and dried under vacuum. Recrystallisation as above gave spectroscopically and analytically products.

General method 3. Under nitrogen, a THF solution of lithium diisopropylamide or potassium bis(trimethylsilyl)amide was added dropwise to a dilute THF solution of the corresponding imidazolium salt and (cod)Pd(CH_3)X at −78 °C. The orange/red solution was then allowed to warm to room temperature and stirred for 1 h. After completion, the reaction mixture was filtered, the volatiles were removed under vacuum, and washed with diethyl ether. The resulting solid was dissolved in methanol and filtered through a short silica column. Removal of the volatiles under vacuum gave the air-stable complexes as pale yellow solids. Recrystallisation as above gave spectroscopically and analytically pure products.

Bromo[3-(*tert*-butyl)-1-(α-picolyl)imidazol-2-ylidene]methylpalladium(II) 1a

This was prepared following the general method 3 from 3-(*tert*-butyl)-1-(α-picolyl)imidazolium bromide (0.222 g, 0.75 mmol) and (cod)Pd(CH_3)Br (0.23 g, 0.75 mmol) in THF (100 cm^3) at −78 °C. To this suspension was added a solution of lithium diisopropylamide (0.08 g, 0.75 mmol) in THF (50 cm^3). The product was obtained as a yellow solid. Yield: 70% (Found: C, 40.45; H, 4.91; N, 10.05. Calc. for $C_{14}H_{20}BrN_3Pd$: C, 40.36; H, 4.84; N, 10.09%). MS (ES): *m*/*z* 377, [(ligand)PdMe + MeCN]$^+$. NMR: δ_H ($CDCl_3$): 0.2 (3H, s, PdCH_3), 2.0 [9H, s, C(CH_3)$_3$], 5.2, 5.9 (2H, 2 × d, CH_2), 6.7 (1H, d, 3-picolyl *H*), 7.1 (1H, d, 5-imidazol-2-ylidene *H*), 7.2 (1H, d, 4-imidazol-2-ylidene *H*), 7.3 (1H, m, 5-picolyl *H*), 7.7 (1H, td, 4-picolyl *H*), 9.2 (1H, d, 6-picolyl *H*). δ_C ($CDCl_3$): −8 (Pd*C*H$_3$), 32 [C(*C*H$_3$)$_3$], 59 (*C*H$_2$), 60 [*C*(CH$_3$)$_3$)], 119 (4-imidazol-2-ylidene *C*), 120 (5-imidazol-2-ylidene *C*), 122 (5-picolyl *C*H), 124 (3-picolyl *C*H), 138 (4-picolyl *C*H), 153 (6-picolyl *C*H), 160 (2-picolyl *C*), 175 (2-imidazol-2-ylidene *C*).

Bromo[3-(mesityl)-1-(α-picolyl)imidazol-2-ylidene]methylpalladium(II) 2a

This was prepared by following: (i) The general method 1 from [3-(mesityl)-1-(α-picolyl)imidazol-2-ylidene] silver bromide (0.3 g, 0.64 mmol) and (cod)Pd(CH_3)Br (0.2 g, 0.64 mmol) in dichloromethane (60 cm^3) by stirring at room temperature for 12 h. Yield was quantitative. (ii) The general method 3 from 3-(mesityl)-1-(α-picolyl)imidazolium bromide (3.0 g, 12.0 mmol) and (cod)Pd(CH_3)Br (2.2 g, 12.0 mmol) in THF (100 cm^3) at −78 °C.To this suspension was added a solution of lithium diisopropylamide (1.3 g, 12.0 mmol) in THF (50 cm^3). The product was obtained as a yellow solid. Yield: 3.5 g, 65%. X-Ray diffraction quality crystals were obtained by layering a dichloromethane solution with diethyl ether (Found: C, 47.69; H, 4.42; N, 8.77. Calc. for $C_{19}H_{22}BrN_3Pd$: C, 47.67; H, 4.63; N, 8.78%). MS (ES): *m*/*z* 439, [(ligand)PdMe + MeCN]$^+$. δ_H ($CDCl_3$): 0.2 (3H, s, PdCH_3), 2.1 (6H, s, mesityl CH_3), 2.3 (3H, s, mesityl CH_3), 5.5 (2H, br, CH_2), 6.8 (1H, d, 5-imidazol-2-ylidene *H*), 6.9 (2H, s, mesityl *H*), 7.3 (1H, d, 4-imidazol-2-ylidene *H*), 7.4 (1H, m, 5-picolyl *H*), 7.5 (1H, d, 3-picolyl *H*), 7.8 (1H, td, 4-picolyl *H*), 9.3 (1H, d, 6-picolyl *H*). δ_C ($CDCl_3$): −14 (Pd*C*H$_3$), 19, 21 (mesityl *C*H$_3$), 55 (*C*H$_2$), 121 (4-imidazol-2-ylidene *C*), 122 (5-imidazol-2-ylidene *C*), 124 (5-picolyl *C*H), 124 (3-picolyl *C*H), 128 (mesityl *C*H), 129, 134, 135 (mesityl *C*), 139 (4-picolyl *C*H), 153 (6-picolyl *C*H), 153 (2-picolyl *C*), 173 (2-imidazol-2-ylidene *C*).

Bromo[3-(2,6-diisopropylphenyl)-1-(α-picolyl)imidazol-2-ylidene]methylpalladium(II) 3a

This was prepared by following: (i) the general method 1 from [3-(2,6-diisopropylphenyl)-1-(α-picolyl)imidazol-2-ylidene]-silver bromide, (1.5 g, 3.2 mmol) and Pd(cod)(CH_3)Br (1.0 g, 3.2 mmol) in dichloromethane (200 cm^3) by stirring at room temperature for 12 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 petrol. (ii) The general method 3 from 3-(2,6-diisopropylphenyl)-1-(α-picolyl)imidazolium bromide (0.14 g, 0.32 mmol) and (cod)-Pd(CH_3)Br, (0.1 g, 0.32 mmol) in THF (50 cm^3) at −78 °C. To this suspension was added a solution of lithium diisopropylamide (0.09 g, 0.88 mmol) in THF (20 cm^3). The product was obtained in good yield as a yellow solid. Yield: 0.11 g, 72% (Found: C, 50.63; H, 5.53; N, 7.94. Calc. for $C_{22}H_{28}PdBr$: C, 50.74; H, 5.42; N, 8.07%). MS (ES): *m*/*z* 481, [(ligand)PdMe + MeCN]$^+$. δ_H (CD_2Cl_2, −40 °C): −0.1 (3H, s, PdCH_3), 0.8, 1.1, 1.2, 1.6 [4 × 3H, d, CH(CH_3)$_2$], 2.0, 2.6 [2 × 1H, septet, C*H*(CH$_3$)$_2$], 5.2, 5.7 (2 × 1H, 2 × d,, CH_2), 6.8 (1H, d, 5-imidazol-2-ylidene *H*), 7.2, 7.2 (2 × 1H, d, Pr$^i_2$C$_6$*H*$_2$H), 7.3 (1H, d, 4-imidazol-2-ylidene *H*), 7.3 (1H, m, 5-picolyl *H*), 7.4 (1H, t, Pr$^i_2$C$_6$H$_2$*H*), 7.5 (2H, d, 3-picolyl *H*), 7.8 (1H, dt, 4-picolyl *H*), 9.1 (1H, br d, 6-picolyl *H*).

Bromo[3-(2,6-diisopropylphenyl)-1-(α-lutidyl)imidazol-2-ylidene]methylpalladium(II) 4

This was prepared following the general method 1 from [3-(2,6-diisopropylphenyl)-1-(α-lutidyl)imidazol-2-ylidene] silver bromide (0.5 g, 1.1 mmol) and (cod)Pd(CH_3)Br (0.3 g, 1.1 mmol) in dichloromethane (100 cm^3) by stirring at room temperature for 12 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 (Found: C, 52.06; H, 5.80; N, 7.91. Calc. for $C_{23}H_{30}BrN_3Pd$: C, 51.65; H, 5.65; N, 7.86%). MS (ES): *m*/*z* 482, [(ligand)PdMe + MeCN]$^+$. δ_H ($CDCl_3$): 0.2, 0.3 (3H, s, PdCH_3), 0.8, 1.1, 1.2, 1.5 [4 × 3H, d, CH(CH_3)$_2$], 2.4, 2.7 [2 × 1H, septet, C*H*(CH$_3$)$_2$], 3.0 (3H, s, lutidyl CH_3), 5.1, 6.0 (2 × 1H, 2 × d, CH_2), 6.7 (1H, d, 5-imidazol-2-ylidene *H*), 7.1 (2H, br d, Pr$^i_2$C$_6$*H*$_2$H), 7.3 (1H, d, 4-imidazol-2-ylidene *H*), 7.2 (1H, d, 5-lutidyl *H*), 7.3 (1H, t, Pr$^i_2$C$_6$H$_2$*H*), 7.3 (1H, d, 3-lutidyl *H*), 7.5 (1H, t, 4-lutidyl *H*). δ_C ($CDCl_3$): −5 (Pd*C*H$_3$), 22, 24, 25, 26 (CH(*C*H$_3$)$_2$), 28 (lutidyl *C*H$_3$), 29 (*C*H(CH$_3$)$_2$), 57 (CH_2), 120 (3-lutidyl *C*H), 120 (4-imidazol-2-ylidene *C*), 123 (5-lutidyl *C*H), 123, 125, 130, 145 (Pr$^i_2$*C*$_6$H$_3$), 128 (5-imidazol-2-ylidene *C*), 138 (4-lutidyl *C*H), 152 (6-lutidyl *C*H), 152 (2-lutidyl *C*), 163 (2-imidazol-2-ylidene *C*).

Bromo[3-(2,6-diisopropylphenyl)-1-(2-pyridyl)imidazol-2-ylidene]methylpalladium(II) 5a

This was prepared by following: (i) the general method 1 from [3-(2,6-diisopropylphenyl)-1-(2-pyridyl)imidazol-2-ylidene] silver bromide (1.5 g, 3.2 mmol) and (cod)Pd(CH_3)Br (1.0 g, 3.2 mmol) in dichloromethane (200 cm^3) by stirring at room temperature for 12 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. (ii) The general method 2 from [3-(2,6-diisopropylphenyl)-1-(2-pyridyl)imidazol-2-ylidene] (1.273 g, 3.3 mmol) and (cod)Pd(CH_3)Br (1.0 g, 3.2 mmol) in toluene (50 cm^3) at room temperature. Yield: 1.31g, 90% (Found: C, 49.79; H, 5.25; N, 8.15. Calc. for $C_{21}H_{25}PdBr$: C, 49.77; H, 5.17; N, 8.29%). MS (ES): *m*/*z* 455, [(ligand)PdMe + MeCN]$^+$. δ_H ($CDCl_3$): 0.4 (3H, s, PdCH_3), 1.1, 1.3 [2 × 6H, d, CH(CH_3)$_2$], 2.7 [2H, septet, CH(CH_3)$_2$], 7.0 (1H, d, 5-imidazol-2-ylidene *H*), 7.3 (2H, d, Pr$^i_2$C$_6$$H_2$H), 7.4 (1H, m, 5-pyridyl *H*), 7.5 (1H, t, Pr$^i_2$C$_6$H$_2$*H*), 7.7 (2H, d, 3-pyridyl *H*), 8.0 (1H, d, 4-imidazol-2-ylidene *H*), 8.0 (1H, dt, 4-pyridyl *H*), 9.4 (1H, br d, 6-pyridyl *H*). δ_C ($CDCl_3$): −11 (PdCH_3), 23, 25 (CH(CH_3)$_2$), 29 (CH(CH_3)$_2$), 110 (3-picolyl *C*H), 116 (4-imidazol-2-ylidene *C*), 123 (5-picolyl *C*H), 124, 131, 134, 146 (Pr$^i_2$$C_6H_3$), 126 (5-imidazol-2-ylidene *C*), 141 (4-picolyl *C*H), 150 (6-picolyl *C*H), 150 (2-picolyl *C*), 174 (2-imidazol-2-ylidene *C*).

Bromo{3-(2,6-diisopropylphenyl)-1-[(6-trimethylsilyl)-2-pyridyl)]imidazol-2-ylidene}methylpalladium(II) 6

This was prepared by following general method 1 from {3-(2,6-diisopropylphenyl)-1-[(6-trimethysilyl)-2-pyridyl)]imidazol-2-ylidene} silver chloride (0.25 g, 0.5 mmol) and (cod)Pd(CH_3)Br (0.16 g, 0.5 mmol) in dichroromethane. After stirring at room temperature for 12 h the product was isolated as a white air-stable powder by filtering off the precipitated AgCl and evaporating the volatiles under reduced pressure. Yield: 0.18 g, 60%. X-Ray quality crystals were obtained by layering dichloromethane solutions with light petroleum (Found: C,50.23; H, 6.09; N, 7.35. Calc. for $C_{24}H_{34}BrN_3PdSi$: C, 49.79; H, 5.92; N, 7.26%). MS (ES): *m*/*z* 907, [(ligand)$_2$PdMe]+. δ_H (CD_2Cl_2): 0.3 (3H, s, PdCH_3), 0.4 [9H, s, Si(CH_3)$_3$], 1.2, 1.3 [2 × 6H, d, CH(CH_3)$_2$], 2.5 [2H, septet, CH(CH_3)$_2$], 7.0 (1H, d, 5-imidazol-2-ylidene *H*), 7.8 (1H, d, 4-imidazol-2-ylidene *H*), 7.3 (2H, d, Pr$^i_2$C$_6$$H_2$H), 7.4 (1H, t, Pr$^i_2C_6H_2$*H*), 7.7 (1H, d, 3-pyridyl *H*), 8.1 (1H, t, 4-pyridyl *H*), 9.2 (1H, d, 5-pyridyl *H*).

Bromo[3-(2,6-diisopropylphenyl)-1-(5-trimethylsilyl)-2-pyridyl)-imidazol-2-ylidene]methylpalladium(II) 7

This was prepared by following general method 1 from {3-(2,6-diisopropylphenyl)-1-[(6-trimethysilyl)-2-pyridyl)]imidazol-2-ylidene} silver chloride (0.25 g, 0.5 mmol) and (cod)Pd(CH_3)Br (0.16 g, 0.5 mmol) in dichroromethane. After stirring at room temperature for 12 h the product was isolated as a white air-stable powder by filtering off the precipitated AgCl and evaporating the volatiles under reduced pressure. Yield: 0.22 g, 75%. X-Ray quality crystals were obtained by layering dichloromethane solutions with light petroleum (Found: C,50.62; H, 6.31; N, 6.42. Calc. for $C_{24}H_{34}SiN_3PdBr$: C, 49.79; H, 5.92; N, 7.26%). MS (ES): *m*/*z* 540, [(ligand)PdMe + MeCN]$^+$. δ_H (CD_2Cl_2): 0.3 (3H, s, PdCH_3), 0.4 [9H, s, Si(CH_3)$_3$], 1.1, 1.3 [2 × 6H, d, CH(CH_3)$_2$], 2.7 [2H, septet, CH(CH_3)$_2$], 6.9 (1H, d, 5-imidazol-2-ylidene *H*), 7.0 (2H, d, Pr$^i_2$C$_6$$H_2$H), 7.4 (1H, t, Pr$^i_2C_6H_2$*H*), 7.8 (1H, br t, 3-pyridyl *H*), 8.1 (1H, d, 4-imidazol-2-ylidene *H*), 8.2 (1H, d, 4-pyridyl *H*), 9.2 (1H, br d, 6-pyridyl *H*). δ_C ($CDCl_3$): −1 (PdCH_3), 1 [Si(CH_3)$_3$] 23, 25 (CH(CH_3)$_2$), 28 (CH(CH_3)$_2$), 109 (3-pyridyl *C*H), 114 (4-imidazol-2-ylidene *C*), 123 (5-pyridyl *C*H), 122, 125, 129, 145 (Pr$^i_2$$C_6H_3$), 128 (5-imidazol-2-ylidene *C*), 135 (4-pyridyl *C*H), 153 (6-pyridyl *C*H), 162 (2-pyridyl *C*).

Bromo[3-(2,6-diisopropylphenyl)-1-(5-trifluoromethyl)-2-pyridyl)imidazol-2-ylidene]methylpalladium(II) 8

This was prepared by following general method 1 from {3-(2,6-diisopropylphenyl)-1-[(5-trifluoromethyl)-2-pyridyl)]imidazol-2-ylidene} silver bromide (0.28 g, 0.5 mmol) and (cod)Pd(CH_3)Br (0.16 g, 0.5 mmol) in dichroromethane. After stirring at room temperature for 12 h the product was isolated as a white air-stable powder by filtering off the precipitated AgBr and evaporating the volatiles under reduced pressure. X-Ray quality crystals were obtained by layering dichloromethane solutions with light petroleum. Yield: 0.31 g, 85% (Found: C,44.84; H, 4.42; N, 6.95. Calc. for $C_{22}H_{25}F_3N_3PdBr$: C, 45.97; H, 4.38; N, 7.31%). MS (ES): *m*/*z* 535, [(ligand)PdMe + MeCN]$^+$. δ_H (CD_2Cl_2): 0.1 (3H, s, PdCH_3), 1.1, 1.3 [2 × 6H, d, CH(CH_3)$_2$], 2.7 [2H, septet, CH(CH_3)$_2$], 6.9 (1H, d, 5-imidazol-2-ylidene *H*), 7.0 (2H, d, Pr$^i_2$C$_6$$H_2$H), 7.4 (1H, t, Pr$^i_2C_6H_2$*H*), 7.7 (1H, d, 3-pyridyl *H*), 7.9 (1H, d, 4-imidazol-2-ylidene *H*), 8.0 (1H, d, 4-pyridyl *H*), 9.4 (1H, br d, 6-pyridyl *H*). δ_C ($CDCl_3$): −2 (PdCH_3), 22 (CF_3) 23, 25 (CH(CH_3)$_2$), 29 (CH(CH_3)$_2$), 101 (3-pyridyl *C*H), 114 (4-imidazol-2-ylidene *C*), 121 (5-pyridyl *C*H), 122, 125, 129, 147 (Pr$^i_2$$C_6H_3$), 123 (5-imidazol-2-ylidene *C*), 136 (4-pyridyl *C*H), 153 (6-pyridyl *C*H), 154 (2-pyridyl *C*), 205 (2-imidazol-2-ylidene *C*).

Tris(chloro/bromo)[3-(2,6-diisopropylphenyl)-1-(α -picolyl)-imidazolium]palladium(II) 9

To a solution of $PdCl_2$ (0.044 g, 0.25 mmol) dissolved in acetonitrile (10 cm^3) was added a solution of 3-(2,6-diisopropylphenyl)-1-(α -picolyl)imidazolium chloride (0.089 g, 0.25 mmol) in the same solvent. The mixture was stirred at room temperature until yellow **9** precipitated as a microcrystalline powder. Recrystallisation from acetonitrile yielded yellow X-ray quality crystals. δ_H (CD_3CN): 2.0, [2 × 6H, d, CH(CH_3)$_2$], 3.3 [2H, septet, CH(CH_3)$_2$], 6.4 (2H, br s, CH_2), 7.7 (1H, d, 5-imidazol-2-ylidene *H*), 8.4 (1H, d, 4-imidazol-2-ylidene *H*), 8.5 (2H, br d, Pr$^i_2$C$_6$$H_2$H), 8.8 (1H, m, 5-picolyl *H*), 9.0 (1H, t, Pr$^i_2$C$_6$H$_2$*H*), 10.0 (2H, br, 3,4-picolyl *H*), 10.1 (1H, d, 6-picolyl *H*).10.7 (1H, s, 2-imidazol-2-ylidene *H*).

Dichloro(μ-chloro)bis[3-(2,6-diisopropylphenyl)(1-methoxymethyl)imidazol-2-ylidene]dipalladium(II) 10 and dichloro{*trans*-bis[3-(2,6-diisopropylphenyl)(1-methoxymethyl)imidazol-2-ylidene]}palladium(II) 11

This was prepared following the general method 1 from {1-[3-(2,6-diisopropylphenyl)imidazol-2-ylidene]-1-methoxymethane} silver chloride (0.39 g, 1.05 mmol) and (cod)$PdCl_2$ (0.15 g, 0.53 mmol) in dichloromethane (75 cm^3) by stirring at room temperature for 12 h. The orange–yellow solid obtained in good yields was dissolved in a small volume (*ca* 10 cm^3) of dichloromethane, the undissolved material was removed by filtration and the filtrate was layered with diethyl ether. Orange–yellow crystals of **10** appeared after one week, which were collected and dried. Yield: 0.1 g, 45% based on Pd (Found: C, 57.49; H, 7.41; N, 6.89. Calc. for $C_{34}H_{48}Cl_2N_4O_2PdCl_2\cdot C_4H_{10}O$: C, 57.18; H, 7.58; N, 7.02%). MS (ES): *m*/*z* 455, [(ligand)$_2$PdCl]$^+$. δ_H ($CDCl_3$): 1.0, 1.3 [2 × 6H, d, CH(CH_3)$_2$], 2.8 [2H, septet, CH(CH_3)$_2$], 3.0 (3H, s, OCH_3), 5.6 (2H, d, CH_2), 6.2 (1H, d, 5-imidazol-2-ylidene *H*), 6.9 (1H, d, 4-imidazol-2-ylidene *H*), 7.4 (2H, d, Pr$^i_2$C$_6$$H_2$H), 7.5 (1H, t, Pr$^i_2C_6H_2$*H*). δ_C ($CDCl_3$): 22, 26 (CH(CH_3)$_2$), 26 (OCH_3), 29 (CH(CH_3)$_2$), 58 (CH_2), 117 (4-imidazol-2-ylidene *C*), 119, 126, 130, 147 (Pr$^i_2$$C_6H_3$), 124 (5-imidazol-2-ylidene *C*), 174 (2-imidazol-2-ylidene *C*). The less soluble in dichloromethane solid material was dissolved by addition of more solvent and the resultant solution was allowed to evaporate slowly giving a few X-ray quality crystals of **11**. Yield: *ca.* 0.05 g.

Dichloro-bis{1-[3-(mesityl)imidazol-2-ylidene]-1-diethylcarbamoylmethyl}palladium(II) 12

This was prepared following the general method 1 from {1-[3-(mesityl)imidazol-2-ylidene]-1-diethylcarbamoylmethyl} silver chloride (0.20 g, 0.45 mmol) and (cod)$PdCl_2$ (0.13 g, 0.45 mmol) in dichloromethane (50 cm^3) by stirring at room temperature for 12 h. The crude product was washed with methanol, dissolved in dichloromethane and passed through a short silica gel column. Evaporation of the volatiles gave spectroscopically pure **12**. Yield: 0.12 g (Found: C, 55.29; H, 6.21; N, 10.49. Calc. for $C_{36}H_{50}Cl_2N_6O_2PdCl_2$: C, 55.71; H, 6.49; N, 10.82%). X-Ray quality crystals were obtained by layering a saturated dichloromethane solution with diethyl ether. δ_H ($CDCl_3$): 1.2 [6H, t, $N(CH_2CH_3)$], 2.5 (6H, br s, mesityl CH_3), 2.9 (12H, br s, mesityl CH_3), 3.4 [4H, q, $N(CH_2CH_3)$], 5.3 (4H, s, CH_2), 6.3 (6H, br s, mesityl *H* and 4- imidazol-2-ylidene *H*), 7.2 (2H, s, 5-imidazol-2-ylidene *H*).

Anion exchange reactions

General method. A dichloromethane or acetonitrile solution of the corresponding silver salt was added dropwise to a solution of the corresponding palladium carbene complex (**1a**, **2a**, **3a**, **4a** or **5a**) and stirred at room temperature for 2–12 h. After completion, the reaction mixture was filtered, the volatiles were removed under vacuum and the resulting solid washed with diethyl ether. Drying under vacuum gave the products as pale yellow solids. In most cases, the products obtained at this stage were spectroscopically and analytically pure. If necessary, they were purified by recrystallisation from saturated solution of dichloromethane and diethyl ether or by extraction into hot toluene and crystallisation by slow cooling to room temperature.

[3-(*tert*-Butyl)-1-(α-picolyl)imidazol-2-ylidene]methyl(tosylato)-palladium(II) 1b

This was prepared following the general method from [3-(*tert*-butyl)-1-(α-picolyl)imidazol-2-ylidene] palladium(II) methyl bromide **1a** (0.1 g, 0.27 mmol) and silver tosylate (0.07 g, 0.27 mmol) in acetonitrile (50 cm^3) by stirring at room temperature for 2 h. The product was obtained in good yields as a yellow solid. Yield: quantitative. Crystals were obtained by cooling a saturated THF solution (Found: C, 49.86; H, 4.98; N, 8.02. Calc. for $C_{21}H_{27}N_3O_3PdS$: C, 49.66; H, 5.36; N, 8.27%). MS (ES): *m*/*z* 377, [(ligand)PdMe + MeCN]$^+$. δ_H (CD_3CN) 0.4 (3H, s, $PdCH_3$), 1.6 (9H, s, $C(CH_3)_3$), 2.2 (3H, s, OTs CH_3), 5.4, 5.6 (2H, 2 × d, CH_2), 7.0 (2H, d, OTs *H*), 7.2 (1H, d, 5-imidazol-2-ylidene *H*), 7.3 (1H, m, 5-picolyl *H*), 7.4 (1H, d, 4-imidazol-2-ylidene *H*), 7.5 (2H, d, OTs *H*), 7.6 (1H, d, 3-picolyl *H*), 7.8 (1H, td, 4-picolyl *H*), 8.5 (1H, d, 6-picolyl *H*). δ_C (CD_3CN) −9 ($PdCH_3$), 21 (OTs CH_3), 33 [$C(CH_3)_3$], 57 (CH_2), 60 [$C(CH_3)_3$)], 119, 140, (OTs *C*), 121 (5-imidazol-2-ylidene *C*), 123 (5-picolyl *C*H), 126 (4-imidazol-2-ylidene *C*), 126 (3-picolyl *C*H), 127, 129 (OTs *C*H), 140 (4-picolyl *C*H), 152 (6-picolyl *C*H), 155 (2-picolyl *C*), 166 (2-imidazol-2-ylidene *C*).

[3-(*tert*-Butyl)-1-(α-picolyl)imidazol-2-ylidene]methyl(triflato)-palladium(II) 1c

This was prepared following the general method from bromo-[3-(*tert*-butyl)-1-(α-picolyl)imidazol-2-ylidene]methylpalladium(II) **1a** (0.10 g, 0.27 mmol) and silver triflate (0.07 g, 0.27 mmol) in acetonitrile (50 cm^3) by stirring at room temperature for 2 h. The product was obtained in quantitative yields as a yellow solid (Found: C, 36.87; H, 4.77; N, 8.21. Calc. for $C_{15}H_{21}F_3N_3O_3PdS$: C, 37.01; H, 4.35; N, 8.63%). MS (ES): *m*/*z* 377, [(ligand)PdMe + MeCN]$^+$. δ_H (CD_3CN) 0.5 (3H, s, $PdCH_3$), 1.7 (9H, s, $C(CH_3)_3$), 5.3, 5.7 (2H, 2 × d, CH_2), 7.2 (1H, d, 5-imidazol-2-ylidene *H*), 7.3 (1H, d, 4-imidazol-2-ylidene *H*), 7.4 (1H, m, 5-picolyl *H*), 7.6 (1H, d, 3-picolyl *H*), 7.9 (1H, td, 4-picolyl *H*), 8.5 (1H, d, 6-picolyl *H*). δ_C (CD_3CN): −10 ($PdCH_3$), 32 [$C(CH_3)_3$], 58 (CH_2), 60 [$C(CH_3)_3$)], 118 (CF_3), 121 (5-imidazol-2-ylidene *C*), 123 (5-picolyl *C*H), 126 (4-imidazol-2-ylidene *C*), 126 (3-picolyl *C*H), 140 (4-picolyl *C*H), 152 (6-picolyl *C*H), 155 (2-picolyl *C*), 169 (2-imidazol-2-ylidene *C*).

[3-(*tert*-Butyl)-1-(α-picolyl)imidazol-2-ylidene]methyl(trifluoroacetato)palladium(II) 1d

This was prepared following the general method from bromo-[3-(*tert*-butyl)-1-(α-picolyl)imidazol-2-ylidene]methylpalladium(II) **1a** (0.1 g, 0.27 mmol) and silver trifluoroacetate (0.059 g, 0.27 mmol) in acetonitrile (50 cm^3) by stirring at room temperature for 2 h. The product was obtained in quantitative yield as a yellow solid. X-Ray quality crystals were obtained by layering a saturated solution of dichloromethane with diethyl ether (Found: C, 42.42; H, 4.14; N, 9.06. Calc. for $C_{16}H_{20}F_3N_3O_2Pd$: C, 42.73; H, 4.48; N, 9.34%). MS (ES): *m*/*z* 336, [(ligand)PdMe]$^+$; 377, [(ligand)PdMe + MeCN]$^+$. δ_H ($CDCl_3$): 0.5 (3H, br s, $PdCH_3$), 1.7 (9H, s, $C(CH_3)_3$), 5.3 (2H, s, CH_2), 6.4 (1H, d, 5-imidazol-2-ylidene *H*), 7.0 (1H, d, 4-imidazol-2-ylidene *H*), 7.1 (1H, d, 3-picolyl *H*), 7.2 (1H, t, 5-picolyl *H*), 7.5 (1H, td, 4-picolyl *H*), 8.8 (1H, d, 6-picolyl *H*). δ_C ($CDCl_3$): −8 ($PdCH_3$), 32 [$C(CH_3)_3$], 57 (CH_2), 58 [$C(CH_3)_3$)], 119 (CF_3), 120 (5-picolyl *C*H), 121 (5-imidazol-2-ylidene *C*), 123 (3-picolyl *C*H), 125 (4-imidazol-2-ylidene *C*), 138 (4-picolyl *C*H), 151 (6-picolyl *C*H), 152 (2-picolyl *C*), 159 (2-imidazol-2-ylidene *C*), 174 (CO_2).

[3-(Mesityl)-1-(α-picolyl)imidazol-2-ylidene]methyl(tosylato)-palladium(II) 2b

This was prepared following the general method from [3-(mesityl)-1-(α-picolyl)imidazol-2-ylidene] palladium(II) methyl bromide **2a** (0.1 g, 0.23 mmol) and silver tosylate (0.060 g, 0.23 mmol) in acetonitrile (50 cm^3) by stirring at room temperature for 2 h. The product was obtained in quantitative yields as a yellow solid. (Found: C, 55.10; H, 4.86; N, 7.85. Calc. for $C_{26}H_{29}N_3O_3PdS$: C, 54.78; H, 5.13; N, 7.37%). MS (ES): *m*/*z* 439, [(ligand)PdMe + MeCN]$^+$. δ_H (CD_3CN) 0.0 (3H, s, $PdCH_3$), 2.1 (6H, s, mesityl CH_3), 2.4 (3H, s, OTs CH_3), 2.4 (3H, s, mesityl CH_3), 5.7 (2H, s, CH_2), 7.1 (2H, s, mesityl *H*), 7.1 (1H, d, 5-imidazol-2-ylidene *H*),7.3 (2H, d, OTs *H*), 7.6 (1H, m, 5-picolyl *H*), 7.7 (2H, d, OTs *H*), 7.8 (1H, d, 4-imidazol-2-ylidene *H*), 7.9 (1H, d, 3-picolyl *H*), 8.1 (1H, td, 4-picolyl *H*), 8.8 (1H, d, 6-picolyl *H*). δ_C (CD_3CN) −5 ($PdCH_3$), 18, 21 (mesityl CH_3), 21 (OTs CH_3), 55 (CH_2), 119, 140, (OTs *C*), 123 (5-imidazol-2-ylidene *C*), 124 (4-imidazol-2-ylidene *C*), 126 (5-picolyl *C*H), 126 (3-picolyl *C*H), 127, 129 (OTs *C*H), 130 (mesityl *C*H), 136, 140, 140 (mesityl *C*),141 (4-picolyl *C*H), 152 (6-picolyl *C*H), 154 (2-picolyl *C*), 168 (2-imidazol-2-ylidene *C*).

[3-(Mesityl)-1-(α-picolyl)imidazol-2-ylidene]methyl(triflato)-palladium(II) 2c

This was prepared following the general method from bromo[3-(mesityl)-1-(α-picolyl)imidazol-2-ylidene]methylpalladium(II) **2a** (0.1 g, 0.23 mmol) and silver triflate (0.059 g, 0.23 mmol) in acetonitrile (50 cm^3) by stirring at room temperature for 2 h. The product was obtained in quantitative yield as a yellow solid (Found: C, 43.98; H, 4.54; N, 7.43. Calc. for $C_{20}H_{23}F_3N_3O_3PdS$: C, 43.76; H, 4.22; N, 7.66%). MS (ES): *m*/*z* 439, [(ligand)PdMe + MeCN]$^+$. δ_H (CD_3CN) 0.0 (3H, s, $PdCH_3$), 2.1 (6H, s, mesityl CH_3), 2.4 (3H, s, mesityl CH_3) 5.6 (2H, s, CH_2), 7.1 (2H, s, mesityl *H*), 7.1 (1H, d, 5-imidazol-2-ylidene *H*), 7.6 (1H, m, 5-picolyl *H*), 7.6 (1H, d, 4-imidazol-2-ylidene *H*), 7.9 (1H, d, 3-picolyl *H*), 8.1 (1H, td, 4-picolyl *H*), 8.8 (1H, d, 6-picolyl *H*). δ_C (CD_3CN) −9 ($PdCH_3$), 18, 21 (mesityl CH_3), 56 (CH_2), 119 (CF_3), 123 (5-imidazol-2-ylidene *C*), 124 (4-imidazol-2-ylidene *C*), 126 (5-picolyl *C*H), 126 (3-picolyl *C*H), 130 (mesityl *C*H),

136, 140, 140 (mesityl *C*), 140 (4-picolyl *C*H), 152 (6-picolyl *C*H), 154 (2-picolyl *C*), 168 (2-imidazol-2-ylidene *C*).

[3-(Mesityl)-1-(α-picolyl)imidazol-2-ylidene]methyl(trifluoroacetato)palladium(II) 2d and compound 13

This was prepared following the general method from bromo[3-(mesityl)-1-(α-picolyl)imidazol-2-ylidene]methylpalladium(II) **2a** (0.1 g, 0.23 mmol) and silver trifluoroacetate (0.05 g, 0.23 mmol) in acetonitrile (50 cm^3) by stirring at room temperature for 2 h. The product was obtained in quantitative yields as a yellow solid. Crystals were obtained by layering a saturated solution of dichloromethane with diethyl ether (Found: C, 48.98; H, 4.64; N, 7.82. Calc. for $C_{21}H_{23}F_3N_3O_2Pd$: C, 49.18; H, 4.52; N, 8.19%). MS (ES): *m*/*z* 439, [(ligand)PdMe + MeCN]$^+$. δ_H ($CDCl_3$): 0.1 (3H, s, PdCH_3), 2.0 (6H, s, mesityl CH_3), 2.3 (3H, s, mesityl CH_3) 5.6 (2H, v br, CH_2), 6.8 (1H, d, 5-imidazol-2-ylidene *H*), 6.9 (2H, s, mesityl *H*), 7.2 (1H, d, 4-imidazol-2-ylidene *H*), 7.4 (1H, br m, 5-picolyl *H*), 7.5 (1H, br, 3-picolyl *H*), 7.9 (1H, br t, 4-picolyl *H*), 8.6 (1H, br d, 6-picolyl *H*). δ_C ($CDCl_3$): −9 (Pd*C*H_3), 18, 21 (mesityl *C*H_3), 56 (*C*H_2), 122 (*C*F_3), 123 (5-imidazol-2-ylidene *C*), 125 (5-picolyl *C*H), 125 (3-picolyl *C*H), 128 (4-imidazol-2-ylidene *C*), 130 (mesityl *C*H), 135, 135, 139 (mesityl *C*), 140 (4-picolyl *C*H), 150 (6-picolyl *C*H), 152 (2-picolyl *C*), 164 (2-imidazol-2-ylidene *C*), 174 (CO_2).

Compound **13** was formed by following the above methodology but using a five-fold excess of silver trifluoroacetate. The product cocrystallised with silver trifluoroacetate after filtration of the silver bromide and slow evaporation of the solvent. The ^{1}H NMR spectrum was identical to that of **2d**. Attempts to obtain **13** free from the excess of silver salt by repeated recrystallisations were unsuccessful.

[3-(2,6-Diisopropylphenyl)-1-(α-picolyl)imidazol-2-ylidene]-methyl(tosylato)palladium(II) 3b

This was prepared following the general method using **3a** (0.40 g, 0.77 mmol) and silver tosylate (0.24 g, 0.85 mmol) in dichloromethane (50 cm^3) by stirring at room temperature for 12 h. The product was obtained in quantitative yields as a yellow solid (Found: C, 56.75; H, 5.83; N, 6.55. Calc. for $C_{29}H_{36}N_3O_3PdS$: C, 56.81; H, 5.92; N, 6.85%). MS (ES): *m*/*z* 469, [(ligand)PdMe + MeCN]$^+$. δ_H ($CDCl_3$): −0.1 (3H, s, $PdCH_3$), 1.0, 1.4 [2 × 6H, br d, CH(CH_3)$_2$], 2.3 (3H, s, OTs CH_3), 2.4 [2H, septet, CH(CH_3)$_2$], 5.5 (2H, br s, CH_2), 6.8 (1H, d, 5-imidazol-2-ylidene *H*), 7.1 (2H, d, OTs *H*), 7.2 (1H, d, 4-imidazol-2-ylidene *H*), 7.2 (2H, d, Pr$^i_2$C$_6$$H_2$H), 7.3 (1H, m, 5-picolyl *H*), 7.4 (1H, t, Pr$^i_2$C$_6$H$_2$*H*), 7.5, 7.6 (2H, br, 3,4-picolyl *H*), 7.8 (2H, d, OTs *H*), 8.8 (1H, v br, 6-picolyl *H*).δ_C ($CDCl_3$): −7 (Pd*C*H_3), 21 (OTs *C*H_3), 24, 26 [CH(*C*H_3)$_2$], 28 [*C*H(CH$_3$)$_2$], 56 (*C*H_2), 115, 139, (OTs, *C*), 122, 135 (Pr$^i_2$*C*$_6$H$_3$), 124 (5-picolyl *C*H), 124, 131 (Pr$^i_2$*C*$_6$H$_3$), 125 (4-imidazol-2-ylidene *C*), 129 (3-picolyl *C*H), 126, 129 (OTs *C*H), 138 (5-imidazol-2-ylidene *C*), 142 (4-picolyl *C*H), 145 (6-picolyl *C*H), 152 (2-picolyl *C*), 174 (2-imidazol-2-ylidene *C*).

[3-(2,6-Diisopropylphenyl)-1-(2-pyridyl)imidazol-2-ylidene]-methyl(tosylato)palladium(II) 5b

This was prepared following the general method from bromo-[3-(2,6-diisopropylphenyl)-1-(2-pyridyl)imidazol-2-ylidene]-methylpalladium(II) **5a** (0.38 g, 0.751 mmol) and silver tosylate (0.21 g, 0.754 mmol) in dichloromethane (50 cm^3) by stirring at room temperature for 12 h. The product was obtained in quantitative yield as a yellow solid. X-Ray quality crystals were obtained by layering a saturated solution of dichloromethane with diethyl ether (Found: C, 55.20; H, 5.42; N, 6.52. Calc. for $(C_{28}H_{34}N_3O_3PdS)_4CH_2Cl_2$: C, 54.70; H, 5.61; N, 6.77%). MS (ES): *m*/*z* 455, [(ligand)PdMe + MeCN]$^+$. δ_H ($CDCl_3$): 0.0 (3H, s, PdCH_3), 1.1, 1.2 [2 × 6H, d, CH(CH_3)$_2$], 2.3 (3H, s, OTs CH_3),

Table 5 Crystallographic data for complexes **3a**, **5a**, **5b**, **9**, **10**, **11** and **12**

	3a	**5a**	**5b**	**9**	**10**	**11**	**12**
Chemical formula	$C_{22}H_{28}BrN_3Pd$	$C_{24}H_{26}N_3BrPd$	$C_{28}H_{33}N_3O_3SPd$	$C_{48}H_{61}Cl_6N_9Pd_2$	$C_{34}H_{48}N_4Cl_4O_2Pd_2$	$C_{34}H_{48}N_4Cl_2O_2Pd$	$C_{36}H_{50}N_6Cl_2O_2Pd$
Formula weight	520.78	506.76	598.03	1189.56	899.36	722.11	776.12
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$C2/c$	$P\bar{1}$	$P2_1/c$
a/Å	7.79810(10)	11.29100(10)	15.0071(2)	12.515(5)	21.6662(3)	8.1120(2)	11.448(2)
b/Å	21.8591(2)	13.06100(10)	11.7722(2)	15.993(5)	13.5597(3)	9.1241(2)	10.010(2)
c/Å	13.48780(10)	14.7203(2)	16.2981(2)	16.428(5)	16.6211(4)	12.5173(4)	16.985(2)
α/°	90	90	90	114.512(5)	90	74.511(1)	90
β/°	90.60(1)	90.93(1)	110.042(1)	108.155(5)	129.240(1)	78.054(1)	103.99(3)
γ/°	90	90	90	96.941(5)	90	79.538(1)	90
V/Å^3	2299.00(4)	2170.54(4)	2704.96(7)	2721.3(16)	3781.95(13)	865.61(4)	1888.7(7)
Z	4	4	4	2	4	1	2
T/K	150	150	150	150	150	150	150
μ/mm^{-1}	2.556	2.705	0.797	0.996	1.296	0.726	0.672
No. data collected	24498	25345	23226	77270	13757	7069	15398
No. unique data	6659	6245	6178	7789	4311	3851	4301
R_{int}	0.0434	0.0471	0.0553	0.0421	0.0371	0.0224	0.0781
Final R(|F|) for $F_o > 2\sigma(F_o)$	0.0444	0.0497	0.0408	0.0665	0.0325	0.0303	0.0431
Final R(F^2) for all data	0.1409	0.1586	0.1103	0.2192	0.0789	0.0704	0.1170

2.5 [2H, septet, C*H*$(CH_3)_2$], 6.9 (1H, d, 5-imidazol-2-ylidene *H*), 7.1 (2H, d, OTs *H*), 7.2 (2H, d, $Pr^i_2C_6H_2H$), 7.4 (1H, m, 5-picolyl *H*), 7.5 (1H, t, $Pr^i_2C_6H_2H$), 7.7 (1H, d, 3-picolyl *H*), 7.8 (2H, d, OTs *H*), 7.9 (1H, d, 4-imidazol-2-ylidene *H*), 8.1 (1H, dt, 4-picolyl *H*), 9.1 (1H, br d, 6-picolyl *H*). δ_C ($CDCl_3$): −10 (Pd*C*H_3), 21 (OTs *C*H_3), 23, 25 (CH(*C*$H_3)_2$), 28 (*C*H$(CH_3)_2$), 117, 142 (OTs *C*), 122, 135 ($Pr^i_2C_6H_3$), 124 (4-imidazol-2-ylidene *C*), 124 (5-picolyl *C*H), 124, 131 ($Pr^i_2C_6H_3$),126 (3-picolyl *C*H), 127, 129 (OTs *C*H), 140 (5-imidazol-2-ylidene *C*), 143 (4-picolyl *C*H), 145 (6-picolyl *C*H), 150 (2-picolyl *C*), 174 (2-imidazol-2-ylidene *C*).

Crystallography

A summary of the crystal data, data collection and refinement for compounds **3a**, **5a**, **5b**, **9**, **10**, **11** and **12** are given in Table 5. Data for compounds **4**, **7** and **8** and **13** 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.[12] 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[13] and all software packages within. All figures were plotted using ORTEP (ref. 14) except Fig. 8 which was plotted using the CAMERON package (ref. 15). All non-hydrogen atoms were refined using anisotropic thermal parameters and hydrogens were added using a riding model. The orange crystals of **10** and clear crystals of **11** were taken from a single reaction mixture which gave two different crystalline species with **11** being the major product. Compound **12** has a residual density peak of 1.55 e Å which is located within 1.08 Å of a palladium centre and does not represent an atom. The data for **13** is of poor quality due to the nature of the crystals. Attempts to grow better quality crystals were unsuccessful. The data was refined to an error factor of 12.7% allowing to establish with certainty atom connectivity, even though the accuracy in the measurements of bond lengths and angles is limited. The crystal data is included in the CIF file.

CCDC reference numbers 194155–194165.

See http://www.rsc.org/suppdata/dt/b2/b209231j/ for crystallographic data in CIF or other electronic format.

Acknowledgements

We thank the EPSRC for partial support of this project and Prof. Robert P. Tooze for helpful discussions.

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