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O,N,N-Pincer ligand effects on oxidatively induced carbon–chlorine coupling reactions at palladium†

Luka A. Wright,[a] Eric G. Hope,[a] Gregory A. Solan,*[a] Warren B. Cross[a,b] and Kuldip Singh[a]

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The syntheses of two families of sterically tuneable *O,N,N* pro-ligands are reported, namely the 2-(phenyl-2′-ol)-6-imine-pyridines, 2-(C_6H_4-2′-OH),6-(CMe=NAr)C_5H_3N [Ar = 4-i-PrC_6H_4 (H**L1**$_a$), 2,6-i-$Pr_2C_6H_3$ (H**L1**$_b$)] and the 2-(phenyl-2′-ol)-6-(amino-prop-2-yl)pyridines, 2-(C_6H_4-2′-OH),6-(CMe_2NHAr)-C_5H_3N [Ar = 4-i-PrC_6H_4 (H**L2**$_a$), 2,6-i-$Pr_2C_6H_3$ (H**L2**$_b$)], using straightforward synthetic approaches and in reasonable overall yields. Interaction of H**L1**$_{a/c}$ and H**L2**$_{a/b}$ with palladium(II) acetate affords the *O,N,N*-pincer complexes, [{2-(C_6H_4-2′-O)-6-(CMe=NAr)C_5H_3N}Pd(OAc)] (Ar = 4-i-PrC_6H_4 (**1a**), 2,6-i-$Pr_2C_6H_3$ (**1b**)) and [{2-(C_6H_4-2′-O)-6-(CMe_2NHAr)C_5H_3N}Pd(OAc)] (Ar = 4-i-PrC_6H_4 (**2a**), 2,6-i-$Pr_2C_6H_3$ (**2b**)), which can be readily converted to their chloride derivatives, [{2-(C_6H_4-2′-O)-6-(CMe=NAr)C_5H_3N}PdCl] (Ar = 4-i-PrC_6H_4 (**3a**), 2,6-i-$Pr_2C_6H_3$ (**3b**)) and [{2-(C_6H_4-2′-O)-6-(CMe_2NHAr)C_5H_3N}PdCl] (Ar = 4-i-PrC_6H_4 (**4a**), 2,6-i-$Pr_2C_6H_3$ (**4b**)), respectively, on reaction with an aqueous sodium chloride solution. Treating each of **3a**, **3b**, **4a** and **4b** with two equivalents of di-*p*-tolyliodonium triflate at 100 °C in a toluene/acetonitrile mixture affords varying amounts of 4-chlorotoluene along with the 4-iodotoluene by-product with the conversions highly dependent on the steric and backbone properties of the pincer complex employed (*viz.* **4a** > **3a** > **4b** > **3b**); notably, the least sterically bulky and most flexible amine-containing **4a** reaches 90% conversion to 4-chlorotoluene in 15 h as opposed to 17% for imine-containing **3b**. In the case of **3a**, the inorganic palladium species recovered from the reaction has been identified as the Pd(II) salt [{2-(C_6H_4-2′-O)-6-(CMe=N(4-i-PrC_6H_4)C_5H_3N}Pd(NCMe)][O_3SCF_3] (**5a**), which was independently prepared by the reaction of **3a** with silver triflate in acetonitrile. Single crystal X-ray structures are reported for H**L1**$_a$, H**L2**$_a$, **1a**, **1b**, **2a**, **2b**, **3a** and **5a**.

Introduction

While hypervalent iodine salts of the type [Ar_2I][X] (X = OTf, BF_4) have been widely used in Pd(0)/(II) cross coupling reactions,[1] their application in Pd(II)/(IV) and/or Pd(II)/(III) chemistry has only started to emerge over the last decade.[2,3] With regard to the Pd(II)/(IV) couple, stable palladium(IV) species have been characterised,[4] computationally modelled[5] and highlight the ability of the I(III) reagent to transfer an "Ar^+" group to the palladium(II) centre; decomposition can ensue *via* reductive elimination of an aryl-containing product. The chlorination of Pd(II)–C and Pd(II)–Cl containing complexes with $PhICl_2$ represents another transformation that has been more extensively studied and these reactions are considered to proceed *via* a facile C–Cl bond forming reductive elimination from a Pd(IV) intermediate.[6,7] For example, van Koten has spectroscopically characterised a transient Pd(IV) species from the reaction of an Pd(II) chloride N,C_{ph},N-pincer complex with $PhICl_2$, which is presumed to then undergo C–Cl bond forming reductive elimination with the phenyl moiety of the pincer ligand.[8] Indeed, a variety of pincer ligand frameworks including symmetrical (*e.g.*, *N,C,N*[5,8]) and unsymmetrical (*e.g.*, *C,N,N*,[9] *O,N,C*,[10] *O,N,N*[11]) variations have proved conducive to promoting the formation of related electron deficient Pd(IV) intermediates, a feature that is likely to be attributable to the electron supplying nature of the tridentate manifold.

In this article we report the stoichiometric reactivity of a range of palladium(II) chloride *O,N,N*-pincer complexes towards di-*p*-tolyliodonium triflate with a view to monitoring the effect that the *O,N,N*-spectator ligand has on the anticipated formation of 4-chlorotoluene. In particular, we target two families of pyridine-based O,N_{py},N pincers in order to investigate how structural features within their respective O,N_{py},N ligand manifold influence the C–Cl bond forming process; the effects of imine (**L1**) *vs.* amine (**L2**) nitrogen donor

[a]*Department of Chemistry, University of Leicester, University Road, Leicester LE1 7RH, UK. E-mail: gas8@leicester.ac.uk*
[b]*School of Science and Technology, Nottingham Trent University, Clifton Lane, Nottingham NG11 8NS, UK*

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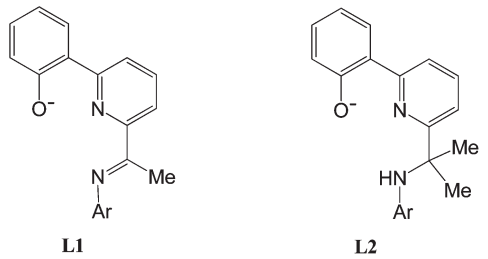


Fig. 1 Monoanionic 2-(phenyl-2′-olate)-6-ketimine-pyridine (**L1**) and 2-(phenyl-2′-olate)-6-(amino-prop-2-yl)pyridine (**L2**) pincer ligands.

and steric factors within the *N*-aryl group (Ar = 4-i-PrC_6H_4, 2,6-i-Pr$_2C_6H_3$) will be examined (Fig. 1). Full details of the synthetic and characterisation data for the pro-ligands, 2-(phenyl-2′-ol)-6-ketimine-pyridines (**HL1**) and 2-(phenyl-2′-ol)-6-(amino-prop-2-yl)pyridines (**HL2**), will be reported as will the corresponding data for their palladium(II) acetate (**1** and **2**) and chloride (**3**, **4**) complexes.

Results and discussion

(a) Preparation of pro-ligands HL1 and HL2

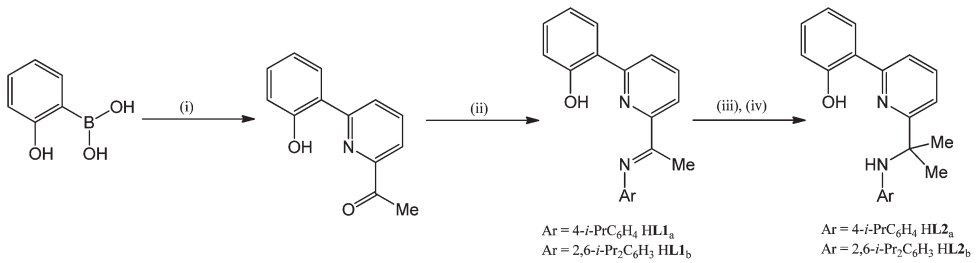
The 2-(phenyl-2′-ol)-6-imine-pyridines, 2-(C_6H_4-2′-OH),6-(CMe=NAr)C_5H_3N [Ar = 4-i-PrC_6H_4 (**HL1$_a$**), 2,6-i-Pr$_2C_6H_3$ (**HL1$_b$**)], have been prepared in modest to good yield *via* sequential Suzuki coupling and condensation reactions from 2-hydroxyphenylboronic acid and 2-bromo-6-acetyl pyridine (Scheme 1). As a slight modification to the reported synthesis of ketone precursor, 2-(C_6H_4-2′-OH),6-(CMe=O)C_5H_3N, it was found that the cross coupling proceeds more efficiently and over a shorter reaction time using a catalyst composed of Pd(OAc)$_2$ and PPh_3 in a reaction vessel open to the air.[12] Treatment of **HL1$_a$** and **HL1$_b$** with trimethylaluminium in toluene at elevated temperature followed by hydrolysis gave the 2-(phenyl-2′-ol)-6-(amino-prop-2-yl)pyridines, 2-(C_6H_4-2′-OH),6-(CMe$_2$NHAr)C_5H_3N [Ar = 4-i-PrC_6H_4 (**HL2$_a$**), 2,6-i-Pr$_2C_6H_3$ (**HL2$_b$**)], in good yield. The new compounds, **HL1$_a$**, **HL2$_a$** and **HL2$_b$**, have been characterised by a combination of ^{1}H, ^{13}C{^{1}H} NMR, IR spectroscopy and ESI mass spectrometry (see Experimental).

Compounds, **HL1$_a$**, **HL2$_a$** and **HL2$_b$**, all display protonated molecular ions peaks in their electrospray mass spectra and downfield shifted signals for the phenolic protons (range: δ 14.18–14.60) in their ^{1}H NMR spectra. For **HL1$_a$**, the imine methyl substituent is seen as a singlet at δ 2.32 in the ^{1}H NMR spectrum while the IR spectrum reveals a characteristic ν(C=N)$_{imine}$ stretch at 1635 cm^{-1}. For amine-containing **HL2$_a$** and **HL2$_b$**, broad singlets are visible for the NH protons between δ 3.3–4.0 in their ^{1}H NMR spectra along with sharp singlets for the equivalent *gem*-dimethyl protons. Further confirmation of the composition of **HL1$_a$** and **HL2$_a$** was achieved using single crystal X-ray diffraction.

Perspective views of **HL1$_a$** and **HL2$_a$** are depicted in Fig. 2a and b; selected bond distances and angles for both structures are listed in Table 1. Each structure consists of a central pyridine ring that is substituted at its 2-position by a phenyl-2′-ol group but differs at the 6-position with a *trans*-configured *N*-arylimine unit for **HL1$_a$** [C(12)–N(2) 1.2692(19) Å] or a saturated CMe$_2$NH(4-i-PrC_6H_4) unit for **HL2$_a$** [C(11)–C(12)–N(2) 108.97(16)°]. In general, the pyridine nitrogen atoms adopt a *cis* conformation with respect to the neighbouring phenol oxygen as a result of a hydrogen-bonding interaction between the phenol hydrogen atom and the pyridine nitrogen [O(1)···N(1) 2.563 (**HL1$_a$**), 2.537 Å (**HL2$_a$**)], a conformation that has been observed in related structures.[12–14]

(b) Palladium(II) complexes of L1 and L2

Interaction of **HL1$_{a/b}$** and **HL2$_{a/b}$** with palladium(II) acetate affords the *O*,*N*,*N*-pincer complexes, [{2-(C_6H_4-2′-O)-6-(CMe=NAr)C_5H_3N}Pd(OAc)] (Ar = 4-i-PrC_6H_4 (**1a**), 2,6-i-Pr$_2C_6H_3$ (**1b**)) and [{2-(C_6H_4-2′-O)-6-(CMe$_2$NHAr)C_5H_3N}Pd(OAc)] (Ar = 4-i-PrC_6H_4 (**2a**), 2,6-i-Pr$_2C_6H_3$ (**2b**)), in good yield (Scheme 2). Compounds **1** and **2** can be readily converted to their chloride analogues [{2-(C_6H_4-2′-O)-6-(CMe=NAr)C_5H_3N}PdCl] (Ar = 4-i-PrC_6H_4 (**3a**), 2,6-i-Pr$_2C_6H_3$ (**3b**)) and [{2-(C_6H_4-2′-O)-6-(CMe$_2$NHAr)C_5H_3N}PdCl] (Ar = 4-i-PrC_6H_4 (**4a**), 2,6-i-Pr$_2C_6H_3$ (**4b**)) by treating their chloroform or dichloromethane solutions with aqueous sodium chloride. Alternatively, **1a** can be prepared more conveniently by the template reaction of 2-(C_6H_4-2′-OH),6-(CMe=O)C_5H_3N, Pd(OAc)$_2$ and 4-isopropylaniline in toluene. Complexes **1–4** are air stable and have been characterised using a combination of mass spectrometry (FAB, ESI and ToF), IR and NMR (^{1}H and ^{13}C) spectroscopy and elemental analyses (see Experimental section). In addition,



Scheme 1 Reagents and conditions: (i) 2-Br-6-{MeC(O)}C_5H_3N, cat. Pd(OAc)$_2$/PPh_3, toluene, 90 °C, 12 h; (ii) ArNH_2, MeOH, cat. CH_3COOH, reflux; (iii) $AlMe_3$, toluene, 110 °C, 12 h; (iv) H_2O.

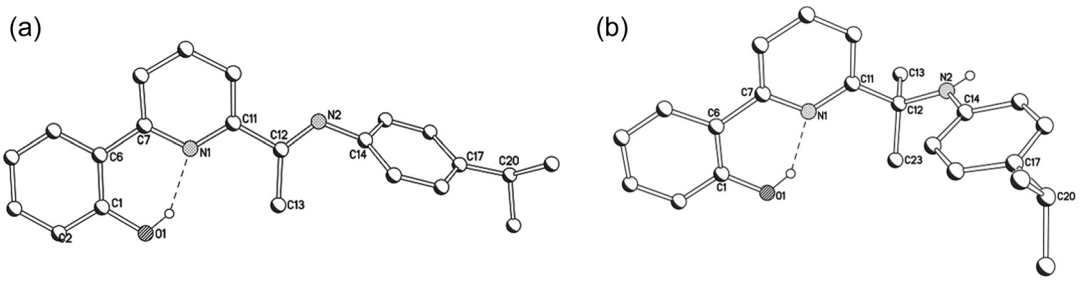
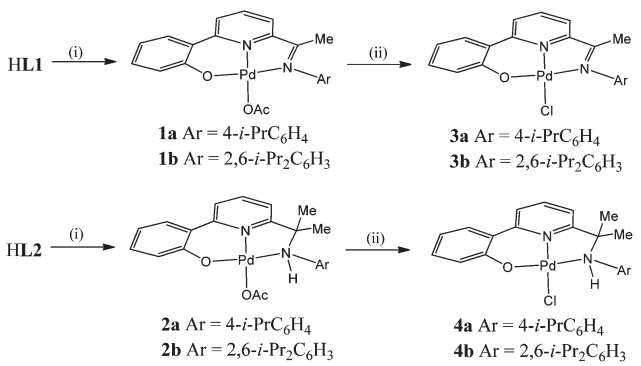


Fig. 2 (a) Molecular structure of HL1$_a$, including a partial atom numbering scheme. All hydrogen atoms, apart from H1, have been omitted for clarity. (b) Molecular structure of HL2$_a$, including a partial atom numbering scheme. All hydrogen atoms, apart from H1 and H2, have been omitted for clarity.

Table 1 Selected bond distances (Å) and angles (°) for HL1$_a$ and HL2$_a$

	HL1$_a$	HL2$_b$
Bond lengths		
C(1)–O(1)	1.3455(19)	1.353(2)
C(12)–N(2)	1.2692(19)	1.460(2)
C(6)–C(7)	1.466(2)	1.480(2)
C(11)–C(12)	1.482(2)	1.530(3)
Bond angles		
C(11)–C(12)–N(2)	115.71(15)	108.97(16)
C(12)–N(2)–C(14)	123.06(15)	125.80(16)



Scheme 2 Reagents and conditions: (i) Pd(OAc)$_2$, toluene, 75–80 °C; (ii) NaCl(aq.), $CHCl_3$ or CH_2Cl_2, RT.

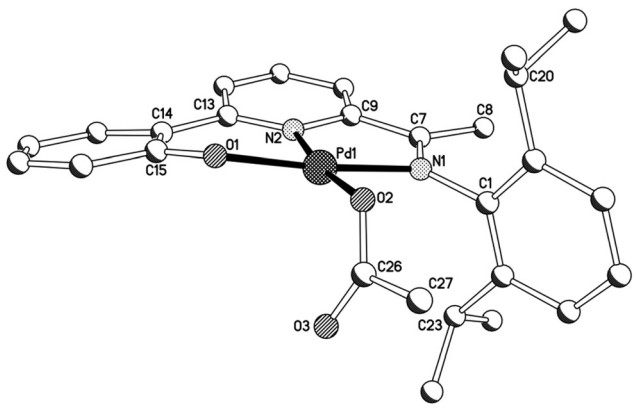


Fig. 3 Molecular structure of **1b** including a partial atom numbering scheme. All hydrogen atoms have been omitted for clarity.

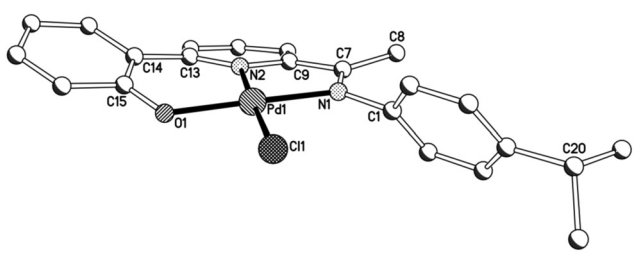


Fig. 4 Molecular structure of **3a** including a partial atom numbering scheme. All hydrogen atoms have been omitted for clarity.

crystals of **1a**, **1b**, **2a**, **2b** and **3a** have been the subject of single crystal X-ray diffraction studies.

The molecular structures of imine-based **1a**, **1b** and **3a** are closely related and will be discussed together; amine-containing **2a** and **2b** will be discussed later. Views of **1b** and **3a** are given in Fig. 3 and 4; selected bond distances and angles are collected for all three structures in Table 2. There are four independent molecules for **1a** in the unit cell (molecules A–D) which differ most noticeably in the relative inclinations of the adjacent phenolate and pyridine rings (*vide infra*). The structures (**1a**, **1b** and **3a**) each consist of a single palladium(II) centre bound by a tridentate monoanionic 2-(phenyl-2′-olate)-6-ketimine-pyridine ligand along with a monodentate O-bound acetate (**1**) or chloride (**3**) to complete a distorted square planar geometry. Both 5- and 6-membered chelate rings are present within the complexes with the bite angle for the 6-membered ring being slightly more compatible with the geometrical requirements of the palladium(II) centre [O(1)–Pd(1)–N(2)$_{6\text{-membered}}$: 96.4(4)$_{av.}$ (**1a**), 94.4(1) (**1b**), 93.8 (2)° (**3a**) *vs.* N(2)–Pd(1)–N(1)$_{5\text{-membered}}$ 82.1(4)$_{av.}$ (**1a**), 81.7(1) (**1b**), 81.7(2)° (**3a**)]. In all cases some twisting of the phenolate unit with respect to the pyridyl plane is apparent [tors. N(2)–C(13)–C(14)–C(15) 0.0(3)$_A$, 2.5(3)$_B$, 5.7(3)$_C$, 9.5(3)$_D$ (**1a**), 14.1(3) (**1b**), 22.1(3)° (**3a**)]. In general, the Pd–N$_{imine}$ bond distance is the longest of the three metal–ligand interactions involving the *O*,*N*,*N*-ligand followed by the Pd–N$_{pyridine}$ distance and then by the Pd–O$_{phenolate}$ distance which is best exemplified for complex **3a** [Pd(1)–N(1)$_{imine}$ 2.011(4) > Pd(1)–N(2)$_{pyridine}$

Table 2 Selected bond distances (Å) and angles (°) for **1a**, **1b** and **3a**

	1a					
	Molecule A	Molecule B	Molecule C	Molecule D	**1b**	**3a**
Bond lengths						
Pd(1)–O(1)	1.947(7)	1.928(8)	1.951(8)	1.934(8)	1.953(3)	1.961(3)
Pd(1)–N(1)	1.972(9)	1.980(9)	1.978(10)	1.961(10)	2.006(3)	2.011(4)
Pd(1)–N(2)	1.961(9)	1.972(9)	1.980(9)	2.005(10)	1.969(3)	1.972(4)
Pd(1)–Cl(1)	—	—	—	—	—	2.3039(14)
Pd(1)–O(2)	2.038(8)	2.033(8)	2.016(8)	2.025(8)	2.036(3)	—
C(7)–N(1)	1.319(12)	1.295(13)	1.303(13)	1.302(14)	1.292(5)	1.301(6)
C(7)–C(8)	1.484(13)	1.496(14)	1.515(15)	1.514(15)	1.509(5)	1.497(7)
C(15)–O(1)	1.306(12)	1.310(13)	1.347(13)	1.321(14)	1.317(5)	1.317(6)
Bond angles						
N(1)–Pd(1)–N(2)	82.9(4)	82.2(4)	81.8(4)	81.9(4)	81.68(13)	81.65(17)
N(1)–Pd(1)–O(1)	177.5(4)	177.5(4)	177.2(4)	178.2(4)	174.49(12)	174.56(16)
N(2)–Pd(1)–O(1)	95.2(4)	96.1(4)	96.2(4)	96.4(4)	94.35(12)	93.84(16)
N(2)–Pd(1)–Cl(1)	—	—	—	—	—	177.97(13)
N(2)–Pd(1)–O(2)	176.9(3)	175.0(4)	175.8(4)	176.1(4)	172.47(12)	—

1.972(4) > Pd(1)–$O(1)_{phenolate}$ 1.961(3) Å]. Replacing an O-bound acetate for a chloride has little effect on the *trans* Pd–$N_{pyridine}$ distance [1.972(4) Å (**3a**) *vs.* $1.980(10)_{av.}$ (**1a**)]. The *N*-aryl group in **1b** is inclined towards orthogonality with regard to the neighbouring C=N_{imine} vector [tors. C(7)–N(2)–C(1)–C(2) 86.1(3)°], while in the less sterically bulky **1a** and **3a** the aryl group is tilted [tors. $C(7)–N(2)–C(1)–C(2)\ 66.4(4)_{av}$ (**1a**), 57.8(6) (**3a**)°]. There are no intermolecular contacts of note. The structural features resemble related aldimine-based palladium complexes [{2-(3-$C_{12}H_8$-2-O)-6-(CH=NAr)C_5H_3N}-PdX] (X = OAc, Cl) reported elsewhere.[14,15]

A view of amine-based **2a** is given in Fig. 5; selected bond distances and angles are given for both **2a** and **2b** in Tables 3. The structures are similar to imine-containing **1a** and **1b** with a distorted square planar palladium(II) centre bound by a monoanionic *O*,*N*,*N* ligand and a monodentate O-bound acetate. In this case the more flexible 2-(phenyl-2′-olate)-6-(amino-prop-2-yl)pyridine acts as the *O*,*N*,*N* ligand again forming both 5-membered and 6-membered chelate rings. The presence of both a *gem*-dimethyl sp^3-hybridised carbon (N(1)–C(7)–C(10) 108.9(8) (**2a**) and 109.7(2)° (**2b**)) and secondary amine nitrogen donor results in some puckering of the 5-membered chelate ring while the 6-membered chelate ring shows similar properties to those observed in **1a**, **1b** and **3a** with some twisting of the phenolate unit with respect to the pyridyl plane evident [tors. N(2)–C(14)–C(15)–C(16) 18.3(3) (**2a**), 21.6° (**2b**)]. The Pd–$O_{phenolate}$ and Pd–$N_{pyridine}$ distances are comparable to those in **1a**, **1b** and **3a** while the Pd–N_{amine} length is *ca.* 0.05 Å longer than the average Pd–N_{imine} distance in **1a**, **1b** and **3a** consistent with the poorer donor characteristics of an amine. The pendant oxygen atom on the acetate ligand undergoes an intramolecular hydrogen bond interaction with the amine hydrogen atom [O(3)···N(1) 2.750 (**2a**), 2.895 (**2b**) Å]. It is worthy of note that the isopropyl group on

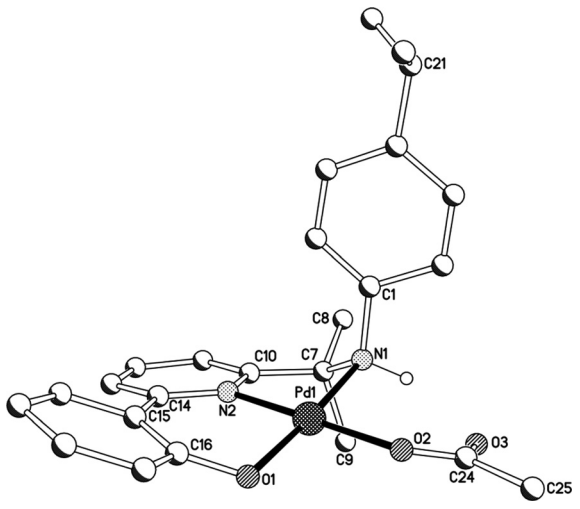
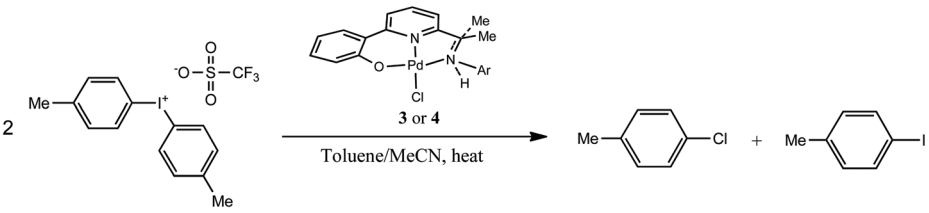


Fig. 5 Molecular structure of **2a** including a partial atom numbering scheme. All hydrogen atoms, apart from H1, have been omitted for clarity.

Table 3 Selected bond distances (Å) and angles (°) for **2a** and **2b**

	2a	**2b**
Bond lengths		
Pd(1)–O(1)	1.951(6)	1.9541(19)
Pd(1)–N(1)	2.061(6)	2.045(2)
Pd(1)–N(2)	1.983(7)	1.972(2)
Pd(1)–O(2)	2.008(6)	2.034(2)
C(7)–C(8)	1.519(11)	1.533(4)
C(7)–C(9)	1.557(11)	1.529(4)
C(7)–N(1)	1.467(10)	1.525(4)
Bond angles		
N(1)–Pd(1)–N(2)	81.8(3)	84.46(9)
N(1)–Pd(1)–O(1)	176.1(3)	179.16(9)
N(2)–Pd(1)–O(1)	94.5(3)	94.99(9)
N(1)–Pd(1)–O(2)	96.2(3)	94.71(9)
N(2)–Pd(1)–O(2)	176.8(3)	174.90(8)
O(1)–Pd(1)–O(2)	87.6(2)	85.90(8)
N(1)–C(7)–C(10)	108.9(8)	109.7(2)



Scheme 3 Oxidation of **3** and **4** with di-*p*-tolyliodonium triflate to give 4-chlorotoluene and 4-iodotoluene.

C(2) in **2b** occupies a position above the axial site of the N(1)–N(2)–O(1)–Pd(1) square plane (*vide infra*). There are no intermolecular contacts of note.

Complexes **1–4**, display either molecular ion peaks and/or fragmentation peaks corresponding to the loss of an acetate or a chloride in their mass spectra. For imine-based **1** and **3**, the $\nu(C{=}N)_{imine}$ stretch shifts by *ca.* 35 cm^{-1} to lower wavenumber when compared to those for the corresponding free H**L1**, supportive of imine coordination.[16] In **1b** and **3b** two distinct doublets are seen for the isopropyl methyl groups in their ^1H NMR spectra consistent with restricted rotation about the *N*-aryl or Ar–i-Pr bonds in solution. In contrast, there are four distinct doublets in **2b** and **4b** implying all four methyl groups are now inequivalent in the amine-based pincer complexes. The N–H protons in **2a** and **2b** are downfield shifted (between δ 8.7–9.9) consistent with the NH···$O_{acetate}$ hydrogen bonding as seen in the solid state, whilst in their chloride derivatives, **4a** and **4b**, the corresponding protons are found more upfield (between δ 6.1–6.7). The acetate methyl groups in **1** and **2** can be seen at δ *ca.* 1.6 in their ^1H NMR spectra with the Me*C*(O)O carbon atoms observable at δ *ca.* 178.8 in their ^{13}C NMR spectra. In addition strong bands assignable to the symmetric and asymmetric ν(COO) vibrations in **1** and **2**, are in agreement with those expected for monodentate acetate ligands.[17]

(c) Reactivity of 3 and 4 towards [*p*-tolyl$_2$I][O$_3$SCF$_3$]

All four palladium(II) chloride pincer complexes, **3a**, **3b**, **4a** and **4b**, were assessed on their ability to undergo oxidation with a hypervalent iodonium reagent and mediate the formation of a carbon–chlorine coupled product. Typically, **3** and **4** were treated with two equivalents of di-*p*-tolyliodonium triflate at 100 °C in a mixture of toluene–acetonitrile and their reaction mixtures monitored by gas chromatography using an internal standard to quantify the conversions (Scheme 3).

The results of the screening are collected in Table 4. Several points emerge from inspection of the data. Firstly, all the palladium pincer complexes screened afford 4-chlorotoluene in varying amounts along with the expected 4-iodotoluene by-product. Secondly, two structure/reactivity relationships are apparent namely: (i) within each *N*,*N*,*O* family the least sterically bulky *N*-aryl group promotes the highest conversions to 4-chorotoluene, *e.g.*, **4a** (93%, entry 6) *vs.* **4b** (26%, entry 7) and **3a** (80%, entry 4) *vs.* **3b** (17%, entry 5); (ii) amine-containing **4a** and **4b** yield higher conversions than their direct imine counterparts **3a** and **3b**, respectively. Thirdly, periodic monitoring of the conversion for **3a** reveals a rapid initial reaction (33% in 1 h, entry 1) which reaches a plateau over time.

Table 4 Percentage conversion to 4-chorotoluene and 4-iodotoluene on reaction of **3** or **4** with [(*p*-tolyl)$_2$I][O$_3$SCF$_3$][a]

Entry	Pd(II) chloride pincer	Time/h	Conversion/% to 4-chlorotoluene[b]	Conversion/% to 4-iodotoluene[b]
1	**3a**	1	33	27
2	**3a**	2.5	57	42
3	**3a**	6	74	67
4	**3a**	15	80	71
5	**3b**	15	17	7
6	**4a**	15	93	89
7	**4b**	15	26	10

[a] Conditions: **3** or **4** (0.05 mmol), [(*p*-tol)$_2$I][OTf] (0.1 mmol), ([Pd]/[(*p*-tol)$_2$IOTf] = 2), toluene/MeCN, 100 °C. [b] Determined using gas chromatography using naphthalene as an internal standard.

It is uncertain as to the origin of these ligand effects but it would seem likely that the sterically bulky 2,6-i-Pr$_2$Ph substitution pattern in **3b** and **4b** is inhibiting the oxidative transfer of the aryl group to the palladium centre. Indeed, work-up of the reaction between imine-containing **3b** and di-*p*-tolyliodonium triflate at 100 °C over 15 hours (entry 5) gave unreacted starting materials as the major identifiable inorganic components. The increased flexibility of the ligand manifold in amine-containing **4** may, in part, contribute to the improved performance over the corresponding imine.

Unfortunately we were unable to prove or disprove the involvement of a transient Pd(IV) species (*e.g.*, [(ONN)PdCl(*p*-tolyl)(NCMe)][O$_3$SCF$_3$]) by NMR spectroscopy due to the poor solubility of the reaction mixtures at lower temperatures. Nevertheless, we were able, in one case, to identify the palladium-containing decomposition product of the presumed reductive elimination event. Solid residues isolated from the reaction of **3a** with di-*p*-tolyliodonium triflate (entry 4) could be extracted into acetonitrile and found to contain unreacted di-*p*-tolyliodonium triflate and the Pd(II) salt [{2-(C$_6$H$_4$-2′-O)-6-(CMe=N(4-i-PrC$_6$H$_4$)C$_5$H$_3$N}Pd(NCMe)][O$_3$SCF$_3$] (**5a**). Confirmation of the presence of **5a** was obtained through spiking an ^1H NMR solution of the mixture with a genuine sample of **5a** (prepared from the reaction of **3a** with AgO$_3$SCF$_3$ in acetonitrile). Indeed **5a** has been fully characterised by mass spectrometry, IR and NMR (^1H, ^{19}F and ^{13}C) spectroscopy and has been the subject of a single crystal X-ray diffraction study.

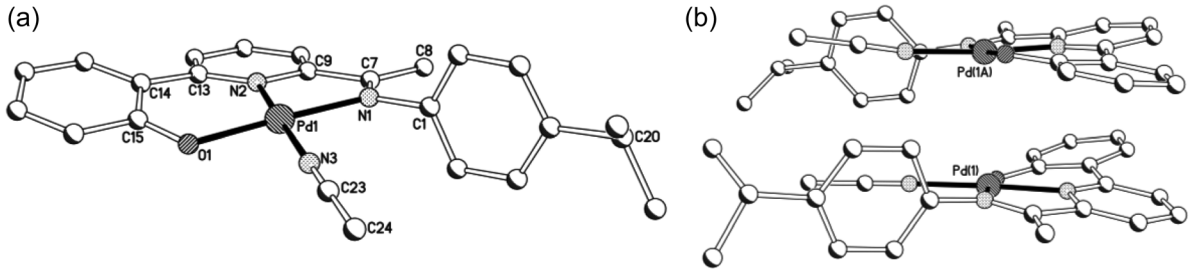


Fig. 6 (a) Molecular structure of the cationic unit in **5a** including a partial atom numbering scheme. All hydrogen atoms have been omitted for clarity. (b) Intermolecular packing of the two independent cationic units in **5a**.

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

	Molecule A	Molecule B
Bond lengths		
Pd(1)–N(1)	2.017(8)	1.997(8)
Pd(1)–N(2)	1.953(8)	1.951(8)
Pd(1)–N(3)	2.007(9)	1.994(10)
Pd(1)–O(1)	1.959(7)	1.979(7)
C(7)–N(1)	1.277(13)	1.297(13)
C(9)–C(7)	1.515(14)	1.473(15)
C(23)–N(3)	1.138(13)	1.176(14)
Range S(1)–$O_{triflate}$	1.416(9)–1.434(11)	
Bond angles		
N(1)–Pd(1)–N(2)	82.0(3)	82.5(3)
N(1)–Pd(1)–O(1)	175.0(3)	176.1(3)
N(1)–Pd(1)–N(3)	95.9(3)	94.5(3)
N(2)–Pd(1)–O(1)	94.5(3)	95.0(3)
N(2)–Pd(1)–N(3)	177.3(3)	174.9(3)

A view of **5a** is given in Fig. 6a; selected bond distances and angles are collected in Table 5. There are two independent cations and associated anions in the unit cell with the main differences between the cations being the inclinations of *N*-aryl groups. The structure of **5a** comprises a cationic palladium(II) unit charged balanced by a non-coordinating triflate anion. The cationic unit adopts a distorted square planar geometry [max. distortion: N(1)–Pd(1)–N(2) $82.0(3)_A$, $82.5(3)_B$°] with the 2-(phenyl-2′-olate)-6-ketimine-pyridine ligand occupying three coordination sites and the η^1-N acetonitrile molecule the fourth. The structural parameters displayed by the pincer ligand closely mirror the features observed in neutral precursor **3a** with the Pd–N_{imine} distance again the longest [Pd(1)–N(1) 2.017(8) Å, 1.997(8) Å] of the three donor atoms. Interestingly, the independent cations assemble in such a way as to maintain the Pd(II) centres in close proximity (Pd(1)···Pd(1A) 3.313 Å) and only slightly further apart than the sum of the van der Waals radii (3.26 Å) (Fig. 6b). Further confirmation of the salt-like nature of **5a** comes from the positive ESI mass spectrum (recorded in MeCN) which reveals peaks corresponding to the cationic unit while the negative spectrum the triflate anion. The ^{19}F NMR spectrum (in CD_3CN) displays a single peak at δ −79.3 comparable with that observed in related triflate salts of Pd-acetonitrile species.[18]

Conclusions

Two families of palladium(II) chloride *O*,*N*,*N* pincer complexes (**3** and **4**), differing in the type of exterior nitrogen donor and, within each family, the steric properties of the *N*-aryl ring, have been prepared *via* their respective acetate analogues (**1** and **2**) and fully characterised. Oxidation of **3** and **4** with di-*p*-tolyliodonium triflate leads in all cases to carbon–chloride coupling to give 4-chlorotoluene with the conversion highly dependent on the *O*,*N*,*N* pincer framework employed; the recovery of **5a** with an intact pincer framework highlights the robustness of the ligand manifold to oxidation. Notably, the least sterically hindered member of each family (**3a** and **4a**) leads to the highest conversion with amine-containing **4a** the highest. These observations set the stage for an investigation of these and related pincer systems in various Pd(II)/(IV)-mediated C–X coupling reactions. These results will be reported in due course.

Experimental

General

All operations, unless otherwise stated, were carried out under an inert atmosphere of dry, oxygen-free nitrogen using standard Schlenk and cannular techniques or in a nitrogen purged glove box. Solvents were distilled under nitrogen from appropriate drying agents[19] or were employed directly from a Solvent Purification System (Innovative Technology, Inc). The electrospray (ESI) mass spectra were recorded using a micromass Quattra LC mass spectrometer with acetonitrile or methanol as the matrix. FAB mass spectra (including high resolution) were recorded on a Kratos Concept spectrometer with NBA as matrix or on a Water Xevo QToF mass spectrometer equipped with an atmospheric solids analysis probe (ASAP). The infrared spectra were recorded in the solid state with Universal ATR sampling accessories on a Perkin Elmer Spectrum One FTIR instrument. NMR spectra were recorded on a Bruker DPX 300 spectrometer operating at 300.03 (^{1}H) and 75.4 MHz (^{13}C) or a Bruker DRX400 spectrometer at 400.13 (^{1}H), 376.46 (^{19}F) and 100.61 MHz (^{13}C) or a Bruker Avance III 500 spectrometer at 125 MHz (^{13}C), at ambient temperature unless otherwise

stated; chemical shifts (ppm) are referred to the residual protic solvent peaks and coupling constants are expressed in hertz (Hz). Melting points (mp) were measured on a Gallenkamp melting point apparatus (model MFB-595) in open capillary tubes and were uncorrected. Elemental analyses were performed at the Science Technical Support Unit, London Metropolitan University. The reagents 2,6-diisopropylaniline, 4-isopropylaniline, silver triflate and trimethylaluminium (2 M solution in toluene) were purchased from Aldrich Chemical Co. and used without further purification. The compounds 2-hydroxyphenylboronic acid,[12] 2-bromo-6-acetyl pyridine[20] and di-*p*-tolyliodonium triflate[21] and H**L1**$_b$[12] were prepared using literature procedures. All other chemicals were obtained commercially and used without further purification.

Synthesis of 2-(phenyl-2′-ol)-6-acetyl-pyridine

A round-bottomed flask equipped with stirrer bar and reflux condenser, open to the air, was loaded with 2-bromo-6-acetyl-pyridine (2.10 g, 10.00 mmol), $Pd(OAc)_2$ (0.047 g, 0.21 mmol), triphenylphosphine (0.110 mg, 0.42 mmol) and 2-hydroxyphenyl boronic acid (1.88 g, 13.7 mmol). Toluene (40 mL), ethanol (22 mL) and aqueous 2 M K_2CO_3 (13 mL, 26.00 mmol) were added and the mixture heated to 90 °C for 12 h. The resultant black reaction mixture was cooled to room temperature followed by the addition of 1 mL H_2O_2 (30% in water) and stirred for a further 30 min. The organic phase was separated and the aqueous phase washed with toluene (3 × 10 mL). The combined organic extracts were washed with water (3 × 30 mL) and brine (10 mL) and concentrated to afford a brown solid. This solid was slurried in methanol (10 mL) for 1 h and the resultant solid filtered and washed with methanol (3 mL) and dried under reduced pressure. 2-(Phenyl-2′-ol)-6-acetyl-pyridine was collected as a yellow solid (1.885 g, 84%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.71 (s, 3H, $CH_3C{=}O$), 6.90 (ddd, $^3J_{HH}$ 8.4, $^3J_{HH}$ 7.4, $^4J_{HH}$ 1.4, 1H, Ar–H), 7.00 (dd, $^3J_{HH}$ 8.3, $^4J_{HH}$ 1.3, 1H, Ar–H), 7.30 (ddd, $^3J_{HH}$ 8.5, $^3J_{HH}$ 7.5, $^4J_{HH}$ 1.7, 1H, Ar–H), 7.78 (dd, $^3J_{HH}$ 8.1, $^4J_{HH}$ 1.7, 1H, Ar–H), 7.94 (m, 2H, Py–H), 8.06 (dd, $^3J_{HH}$ 7.1, $^4J_{HH}$ 2.1, 1H, Py–H), 13.64 (s, 1H, O–H). ESIMS *m*/*z*: 214 $[M + H]^+$. The data was consistent with that reported in ref. 13.

Synthesis of 2-(C_6H_4-2′-OH),6-{CMe=N(4-i-PrC_6H_4)}C_5H_3N (H**L1**$_a$)

2-(Phenyl-2′-ol)-6-acetyl-pyridine (0.405 g, 1.90 mmol), 4-isopropyl aniline (0.473 g, 3.50 mmol) and $MgSO_4$ (2.76 g, 23.0 mmol) were suspended in bench methanol (10 mL) and one drop of acetic acid added. The mixture was stirred and heated at reflux for 9 days whereupon a further drop of acetic acid was added and the mixture stirred at reflux for an additional 12 h. On cooling to room temperature the reaction mixture was filtered and the $MgSO_4$ washed with chloroform (30 mL) and the filtrate concentrated under reduced pressure. The resultant solid was heated in MeOH (10 mL), cooled to room temperature and the suspension collected by filtration and dried under reduced pressure affording H**L1**$_a$ as yellow solid (0.381 g, 61%). Single crystals suitable for an X-ray determination were grown by slow cooling of a saturated solution of H**L1**$_a$ in EtOH. Mp: 123–125 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.20 (d, $^3J_{HH}$ 7.1, 6H, CH*Me*$_2$), 2.32 (s, 3H, $CH_3C{=}N$), 2.84 (sept, $^3J_{HH}$ 7.1, 1H, C*H*Me$_2$), 6.69 (d, $^3J_{HH}$ 8.4, 2H, Ar_{mipp}–H), 6.85 (app. td, $^3J_{HH}$ 8.1, $^4J_{HH}$ 1.2, 1H, Ar_{phenol}–H), 6.96 (dd, $^3J_{HH}$ 8.2, $^4J_{HH}$ 1.2, 1H, Ar_{phenol}–H), 7.16 (d, $^3J_{HH}$ 8.3, 2H, Ar_{mipp}–H), 7.25 (app. td, $^3J_{HH}$ 8.2, $^4J_{HH}$ 1.5, 1H, Ar_{phenol}–H), 7.75 (dd, $^3J_{HH}$ 8.1, $^4J_{HH}$ 1.4, 1H, Ar_{phenol}–H), 7.79–7.91 (m, 2H, Py–H), 8.12 (dd, $^3J_{HH}$ 7.6, $^4J_{HH}$ 1.1, 1H, Py–H), 14.18 (s, 1H, O–H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 15.5 (*C*$H_3C{=}N$), 23.1 (CH*Me*$_2$), 32.6 (*C*HMe$_2$), 117.4 (CH), 117.7 (C), 118.0 (CH), 118.3 (CH), 118.8 (CH), 119.1 (CH), 125.4 (CH), 125.9 (CH), 130.6 (CH), 137.2 (CH), 143.6 (C), 147.2 (C), 152.7 (C), 155.6 (C), 158.6 (C), 163.6 ($C{=}N_{imine}$). IR (cm^{-1}): $\nu(C{=}N)_{imine}$ 1635, $\nu(C{=}N)_{pyridine}$ 1587. ESIMS *m*/*z*: 331 $[M + H]^+$, 329 $[M - H]$. HRMS (ASAP): Calc. for $C_{22}H_{23}N_2O$ $[M + H]^+$ 331.1810, found 331.1803. Anal calc. for ($C_{22}H_{22}N_2O$) C 79.97, N 8.48, H 6.71. Found: C 79.97, N 8.41, H 6.64%.

Synthesis of 2-(C_6H_4-2′-OH),6-(CMe_2NHAr)C_5H_3N (H**L2**)

(a) Ar = 4-i-PrC_6H_4 (H**L2**$_a$): A Schlenk flask equipped with stir bar was evacuated and backfilled with nitrogen. The vessel was loaded with H**L1**$_a$ (0.510 g, 1.50 mmol) and toluene (20 ml) and trimethylaluminium (2.0 ml, 4.00 mmol, 2 M solution in toluene) introduced dropwise. The solution was then stirred and heated to reflux for 12 h before being cooled to room temperature and concentrated under reduced pressure. Petroleum ether (20 ml, 40/60) was added and the solution cooled to 5 °C prior to the slow addition of water (20 ml). The mixture was then stirred for 1 h at room temperature before the organic phase was isolated. The aqueous phase was extracted with chloroform (4 × 50 ml) and the combined organic extracts washed with water (3 × 10 mL) and brine (1 × 10 mL) and then dried over $MgSO_4$. The solvent was removed under reduced pressure to provide H**L2**$_a$ as an orange oil which solidified slowly over time (0.500 g, 96%). Single crystals suitable for an X-ray determination were grown by slow cooling of a saturated solution of H**L2**$_a$ in ethanol. Mp: 109–112 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.07 (d, $^3J_{HH}$ 7.0, 6H, CH*Me*$_2$), 1.66 (s, 6H, N–C-(CH_3)$_2$), 2.66 (sept, $^3J_{HH}$ 7.0, 1H, C*H*Me$_2$), 3.97 (br s, 1H, N–H), 6.19 (d $^3J_{HH}$ 8.6, 2H, Ar_{mipp}–H), 6.81 (d, $^3J_{HH}$ 8.6, 2H, Ar_{mipp}–H), 6.86 (app. td, $^3J_{HH}$ 8.1, $^4J_{HH}$ 1.2, 1H, Ar–H), 6.96 (dd, $^3J_{HH}$ 8.3, $^4J_{HH}$ 1.2, 1H, Ar–H), 7.25 (ddd, $^3J_{HH}$ 8.5, $^3J_{HH}$ 7.2, $^4J_{HH}$ 1.6, 1H, Ar–H), 7.49–7.53 (1H, m, Ar–H), 7.69–7.73 (2H, m, Ar–H), 7.77 (dd, $^3J_{HH}$ 8.0, $^4J_{HH}$ 1.6, 1H, Py–H), 14.55 (s, 1H, O–H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 23.06 (CH*Me*$_2$), 28.2 (N–C-(CH_3)$_2$), 32.0 (*C*HMe$_2$), 56.5 (C–N), 114.3 (CH), 115.8 (CH), 117.4 (CH), 117.7 (C), 177.8 (CH), 118.1 (CH), 125.2 (CH), 125.7 (CH), 130.4 (CH), 137.1 (C), 137.6 (CH), 142.2 (C), 155.9 (C), 158.9 (C), 162.8 (C). IR (cm^{-1}): 1592 $(C{=}N)_{pyridine}$. ESIMS *m*/*z*: 347 $[M + H]^+$. HRMS (EI): Calc. for: $C_{23}H_{27}N_2O$ $[M + H]^+$ 347.2123, found: 347.2140.

(b) Ar = 2,6-i-$Pr_2C_6H_3$ (H**L2**$_b$): A similar procedure to that described for H**L2**$_a$ was followed using H**L1**$_b$ (0.601 g, 2.70 mmol), toluene (20 ml) and trimethylaluminium (3.40 ml, 6.70 mmol 2 M solution in toluene). On work-up, H**L2**$_b$ was afforded as an orange oil which solidified slowly

over time (0.549 g, 88%). Mp: 70–72 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.98 (d, $^3J_{HH}$ 7.0, 12H, CHMe_2), 1.49 (s, 6H, N–C-(CH_3)$_2$), 2.95 (sept, ^3JHH 7.0, 2H, CHMe$_2$), 3.34 (br s, 1H, N–H), 6.85 (ddd, $^3J_{HH}$ 8.2, $^3J_{HH}$ 7.4, $^4J_{HH}$ 1.3, 1H, Ar–H), 6.94 (dd, $^3J_{HH}$ 8.2, $^4J_{HH}$ 1.2, 1H, Ar–H), 6.98 (m (app. s), 3H, Ar–H), 7.23 (ddd, $^3J_{HH}$ 8.4, $^3J_{HH}$ 7.2, $^4J_{HH}$ 1.6, 1H, Ar–H), 7.59 (dd, $^3J_{HH}$ 7.4, $^4J_{HH}$ 1.2, 1H, Py–H), 7.72–7.79 (3H, m, Ar–H), 14.60 (s, 1H, O–H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 22.8 (CHMe_2), 27.4 (CHMe$_2$), 28.2 (N–C(CH_3)$_2$), 58.1 (C–N), 115.7 (CH), 117.2 (CH), 117.4 (CH), 117.7 (CH), 118.1 (C), 122.1 (CH), 123.5 (CH), 125.3 (CH), 130.3 (CH), 137.0 (CH), 138.7 (C), 144.3 (C), 155.5 (C), 159.0 (C), 165.1 (C). IR (cm^{-1}): 1591 (C=N)$_{pyridine}$. ESIMS m/z: 389 [M + H]$^+$. HRMS (EI): Calc. for $C_{26}H_{33}N_2O$ [M + H]$^+$ 389.2593, found 389.2606.

Synthesis of [{2-(C_6H_4-2′-O)-6-(CMe=NAr)C_5H_3N}Pd(OAc)] (1)

(a) Ar = 4-i-PrC_6H_4 (**1a**): A Schlenk flask equipped with stir bar was evacuated and backfilled with nitrogen. The vessel was loaded with H**L1**$_a$ (0.100 g, 0.300 mmol), Pd(OAc)$_2$ (0.068 g, 0.300 mmol) and toluene (10 ml) and then stirred and heated at 80 °C for 12 h. On cooling to room temperature the volatiles were removed under reduced pressure. The resultant solid was dissolved in dichloromethane (5 mL) and hexane (100 mL) introduced affording **1a** as a red solid (0.136 g, 90%). Single crystals suitable for an X-ray determination were grown by slow diffusion of hexane into a solution of **1a** in chloroform. Mp: >240 °C (decomp.). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.22 (d, $^3J_{HH}$ 6.9, 6H, CHMe_2), 1.48 (s, 3H, CH_3C(O)O–), 2.07 (s, 3H, CH_3C=N), 2.90 (sept, $^3J_{HH}$ 6.9, 1H, CHMe$_2$), 6.61 (ddd, $^3J_{HH}$ 8.2, $^3J_{HH}$ 6.6, $^4J_{HH}$ 1.5, 1H, Ar$_{phenolate}$–H), 7.04 (dd, $^3J_{HH}$ 8.5, $^4J_{HH}$ 1.3, 1H, Ar–H), 7.09–7.14 (m, 4H, Ar–H), 7.23 (d, $^3J_{HH}$ 8.2, 2H, Ar$_{mipp}$–H), 8.02 (d, $^3J_{HH}$ 8.5, 1H, Py–H), 8.06 (dd, $^3J_{HH}$ 8.5, $^3J_{HH}$ 8.5, 1H, Py–H), 8.97 (d, $^3J_{HH}$ 8.7, 1H, PyH). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 16.5 (CH$_3$C=N), 21.7 (CH_3C(O)O–), 22.9 (CHMe_2), 32.9 (CHMe$_2$), 114.5 (CH), 118.2 (C), 122.3 (CH), 122.3 (CH), 122.4 (CH), 125.6 (CH), 126.2 (CH), 128.5 (CH), 130.6 (CH), 137.5 (CH), 141.2 (C), 147.5 (C), 150.0 (C), 162.0 (C), 172.4 (C=N$_{imine}$), 177.0 (C=O). IR (cm^{-1}): 1613 (C=N)$_{imine}$, 1590 (COO$_{asymm}$/C=N$_{pyridine}$), 1456 (COO$_{symm}$). FABMS m/z: 435 [M − OAc]$^+$. Anal calc. for ($C_{24}H_{24}N_2O_3Pd$): C 58.25; H 4.89; N 5.66 Found: C 58.12; H 4.83; N 5.67%.

(b) Ar = 2,6-i-Pr$_2C_6H_3$ (**1b**): A similar procedure to that described for **1a** was followed using H**L1**$_b$ (0.100 g, 0.27 mmol), Pd(OAc)$_2$ (0.061 g, 0.27 mmol) afforded **1b** as a red solid (0.135 g, 93%). Crystals suitable for an X-ray determination were grown by slow diffusion of hexane into a solution of **1b** in chloroform. Mp: >240 °C (decomp.). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.04 (d, $^3J_{HH}$ 6.9, 6H, CHMe_2), 1.41 (d, $^3J_{HH}$ 6.7, 6H, CHMe_2), 1.43 (s, 3H, CH_3C(O)C–), 2.24 (s, 3H, CH_3C=N), 3.22 (sept, $^3J_{HH}$ 6.8, 2H, CHMe$_2$), 6.64 (ddd, $^3J_{HH}$ 8.3, $^3J_{HH}$ 6.3, $^4J_{HH}$ 1.9, 1H, Ar$_{phenolate}$–H), 7.14–7.22 (4H, m, under $CHCl_3$), 7.28 (dd, $^3J_{HH}$ 8.2, $^3J_{HH}$ 7.3, 1H, Ar–H), 7.60 (dd, $^3J_{HH}$ 7.5, $^4J_{HH}$ 1.0, 1H, Py–H), 7.79 (d, $^3J_{HH}$ 8.6, 1H, Ar$_{phenolate}$–H), 8.08 (dd, $^3J_{HH}$ 8.8, $^3J_{HH}$ 7.5, 1H, Py–H), 8.43 (d, $^3J_{HH}$ 8.7, 1H, Py–H). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 18.5 (CHMe_2), 22.5 (CHMe_2), 23.7 (CH$_3$C(O)O–), 24.4 (CH$_3$C=N), 28.8 (CHMe$_2$), 115.8 (CH), 119.2 (C), 122.6 (CH), 123.8 (CH), 123.9 (CH), 126.6 (CH), 128.4 (CH), 128.5 (CH), 132.3 (CH), 137.1 (CH), 139.5 (C), 140.8 (C), 152.7 (C), 154.2 (C), 164.1 (C), 174.2 (C=N$_{imine}$), 177.3 (C=O). IR (cm^{-1}): 1600 (C=N$_{imine}$/COO$_{asymm}$/C=N$_{pyridine}$), 1456 (COO$_{symm}$). ESIMS m/z: 477 [M − OAc]$^+$, 518 [(M − OAc + MeCN]$^+$. HRMS (ASAP): Calc. for: $C_{27}H_{30}N_2O_3Pd$ [M]$^+$ 536.1291 Found 536.1333.

Synthesis of [{2-(C_6H_4-2′-O)-6-(CMe$_2$NHAr)C_5H_3N}Pd(OAc)] (2)

(a) Ar = 4-i-PrC_6H_4 (**2a**): A Schlenk flask equipped with a stir bar was evacuated, back-filled with nitrogen and then loaded with H**L2**$_a$ (0.040 g, 0.12 mmol), Pd(OAc)$_2$ (0.026 g, 0.12 mmol) and toluene (4 mL). After stirring and heating at 75 °C for 12 h, the reaction mixture was allowed to cool to room temperature and the volatiles removed under reduced pressure. The residue was dissolved in dichloromethane (1 mL) before hexane (20 mL) was added to precipitate the product. The product was collected on a Celite plug, washed with hexane (10 mL) before being dissolved in dichloromethane (10 mL) and the solution collected. On evaporation of the volatile components, **2a** was obtained as a red powder (0.057 g, 93%). Single crystals suitable for an X-ray determination were grown by slow diffusion of hexane into a solution of **2a** in chloroform. Mp: >240 °C (decomp.). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.09 (d, $^3J_{HH}$ 6.9, 6H, CHMe_2), 1.36 (s, 3H, N–C(CH_3)$_2$), 2.00 (s, 3H, CH_3C(O)C–), 2.40 (s, 3H, N–C(CH_3)$_2$), 2.72 (sept, $^3J_{HH}$ 6.9, 1H, CHMe$_2$), 6.60 (ddd, $^3J_{HH}$ 8.1, $^3J_{HH}$ 6.5, $^4J_{HH}$ 1.8, 1H, Ar$_{phenolate}$–H), 6.67 (d, $^3J_{HH}$ 8.4, 2H, Ar$_{mipp}$–H), 6.87 (dd, $^3J_{HH}$ 6.1, $^4J_{HH}$ 2.3, 1H, Py–H), 6.94 (d, $^3J_{HH}$ 8.3, 2H, Ar$_{mipp}$–H), 7.06–7.14 (m, 2H, Ar$_{phenolate}$–H), 7.57 (d, $^3J_{HH}$ 8.5, 1H, Ar$_{phenolate}$–H), 7.80 (d, $^3J_{HH}$ 8.5, 1H, Py–H), 7.82 (dd, $^3J_{HH}$ 8.5, $^3J_{HH}$ 6.2, 1H, Py–H), 9.92 (br s, 1H, NH). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 23.8 (CHMe_2), 24.1 (CH_3C(O)O–), 24.4 (N–C(CH$_3$)$_2$), 33.6 (CHMe$_2$), 33.6 (N–C(CH$_3$)$_2$), 70.2 (C–N), 116.0 (CH), 116.3 (CH), 121.4 (CH), 121.8 (C), 122.9 (CH), 123.0 (CH), 127.5 (CH), 128.9 (CH), 132.3 (CH), 138.9 (C), 139.7 (C), 147.2 (C), 153.5 (C), 164.4 (C), 168.0 (C), 181.6 (C=O). IR (cm^{-1}): 3400 (NH), 1574 (COO$_{asymm}$/C=N$_{pyridine}$), 1448 (COO$_{symm}$). ESIMS: m/z 510 [M]$^+$, 592 [M − OAc + MeCN]$^+$. HRMS (FAB): m/z Calc. for $C_{25}H_{28}N_2O_3Pd$ [M]$^+$ 510.6296. Found 510.1125.

(b) Ar = 2,6-i-Pr$_2C_6H_3$ (**2b**): A similar procedure to that outlined for **2a** was employed using H**L2**$_b$ (0.024 g, 0.61 mmol) and Pd(OAc)$_2$ (0.014 g, 0.061 mmol) gave **2b** as a yellow solid (0.033 g, 98%). Single crystals suitable for an X-ray determination were grown by slow diffusion of hexane into a solution of **2b** in dichloromethane. Mp: >240 °C (decomp.). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.72 (d, $^3J_{HH}$ 6.9, 3H, CHMe_2), 1.18 (s, 3H, NC(CH_3)$_2$), 1.19 (d, $^3J_{HH}$ 6.9, 3H, CHMe_2), 1.22 (d, $^3J_{HH}$ 6.9, 3H, CHMe_2), 1.54 (d, $^3J_{HH}$ 6.7, 3H, CHMe_2), 1.91 (s, 3H, CH_3C(O)-O–), 2.31 (s, 3H, N–C(CH_3)$_2$), 3.16 (sept, $^3J_{HH}$ 6.7, 1H, CH-(Me)$_2$), 3.72 (sept, $^3J_{HH}$ 6.8, 1H, CH(Me)$_2$), 6.61 (ddd, $^3J_{HH}$ 8.5, $^3J_{HH}$ 6.4, $^4J_{HH}$ 2.0, 1H, Ar$_{phenolate}$–H), 6.84 (dd, $^3J_{HH}$ 6.9, $^4J_{HH}$ 2.1, 1H, Py H), 7.02–7.18 (m, 5H, Ar–H), 7.54 (d, $^3J_{HH}$ 8.3, 1H, Ar$_{phenolate}$–H), 7.74–7.80 (m, 2H, Py–H), 8.66 (br s, 1H, NH). ^{13}C{^{1}H} NMR ($CDCl_3$ 100 MHz): δ 21.9 (CHMe_2), 22.3 (CH_3C(O)-O–), 23.7 (CH_3), 24.1 (CH_3), 24.5 (CHMe_2), 24.6 (CH_3), 27.4

(*C*HMe$_2$), 27.7 (*C*HMe$_2$), 32.3 (N–C(*C*H$_3$)$_2$), 70.8 (C–N), 115.0 (CH), 115.6 (CH), 110.0 (CH), 120.8 (C), 121.5 (CH), 124.2 (CH), 124.7 (CH), 126.9 (CH), 127.9 (CH), 131.4 (CH), 134.5 (C), 137.8 (CH), 143.0 (C), 143.5 (C), 152.3 (C), 163.1 (C), 169.3 (C), 179.2 (C=O). IR (cm^{-1}): 3064 (NH), 1590 (COO_{asymm}/C=$N_{pyridine}$), 1450 (COO_{symm}). TOFMS (ASAP): *m*/*z* 553 [M + H]$^+$, 493 [M − OAc]$^+$. Anal. calc. for ($C_{28}H_{34}N_2O_3Pd{\cdot}3CH_2Cl_2$): C 46.09, H 4.99 N 3.47% Found: C 46.00, H 4.64, N 3.61%.

Synthesis of [{2-(C_6H_4-2′-O)-6-(CMe=NAr)C_5H_3N}PdCl] (3)

(a) Ar = 4-i-PrC_6H_4 (**3a**): A round bottomed flask equipped with stirrer bar and open to the air was loaded with **1a** (0.568 g, 1.15 mmol), chloroform (30 mL) and brine (30 mL). After stirring vigorously at room temperature for 1 h the organic phase was separated, washed with water (3 × 30 ml) and filtered through a Celite plug. The plug was washed with chloroform (10 mL) and the solution concentrated to a smaller volume (*ca.* 5 mL) before hexane (100 mL) was added to precipitate the title compound as dark red solid (0.537 g, 99%). Single crystals suitable for an X-ray determination were grown by slow diffusion of hexane into a solution of **3a** in chloroform. Mp: >240 °C (decomp). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.22 (d, $^3J_{HH}$ 6.9, 6H, CH*Me*$_2$), 2.28 (s, 3H, CH_3C=N), 2.88 (sept, $^3J_{HH}$ 6.9, 1H, C*H*Me$_2$), 6.67 (ddd, $^3J_{HH}$ 8.3, $^3J_{HH}$ 6.1, $^4J_{HH}$ 2.0, 1H, $Ar_{phenolate}$–H), 7.04 (d, $^3J_{HH}$ 8.4, 2H, Ar_{mipp}–H), 7.16–7.24 (m, 4H, Ar–H), 7.61 (dd, $^3J_{HH}$ 7.6, $^4J_{HH}$ 1.0, 1H, Py–H), 7.68 (d, $^3J_{HH}$ 8.4, 1H, $Ar_{phenolate}$–H), 7.89 (dd, $^3J_{HH}$ 8.6, $^3J_{HH}$ 7.5, 1H, Py–H), 8.18 (d, $^3J_{HH}$ 8.7, 1H, Py–H). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 18.5 (*C*H$_3$C=N), 23.9 (CH*Me*$_2$), 33.7 (*C*HMe$_2$), 116.0 (CH), 119.1 (C), 123.2 (CH), 123.6 (CH), 124.1 (CH), 125.7 (CH), 126.5 (CH), 128.9 (CH), 132.1 (CH), 138.0 (CH), 143.7 (C), 148.2 (C), 150.5 (C), 154.7 (C), 162.4 (C), 175.7 (C=N_{imine}). IR (cm^{-1}): ν(C=N)$_{imine}$ 1598. FABMS *m*/*z*: 470 [M]$^+$, 435 [M − Cl]$^+$. Anal calc. for ($C_{22}H_{21}N_2OPdCl$): C 56.07; H 4.49; N 5.94. Found: C 55.99; H 4.38; N 6.01%.

(b) Ar = 2,6-i-$Pr_2C_6H_3$ (**3b**): A similar procedure to that described for **3a** was employed using **1b** (0.289 g, 0.54 mmol) affording **3b** as a red solid (0.221 g, 80%). Mp: >240 °C (decomp.). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.06 (d, $^3J_{HH}$ 6.9, 6H, CH*Me*$_2$), 1.39 (d, $^3J_{HH}$ 6.8, 6H, CH*Me*$_2$), 2.22 (s, 3H, *C*H$_3$C=N), 3.06 (sept, $^3J_{HH}$ 6.8, 2H, C*H*Me$_2$), 6.69 (ddd, $^3J_{HH}$ 8.4, $^3J_{HH}$ 6.8, $^4J_{HH}$ 1.5, 1H, $Ar_{phenolate}$–H), 7.16 (d, $^3J_{HH}$ 7.9, 2H, Ar_{dipp}–H), 7.20–7.32 (m, 3H, Ar–H), 7.71 (dd, $^3J_{HH}$ 7.5, $^4J_{HH}$ 1.0, 1H, Py–H), 7.82 (dd, $^3J_{HH}$ 8.6, $^4J_{HH}$ 1.4, 1H, $Ar_{phenolate}$–H), 8.13 (dd, $^3J_{HH}$ 8.8, $^3J_{HH}$ 7.6, 1H, Py–H), 8.47 (d, $^3J_{HH}$ 8.8, 1H, Py–H). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 18.2 (CH*Me*$_2$), 23.7 (CH*Me*$_2$), 23.9 (*C*H$_3$C=N), 28.9 (*C*HMe$_2$), 116.2 (CH), 118.7 (C), 122.8 (CH), 123.8 (CH), 124.2 (CH), 127.0 (CH), 128.4 (CH), 128.6 (CH), 132.6 (CH), 137.2 (CH), 139.8 (C), 141.3 (C), 152.3 (C), 154.1 (C), 163.5 (C), 175.2 (C=N_{imine}). IR (cm^{-1}): ν(C=N)$_{imine}$ 1607. FABMS: *m*/*z* 512 [M]$^+$, 477 [M − Cl]$^+$. TOFMS (ASAP): *m*/*z* 513 [M + H]$^+$, 477 [M − Cl]$^+$. Anal. calc. for ($C_{25}H_{27}N_2OPdCl$): C 58.49, H 5.30, N 5.46 Found: C 58.38, H 5.27, N 5.52%.

Synthesis of [{2-(C_6H_4-2′-O)-6-(CMe$_2$NHAr)C_5H_3N}PdCl] (4)

(a) Ar = 4-i-PrC_6H_4 (**4a**): A round bottomed flask equipped with stirrer bar and open to the air was loaded with **2a** (0.281 g, 0.55 mmol), dichloromethane (20 mL) and brine (20 mL). After stirring vigorously at room temperature for 12 h the organic phase was separated, washed with water (3 × 30 ml) and filtered through a Celite plug. Hexane (100 mL) was added to precipitate the product which was trapped on a Celite plug and washed with hexane (20 mL). The product was dissolved in dichloromethane and the solution collected. All volatiles were removed under reduced pressure affording **4a** as a yellow solid (0.219 g, 82%). Mp: >240 °C (decomp.). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.19 (d, $^3J_{HH}$ 7.0, 6H, CH*Me*$_2$), 1.53 (s, 3H, N–C(CH$_3$)$_2$), 2.51 (s, 3H, N–C(CH$_3$)$_2$), 2.83 (sept, $^3J_{HH}$ 7.0, 1H, C*H*Me$_2$), 6.67 (br, s, 1H, NH), 6.69–6.73 (m, 1H, Ar–H), 6.94–6.99 (m, 3H, Ar–H), 7.07 (d, $^3J_{HH}$ 8.7, 2H, Ar–H), 7.21 (d, $^3J_{HH}$ 4.3, 2H, Ar–H), 7.69 (d, $^3J_{HH}$ 8.4, 1H, Ar–H), 7.92–8.00 (m, 2H, Ar–H). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 23.8 (CH*Me*$_2$), 24.2 (N–C(*C*H$_3$)$_2$), 33.6 (*C*HMe$_2$), 33.8 (N–C(*C*H$_3$)$_2$), 72.0 (C–N), 116.1 (CH), 116.3 (CH), 121.6 (CH), 121.9 (C), 123.0 (CH), 123.3 (CH), 127.5 (CH), 129.0 (CH), 132.4 (CH), 139.1 (CH), 139.4 (C), 147.5 (C), 152.6 (C), 164.2 (C), 167.0 (C). IR (cm^{-1}): ν(C=$N_{pyridine}$) 1573, ν(NH) 3171. FABMS: *m*/*z* 486 [M]$^+$, 451 [M − Cl]$^+$. HRMS (ASAP): *m*/*z* Calc. for $C_{23}H_{26}N_2OPdCl$ [M + H]$^+$ 487.0768. Found 487.0792. Calc. for $C_{23}H_{25}N_2OPd$ [M − Cl]$^+$ 451.002. Found 451.1026. Calc. for ($C_{23}H_{25}N_2OPdCl{\cdot}CHCl_3$): C 47.51; H 4.32; N 4.62 Found: C 47.54; H 4.19; N 4.71%.

(b) Ar = 2,6-i-$Pr_2C_6H_3$ (**4b**): A similar procedure to that described for **4a** was employed using **2b** (0.221 g, 0.40 mmol) affording **4b** as a yellow solid (0.154 g, 73%). Mp: >240 °C (decomp). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.83 (d, $^3J_{HH}$ 6.9, 3H, CH*Me*$_2$), 1.23 (s, 3H, N–C(CH$_3$)$_2$), 1.27 (d, $^3J_{HH}$ 6.8, 3H, CH*Me*$_2$), 1.41 (d, $^3J_{HH}$ 6.6, 3H, CH*Me*$_2$), 1.51 (d, $^3J_{HH}$ 6.7, 3H, CH*Me*$_2$), 2.16 (s, 3H, N–C(CH$_3$)$_2$), 3.02 (sept, $^3J_{HH}$ 6.7, 1H, C*H*Me$_2$), 3.35 (sept, $^3J_{HH}$ 6.8, 1H, C*H*Me$_2$), 6.10 (br, s, 1H, NH), 6.61 (ddd, $^3J_{HH}$ 8.2, $^3J_{HH}$ 6.3, $^4J_{HH}$ 2.1, 1H, $Ar_{phenolate}$–H), 6.86 (dd, $^3J_{HH}$ 7.5, $^4J_{HH}$ 1.2, 1H, Py–H), 7.05–7.08 (m, 2H, Ar–H), 7.03–7.17 (m, 3H, Ar–H), 7.55 (d, $^3J_{HH}$ 8.3, 1H, $Ar_{phenolate}$–H), 7.81 (dd, $^3J_{HH}$ 8.3, $^3J_{HH}$ 7.4, 1H, Py–H), 7.88 (d, $^3J_{HH}$ 8.4, 1H, Py–H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 22.6 (CH*Me*$_2$), 24.3 (N–C(*C*H$_3$)$_2$), 24.4 (CH*Me*$_2$), 24.9 (CH*Me*$_2$), 25.5 (CH*Me*$_2$), 28.9 (*C*HMe$_2$), 29.3 (*C*HMe$_2$), 34.3 (N–C(*C*H$_3$)$_2$), 72.0 (C–N), 116.1 (CH), 116.1 (CH), 121.4 (C), 123.1 (CH), 124.5 (CH), 125.7 (CH), 128.0 (CH), 129.0 (CH), 132.3 (CH), 135.7 (C), 138.9 (CH), 142.2 (C), 143.0 (C), 153.4 (C), 164.0 (C), 169.0 (C). IR (cm^{-1}): ν(C=$N_{pyridine}$): 1573. FABMS: *m*/*z* 528 [M]$^+$, 493 [M − Cl]$^+$. HRMS (ASAP) *m*/*z*: Calc. for $C_{26}H_{32}N_2OPdCl$ [M + H]$^+$ 529.1238. Found 529.1235. Calc. for $C_{26}H_{31}N_2OPd$ [M − Cl]$^+$ 493.1471 Found 493.1413. Anal calc. for ($C_{26}H_{31}N_2OPdCl{\cdot}0.5CHCl_3$): C 54.03; H 5.39; N 4.76 Found: C 54.44, H 5.75, N 4.78%.

Synthesis of [{2-(C_6H_4-2′-O)-6-(CMe=N{(4-i-PrC_6H_4)}C_5H_3N}-Pd(NCMe)][O_3SCF_3] (5a)

A Schlenk flask was loaded in the glovebox and **3a** (0.124 g, 0.264 mmol) along with $AgOSO_2CF_3$ (68 mg, 0.264 mmol)

introduced. On removal from the glovebox, MeCN (10 mL) was added and the reaction mixture stirred at room temperature for 12 h in the absence of light. The resultant slurry was allowed to settle before the insoluble components were removed by cannular filtration and the filtrate collected in a second dry Schlenk flask. The solvent was removed under reduced pressure affording **5a** as a hygroscopic orange solid (0.160 g, 97%). Single crystals suitable for an X-ray determination were obtained by layering of a solution of **5a** in MeCN–toluene (5 : 95 v/v) with hexane. ^{1}H NMR (CD_3CN, 400 MHz): δ 1.31 (d, $^3J_{HH}$ 7.0, 6H, CHMe_2), 2.45 (s, 3H, $CH_3C{=}N$), 3.05 (sept, $^3J_{HH}$ 7.0, 1H, CHMe$_2$), 6.93 (ddd, $^3J_{HH}$ 8.4, $^3J_{HH}$ 7.0,

Table 6 Crystallographic and data processing parameters for H**L1**$_a$, H**L2**$_a$, **1a**, **1b**, **2a**, **2b**, **3a** and **5a**[a]

Complex	HL1$_a$	HL2$_a$	1a	1b
Formula	$C_{22}H_{22}N_2O$	$C_{23}H_{26}N_2O$	$C_{96}H_{96}N_8O_{12}Pd_4{\cdot}7CHCl_3{\cdot}H_2O$	$C_{27}H_{30}N_2O_3Pd{\cdot}0.75C_6H_{14}$
M	330.42	346.46	2833.00	623.10
Crystal size (mm^3)	0.41 × 0.35 × 0.20	0.35 × 0.30 × 0.26	0.43 × 0.24 × 0.15	0.31 × 0.24 × 0.13
Temperature (K)	150(2)	150(2)	150(2)	150(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2(1)/c$	$P2(1)/c$	$P2(1)/c$	$C2/c$
a (Å)	7.6425(19)	9.166(6)	27.533(6)	26.910(8)
b (Å)	11.027(3)	16.955(11)	19.525(4)	14.159(4)
c (Å)	20.590(5)	13.033(9)	23.435(5)	15.463(5)
α (°)	90	90	90	90
β (°)	93.528(5)	102.965(11)	111.63(3)	110.788(6)
γ (°)	90	90	90	90
U (Å^3)	1731.8(7)	1974(2)	11 711(4)	5508(3)
Z	4	4	4	8
D_c (Mg m^{-3})	1.267	1.166	1.607	1.503
F(000)	704	744	5696	2608
μ(Mo-K$_\alpha$)(mm^{-1})	0.078	0.071	1.144	0.712
Reflections collected	13 311	13 931	22 937	21 197
Independent reflections	3410	3471	22 937	5402
R_{int}	0.0574	0.0595	0.000	0.0834
Restraints/parameters	0/229	0/239	1134/1358	0/304
Final R indices ($I > 2\sigma(I)$)	R_1 = 0.0489	R_1 = 0.0528	R_1 = 0.0958	R_1 = 0.0490
	wR_2 = 0.1054	wR_2 = 0.1289	wR_2 = 0.1419	wR_2 = 0.1019
All data	R_1 = 0.0705	R_1 = 0.0708	R_1 = 0.2822	R_1 = 0.0713
	wR_2 = 0.1147	wR_2 = 0.1385	wR_2 = 0.1947	wR_2 = 0.1084
Goodness of fit on F^2 (all data)	0.981	1.030	0.822	0.959

Complex	2a	2b	3a	5a
Formula	$C_{25}H_{28}N_2O_3Pd{\cdot}1.5CHCl_3$	$C_{28}H_{34}N_2O_3Pd{\cdot}CH_2Cl_2$	$C_{22}H_{21}ClN_2OPd{\cdot}CHCl_3$	$C_{25}H_{24}F_3N_3O_4PdS{\cdot}MeCN$
M	6889.95	637.90	590.63	666.99
Crystal size (mm^3)	0.23 × 0.15 × 0.04	0.37 × 0.24 × 0.20	0.35 × 0.29 × 0.07	0.45 × 0.43 × 0.04
Temperature (K)	150(2)	150(2)	150(2)	150(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2(1)/c$	$P2(1)/c$	$P2(1)/c$	$P\bar{1}$
a (Å)	16.155(4)	16.640(6)	17.785(4)	13.264(11)
b (Å)	13.910(3)	10.960(4)	8.6156(19)	13.822(11)
c (Å)	13.360(3)	17.137(6)	16.469(4)	17.160(14)
α (°)	90	90	90	80.989(15)
β (°)	109.643(5)	116.252(5)	110.168(4)	78.907(15)
γ (°)	90	90	90	64.369(13)
U (Å^3)	2827.5(11)	2803.1(16)	2368.8(9)	2774(4)
Z	4	4	4	4
D_c (Mg m^{-3})	1.621	1.512	1.656	1.597
F(000)	1396	1312	1184	1352
μ(Mo-K$_\alpha$)(mm^{-1})	1.113	0.866	1.253	0.805
Reflections collected	22 017	21 332	18 002	21 653
Independent reflections	5551	5505	4659	10 758
R_{int}	0.1884	0.0497	0.1264	0.1073
Restraints/parameters	277/285	0/341	0/283	36/740
Final R indices ($I > 2\sigma(I)$)	R_1 = 0.0695	R_1 = 0.0373	R_1 = 0.0554	R_1 = 0.0999
	wR_2 = 0.1575	wR_2 = 0.0935	wR_2 = 0.0830	wR_2 = 0.2351
All data	R_1 = 0.1940	R_1 = 0.0439	R_1 = 0.1026	R_1 = 0.1570
	wR_2 = 0.1815	wR_2 = 0.0966	wR_2 = 0.0938	wR_2 = 0.2619
Goodness of fit on F^2 (all data)	0.725	1.059	0.897	1.033

[a] Data in common: graphite-monochromated Mo-K$_\alpha$ radiation, λ = 0.71073 Å; $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, w$R_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, $w^{-1} = [\sigma^2(F_o)^2 + (aP)^2]$, $P = [\max(F_o^2, 0) + 2(F_c^2)]/3$, where a is a constant adjusted by the program; goodness of fit = $[\sum(F_o^2 - F_c^2)2/(n-p)]^{1/2}$ where n is the number of reflections and p the number of parameters.

$^4J_{HH}$ 1.3, 1H, $Ar_{phenolate}$–H), 7.13 (dd, $^3J_{HH}$ 8.6, $^4J_{HH}$ 1.3, 1H, $Ar_{phenolate}$–H), 7.26 (d, $^3J_{HH}$ 8.5, 2H, Ar_{mipp}–H), 7.40 (ddd, $^3J_{HH}$ 8.5, $^3J_{HH}$ 6.8, $^4J_{HH}$ 1.5, 1H, $Ar_{phenolate}$–H), 7.49 (d, $^3J_{HH}$ 8.5, 2H, Ar_{mipp}–H), 8.08–8.13 (2H, m, Ar–H), 8.39 (dd, $^3J_{HH}$ 8.7, $^3J_{HH}$ 7.5, 1H, Py–H), 8.67 (d, $^3J_{HH}$ 8.8, 1H, Py–H), the coordinated CH_3CN ligand was not observed due to rapid exchange with bulk CD_3CN. $^{13}C\{^1H\}$ NMR (CD_3CN, 100 MHz): δ 17.4 ($CH_3C{=}N$), 22.8 ($CHMe_2$), 33.3 ($CHMe_2$), 116.9 (CH), 118.5 (C), 120.7 (CH), 122.4 (CH), 125.6 (CH), 126.8 (CH), 127.2 (CH), 129.5 (CH), 132.9 (CH), 139.4 (CH), 142.9 (C), 149.5 (C), 150.3 (C), 155.2 (C), 160.0 (C), 177.8 ($C{=}N_{imine}$), $CF_3SO_3^-$ not observed. ^{19}F NMR (CD_3CN, 376 MHz): δ −79.3 (s, 3F, CF_3SO_3). IR (cm^{-1}): $\nu(C{=}N)_{imine}$ 1597. ESIMS (+ve): m/z 476 $[M - CF_3SO_3]^+$. ESIMS (−ve): m/z 149 $[CF_3SO_3]^-$. HRMS (ASAP): m/z Calc. for $C_{23}H_{21}N_2O_4SF_3Pd$ $[M - MeCN]^+$ 584.0218 Found 584.0482.

General procedure for reactions of Pd–Cl complexes with the iodonium salt

A microwave vessel equipped with stirrer bar and open to the air was loaded with **3** or **4** (0.05 mmol) and di-*p*-tolyliodonium triflate (0.10 mmol, 2 eq.) and the contents suspended in toluene (4.5 mL) and MeCN (0.5 mL) before the system was sealed. The mixture was then stirred and heated to 100 °C for the specified time period. On cooling to room temperature the internal standard naphthalene (1 eq.) was added in hexane (2 mL). 1 mL of this reaction mixture was removed, diluted with a further 2 mL of hexane and the solids removed by filtration through a silica plug. The plug was washed with hexane (1 mL) and the filtrate was subject to analysis by GC. GC conditions: Hold oven temperature at 40 °C for 2 min; ramp 10 °C min^{-1} for 10 min; hold oven temperature at 180 °C for 12 min; injection temperature 250 °C; injection volume 1 μL; split ratio: 50 : 1. All reactions were repeated in triplicate.

Crystallographic studies

Data for $HL1_a$, $HL2_a$, **1a**, **1b**, **2a**, **2b**, **3a** and **5a** were collected on a Bruker APEX 2000 CCD diffractometer. Details of data collection, refinement and crystal data are listed in Table 6. The data were corrected for Lorentz and polarisation effects and empirical absorption corrections applied. Structure solution by direct methods and structure refinement based on full-matrix least-squares on F^2 employed SHELXTL version 6.10.[22] Hydrogen atoms were included in calculated positions (C–H = 0.93–1.00 Å) riding on the bonded atom with isotropic displacement parameters set to $1.5U_{eq}$(C) for methyl H atoms and $1.2U_{eq}$(C) for all other H atoms. All non-H atoms were refined with anisotropic displacement parameters. Disordered solvent was omitted using the SQUEEZE option in PLATON for **1b** and **2a**.[23]

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