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From discrete monomeric complexes to hydrogen-bonded dimeric assemblies based on sterically encumbered square planar palladium(II) ONN-pincers†

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The 2-(3-biphenyl-2-ol)-6-iminepyridines, 2-(3-$C_{12}H_8$-2-OH)-6-(CH=NAr)C_5H_3N (Ar = 2,6-i-$Pr_2C_6H_3$ (**L1a**-H), 2,4,6-$Me_3C_6H_2$ (**L1b**-H)), have been prepared in high yield *via* sequential Suzuki coupling, deprotection and condensation reactions from 2-methoxybiphenyl-3-ylboronic acid and 2-bromo-6-formylpyridine. Treatment of **L1**-H with $Pd(OAc)_2$ or $(MeCN)_2PdCl_2$ results in deprotonation of **L1**-H to afford the discrete square planar ONN-chelates, [{2-(3-$C_{12}H_8$-2-O)-6-(CH=NAr)C_5H_3N}Pd(OAc)] (Ar = 2,6-i-$Pr_2C_6H_3$ (**1a**), 2,4,6-$Me_3C_6H_2$ (**1b**)) and [{2-(3-$C_{12}H_8$-2-O)-6-(CH=NAr)C_5H_3N}PdCl] (Ar = 2,6-i-$Pr_2C_6H_3$ (**2a**), 2,4,6-$Me_3C_6H_2$ (**2b**)), in good yield, respectively; conversion of **1** to **2** using aqueous sodium chloride has been demonstrated. Selective reduction of the imino unit in **L1**-H with $LiAlH_4$ proceeds smoothly to yield the 2-(3-biphenyl-2-ol)-6-(methylamine)pyridines, 2-(3-$C_{12}H_8$-2-OH)-6-(CH_2-NHAr)C_5H_3N (Ar = 2,6-i-$Pr_2C_6H_3$ (**L2a**-H), 2,4,6-$Me_3C_6H_2$ (**L2b**-H)), which on reaction with $Pd(OAc)_2$ give [{2-(3-$C_{12}H_8$-2-O)-6-(CH_2-NHAr)-C_5H_3N}Pd(OAc)] (Ar = 2,6-i-$Pr_2C_6H_3$ (**3a**), 2,4,6-$Me_3C_6H_2$ (**3b**)). Depending on the temperature of the reaction, the oxidised aldimine products **1a** or **1b** can also be observed as a competitive side-product during the formation of **3a** or **3b**. Similarly, ketimine-containing, [{2-(3-$C_{12}H_8$-2-O)-6-(CMe=N(2,6-i-$Pr_2C_6H_3$))-C_5H_3N}Pd(OAc)] (**5**), can be detected during the preparation of chiral [{2-(3-$C_{12}H_8$-2-O)-6-(CMeH-NH(2,6-i-$Pr_2C_6H_3$))C_5H_3N}Pd(OAc)] (**4**) from 2-(3-$C_{12}H_8$-2-OH)-6-(CH_2-NH(2,6-i-$Pr_2C_6H_3$))C_5H_3N (**L3**-H) and $Pd(OAc)_2$. Complexes **3a**, **3b** and **4** all exist as dimeric species in the solid state in which two anti-aligned square planar monomers are held together by two intermolecular $NH_{amine}\cdots O_{phenolate}$ interactions resulting in palladium–palladium separations of between 3.141–3.284 Å. The structurally related chloride-containing dimeric assemblies, [{2-(3-$C_{12}H_8$-2-O)-6-(CH_2-NHAr)C_5H_3N)}PdCl] (Ar = 2,6-i-$Pr_2C_6H_3$ (**6a**), 2,4,6-$Me_3C_6H_2$ (**6b**)), can also be isolated on treatment of **3** with aqueous sodium chloride or by reaction of **L3**-H with $(MeCN)_2PdCl_2$. Single crystal X-ray diffraction studies have been performed on **L1a**-H, **L3**-H, **1a**, **1b**, **2a**, **2b**, **3a**, **3b**, **4**, **6a** and **6b**.

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Introduction

Pyridine-based pincer-type complexes, in which the heteroaromatic defines the central donor, have attracted considerable interest in recent years due, in large part, to their important applications in organic synthesis, homogeneous catalysis, bond activation and design of new materials.[1] The amenability of the exterior donor atoms of the tridentate ligand to impart electronic and steric flexibility to the metal centre has no doubt impacted on these advances. Moreover, recognition of the aromatisation–dearomatisation processes that can occur at the pyridine core during certain bond activations has help further fuel the research area.[2]

With regard to palladium(II) chemistry, pyridine-based pincer complexes have been reported for a raft of different tridentate ligand sets including symmetrical (*e.g.*, PNP,[3] NNN,[4] CNC,[5] SNS[6]) and non-symmetrical (*e.g.*, NNC,[7] ONC[8]) examples. In contrast, those based on non-symmetric ONN-frameworks are considerably more scarce with anionic O-substituted *N*,*N*-bipyridines/phenanthrolines[9] and neutral 2-imine-6-(methylalcohol)pyridines[10] representative.

With a view to developing new ligand systems that may have catalytic applications, we have been interested in pincers that can not only promote the formation of a sterically protected metal-containing pocket, but also have the potential to

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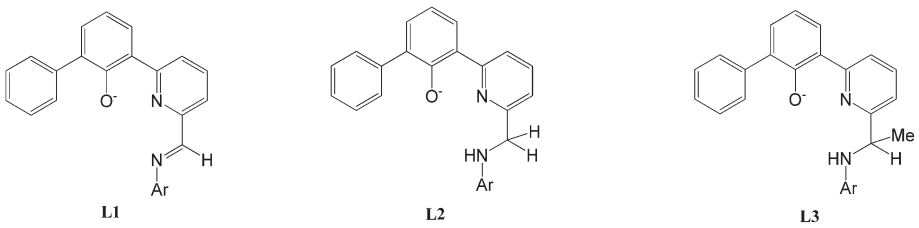


Fig. 1 Monoanionic 2-(3-biphenyl-2-olate)-6-iminepyridine (**L1**), 2-(3-biphenyl-2-olate)-6-(methylamine)pyridine (**L2**) and 2-(3-biphenyl-2-olate)-6-(ethylamine)-pyridine (**L3**).

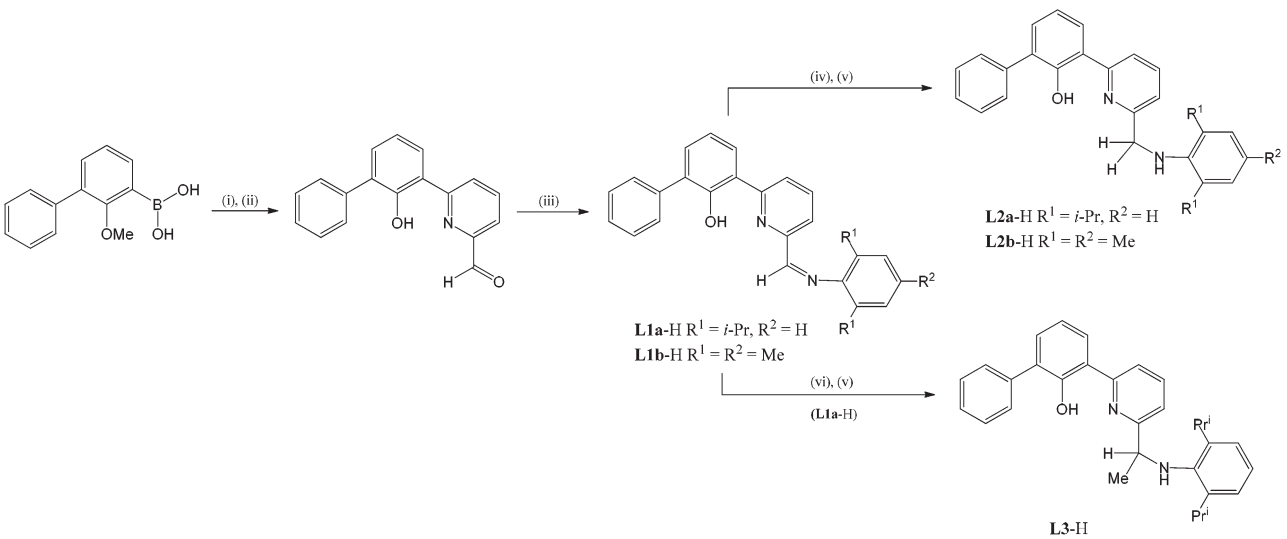
facilitate intermolecular hydrogen-bonding interactions[11,12] within the pocket. To this end, we targeted an ONN ligand framework incorporating a central pyridine group appended by both an anionic oxygen donor and a neutral secondary amine (or imine) donor.[13] It was envisaged that the coordinated amine donor could also serve as a directional hydrogen bond donor (D) and the bound oxygen as an acceptor (A). Herein, we report the synthesis of the protonated forms of the non-symmetrical 2-(biphenyl-2-olate)-6-iminepyridine, **L1**, and the reduced 2-(biphenyl-2-olate)-6-(alkylamine)pyridines, **L2** and **L3**, and then explore their coordination chemistry with palladium(II) (Fig. 1).

Results and discussion

(a) Preparation of pro-ligands L1-H–L3-H

The 2-(3-biphenyl-2-ol)-6-iminepyridines, 2-(3-$C_{12}H_8$-2-OH)-6-(CH=NAr)C_5H_3N (Ar = 2,6-i-$Pr_2C_6H_3$ (**L1a**-H), 2,4,6-$Me_3C_6H_2$ (**L1b**-H)), have been prepared in high yield *via* sequential Suzuki coupling, deprotection and condensation reactions from 2-methoxybiphenyl-3-ylboronic acid and 2-bromo-6-formylpyridine (Scheme 1) using general methodologies we have described elsewhere.[14] The imino unit in **L1**-H could be readily reduced by addition of lithium aluminium hydride to yield the 2-(3-biphenyl-2-ol)-6-(methylamine)pyridines, 2-($C_{12}H_8$-2-OH)-6-(CH_2-NHAr)C_5H_3N (Ar = 2,6-i-$Pr_2C_6H_3$ (**L2a**-H), 2,4,6-Me_3-C_6H_2 (**L2b**-H)), while the 2-(3-biphenyl-2-ol)-6-(ethylamine)pyridine, 2-(3-$C_{12}H_8$-2-OH)-6-(CMeH-NH(2,6-i-$Pr_2C_6H_3$))C_5H_3N (**L3**-H), could be prepared by treating **L1a**-H with trimethylaluminium followed by hydrolysis; this latter approach having been used to derivatize a range of different imine compounds.[15] The five new compounds, **L1a**-H, **L1b**-H, **L2a**-H, **L2b**-H and **L3**-H, have been characterised using a combination of electrospray mass spectrometry, IR, ^{1}H NMR and ^{13}C NMR spectroscopy (see Experimental section).

Compounds, **L1a**-H, **L1b**-H, **L2a**-H, **L2b**-H and **L3**-H, all display protonated molecular ions peaks in their electrospray mass spectra and downfield shifted signals for the phenolic protons (range: δ 14.1–15.2) in their ^{1}H NMR spectra. In addition, broad ν(OH) absorption bands centered *ca.* 2600 cm^{-1} in their IR spectra are consistent with strong intramolecular hydrogen bonds. In the ^{1}H NMR spectrum of imine-based **L1**-H, the C*H*=N protons are seen as singlets at δ *ca.* 8.3 with the corresponding imino carbon appearing at δ *ca.* 161.0 in their ^{13}C NMR spectra. The CH_2-NH moiety in reduced **L2**-H can be seen as a singlet for the methylene protons [δ 4.22 (**L2a**-H), 4.46 (**L2b**-H)] and a broad singlet for the NH proton at δ *ca.*



Scheme 1 *Reagents and conditions*: (i) 2-Br-6-(CHO)C_5H_3N, cat. $Pd(PPh_3)_4$, toluene, K_2CO_3 (aq.), ethanol, 90 °C; (ii) BBr_3, CH_2Cl_2, −78 °C; (iii) $ArNH_2$, ethanol, 40 °C; (iv) $LiAlH_4$, THF, −78 °C; (v) H_2O; (vi) $AlMe_3$, toluene, 100 °C.

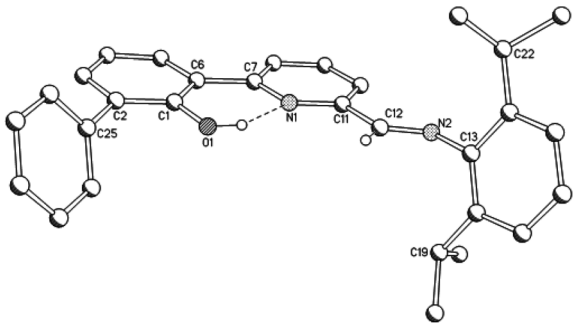


Fig. 2 Molecular structure of **L1a**-H including a partial atom numbering scheme. All hydrogen atoms, apart from H1 and H12, have been omitted for clarity.

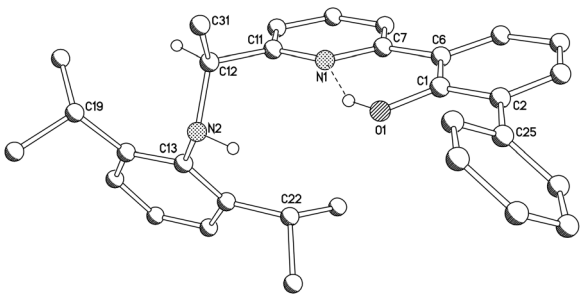


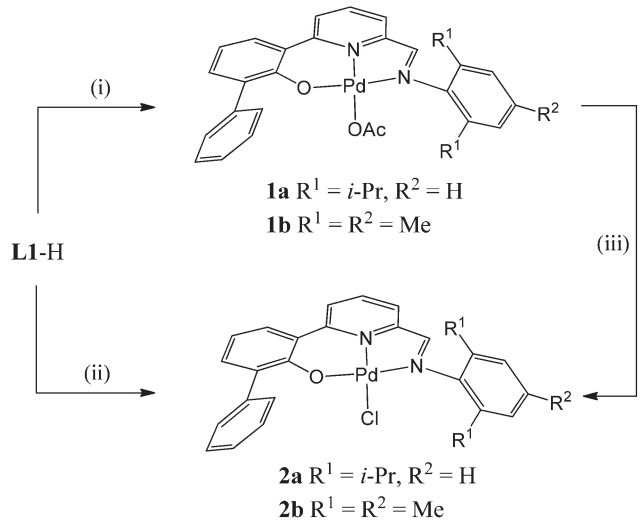
Fig. 3 Molecular structure of **L3**-H including a partial atom numbering scheme. All hydrogen atoms, apart from H1, H2 and H12, have been omitted for clarity.

Table 1 Selected bond lengths (Å) and angles (°) for **L1a**-H and **L3**-H

	L1a-H	**L3**-H
Bond lengths		
C(1)–O(1)	1.348(3)	1.366(3)
C(2)–C(25)	1.489(4)	1.486(5)
C(6)–C(7)	1.482(3)	1.470(4)
C(12)–N(2)	1.262(3)	1.482(4)
C(13)–N(2)	1.429(3)	1.425(4)
Bond angles		
C(11)–C(12)–N(2)	122.0(2)	112.5(3)
C(12)–N(2)–C(13)	119.2(2)	115.2(3)

3.4 in their ^{1}H NMR spectra. Similarly, the CMeH-N*H* proton in **L3**-H appears as a broad singlet at δ 3.48 while a mutually coupled doublet and quartet are seen for the C*Me*H-NH and CMe*H*-NH protons, respectively. Further confirmation of the composition of **L1a**-H and **L3**-H was achieved in the form of single crystal X-ray determinations.

Perspective views of **L1a**-H and **L3**-H are depicted in Fig. 2 and 3; 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 3-biphenyl-2-ol group but differs at the 6-position with a *trans*-configured *N*-arylimine unit for **L1a**-H [C(12)–N(2) 1.262(3) Å] or a saturated CHMeNH(2,6-i-$Pr_2C_6H_3$) unit for **L3**-H. In general, the pyridine nitrogen atoms adopt a *cis* configuration 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) 2.540 (**L1a**-H), 2.543 Å (**L3**-H)].[14] Some tilting of the plane of the 3-phenyl substituent with respect to the neighbouring phenol is evident in both structures [tors. C(1)–C(2)–C(25)–C(26) 48.3(4)° (**L1a**-H), 45.4(5)° (**L3**-H)] in a manner similar to that found in 2-hydroxybiphenyl.[16]



Scheme 2 *Reagents and conditions*: (i) $Pd(OAc)_2$, toluene, 60 °C; (ii) $(MeCN)_2PdCl_2$, THF, RT; (iii) NaCl (aq.), $CHCl_3$, RT.

(b) Palladium(II) complexes of L1

Interaction of **L1**-H with either $Pd(OAc)_2$ at 60 °C in toluene or $(MeCN)_2PdCl_2$ in tetrahydrofuran at room temperature gave, on work-up, [{2-(3-$C_{12}H_8$-2-O)-6-CH=NAr)C_5H_3N}Pd(OAc)] (Ar = 2,6-i-$Pr_2C_6H_3$ (**1a**), 2,4,6-$Me_3C_6H_2$ (**1b**)) and [{(2-(3-$C_{12}H_8$-2-O)-6-CH=NAr)C_5H_3N}PdCl] (Ar = 2,6-i-$Pr_2C_6H_3$ (**2a**), 2,4,6-Me_3-C_6H_2 (**2b**)), respectively, in good yield (Scheme 2). Alternatively, **1** can be converted to **2** in near quantitative yield by treatment of a chloroform solution of **1** with aqueous sodium chloride. The complexes are air stable and have been characterised using a combination of FAB mass spectrometry, IR and NMR (^{1}H and ^{13}C) spectroscopy and elemental analyses (see Experimental section). In addition, crystals of each complex have been the subject of single crystal X-ray diffraction studies.

The molecular structures of **1a**, **1b**, **2a**, and **2b** are closely related and will be discussed together. Perspective views of **1a** and **2b** are given in Fig. 4 and 5; selected bond distances and angles are collected for all the structures in Tables 2 and 3. There are two independent molecules for **1a** in the unit cell (molecules A and B) and five for **2b** (molecules A–E) which differ most noticeably in the inclination of the *N*-aryl plane to the adjacent imine unit (*vide infra*). Each structure consists of a single palladium centre bound by a tridentate monoanionic 2-(3-biphenyl-2-olate)-6-iminepyridine ligand along with a monodentate O-bound acetate (**1**) or chloride (**2**) to complete a distorted square planar geometry. Within the ONN-ligand

there are both 5- and 6-membered chelate rings with the bite angle for the 6-membered ring being more compatible with the geometrical requirements of the palladium(II) centre [O(1)–Pd(1)–$N(1)_{6\text{-membered}}$: $94.5(2)_A$, $92.9(2)_B$ (**1a**), 94.9(3) (**1b**), 92.6(2) (**2a**), $93.3(3)_{av.}°$ (**2b**) *vs.* N(2)–Pd(1)–$N(1)_{5\text{-membered}}$ $83.1(3)_A$, $83.8(3)_B$ (**1a**), 81.8(3) (**1b**), 82.1(2) (**2a**), $82.0(3)_{av.}°$ (**2b**)]. In all cases some twisting of the phenolate unit with respect to the pyridyl plane is apparent [tors. N(1)–C(13)–C(2)–C(1) 6.0(10) (**2a**), $13.4(15)_{av.}°$ (**2b**) compared with tors. N(1)–C(13)–C(2)–C(1) $9.2(11)_A$, $8.8(11)_B$ (**1a**), 2.1(12)° (**1b**)]. For a given complex, the Pd–N(imine) bond distance is the longest of the three metal–ligand interactions involving the ONN-ligand followed by the Pd–N(pyridine) distance and then by the Pd–O(phenolate) distance which is best exemplified for complex **1b** [Pd(1)–$N(2)_{imine}$ 2.004(6) > Pd(1)–$N(1)_{pyridine}$ 1.973(6) > Pd(1)–$O(1)_{phenolate}$ 1.942(5) Å]. Replacing a chloride for an O-bound acetate has little effect on the *trans* Pd–N(pyridine) distance [$1.958(6)_{A/B}$ (**1a**), 1.973(6) (**1b**), 1.986(5) (**2a**), $1.968(8)_{av.}$ Å (**2b**)]. The *N*-aryl groups are inclined towards orthogonality with regard to the neighbouring C=N_{imine} vector [tors. C(18)–N(2)–C(19)–C(20) $105.6(8)_A$, $86.9(9)_B$ (**1a**), 75.2(10) (**1b**), 98.5(7) (**2a**), $72.9(13)_A$–$103.4(11)_E°$ (**2b**)], while the 3-phenyl group is tilted [tors. C(1)–C(6)–C(7)–C(12) $53.4(10)_A$, $50.4(12)_B$ (**1a**), 44.6(12) (**1b**), 49.5(10) (**2a**), $44.0(14)_{av.}°$ (**2b**)] with respect to the adjacent phenolate group. There are no intermolecular contacts of note. The closest crystallographically characterised comparators to **1** and **2** are [2-(2,2′-bipyridin-6-yl)phenolate]PdCl[9b] and [3-fluoro-2-(1,10-phenanthrolin-2-yl)phenolate]Pd(OAc),[9d] which display similar bonding characteristics.

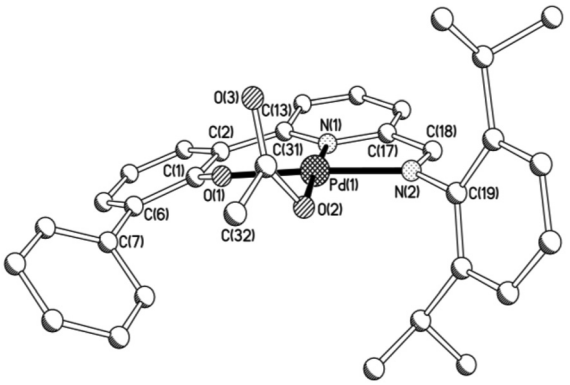


Fig. 4 Molecular structure of **1a** (*molecule A*) including a partial atom numbering scheme. All hydrogen atoms have been omitted for clarity.

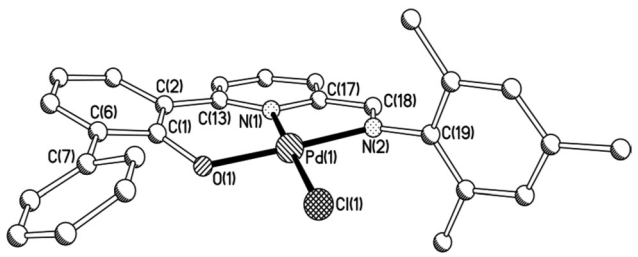


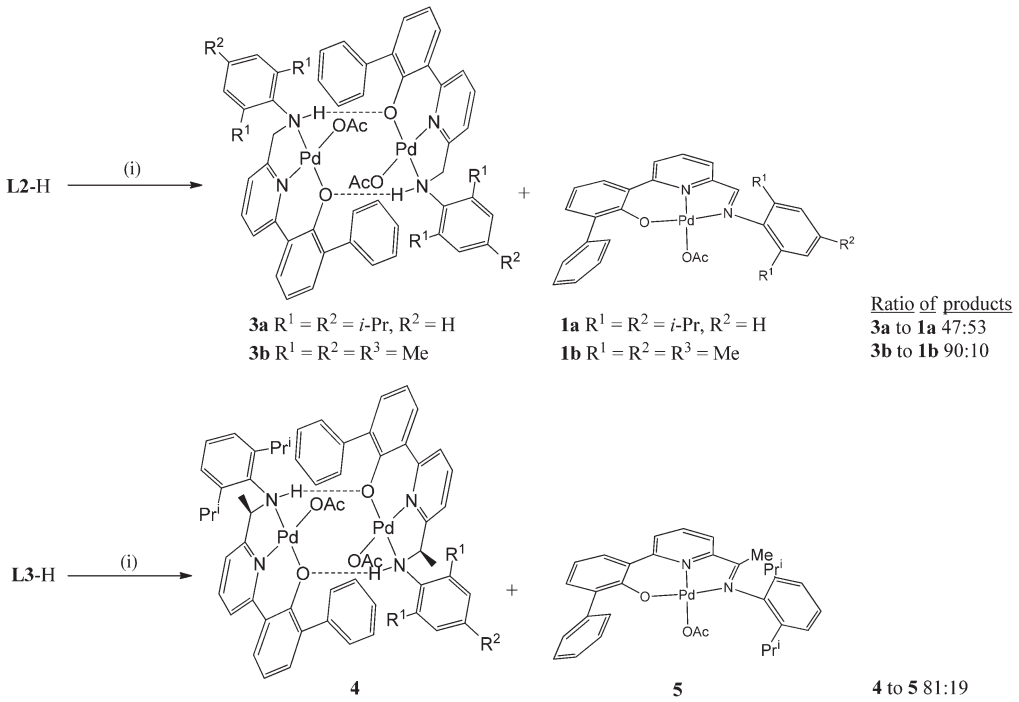
Fig. 5 Molecular structure of **2b** (*molecule A*) including a partial atom numbering scheme. All hydrogen atoms have been omitted for clarity.

Table 2 Selected bond lengths (Å) and angles (°) for **1a** and **1b**

	1a	**1b**	
	Molecule A	*Molecule B*	
Bond lengths			
Pd(1)–O(1)	1.934(5)	1.948(5)	1.942(5)
Pd(1)–O(2)	1.997(5)	2.004(5)	2.018(5)
Pd(1)–N(1)	1.958(6)	1.958(6)	1.973(6)
Pd(1)–N(2)	1.973(6)	1.993(6)	2.004(6)
C(18)–N(2)	1.292(8)	1.297(8)	1.299(10)
C(6)–C(7)	1.483(10)	1.503(11)	1.508(12)
C(31)–O(2)	1.303(9)	1.293(9)	1.313(11)
C(31)–O(3)	1.225(9)	1.224(8)	1.234(10)
Bond angles			
N(1)–Pd(1)–N(2)	83.1(3)	83.8(3)	81.8(3)
N(1)–Pd(1)–O(1)	94.5(2)	92.9(2)	94.9(3)
N(2)–Pd(1)–O(2)	95.0(2)	94.7(2)	95.5(3)
O(1)–Pd(1)–O(2)	87.3(2)	88.6(2)	88.0(2)
N(1)–Pd(1)–O(2)	176.8(2)	178.2(2)	176.7(2)

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

		2b				
	2a	*Molecule A*	*Molecule B*	*Molecule C*	*Molecule D*	*Molecule E*
Bond lengths						
Pd(1)–O(1)	1.976(4)	1.943(6)	1.934(6)	1.950(6)	1.946(6)	1.937(6)
Pd(1)–N(1)	1.986(5)	1.959(7)	1.969(8)	1.966(8)	1.973(8)	1.973(8)
Pd(1)–N(2)	2.010(5)	1.981(8)	1.999(8)	2.006(8)	1.990(8)	1.990(8)
Pd(1)–Cl(1)	2.299(2)	2.287(3)	2.287(3)	2.298(3)	2.286(3)	2.291(3)
C(18)–N(2)	1.289(7)	1.257(11)	1.305(11)	1.276(11)	1.283(11)	1.271(11)
C(6)–C(7)	1.492(14)	1.494(12)	1.451(13)	1.484(13)	1.491(13)	1.500(13)
Bond angles						
N(1)–Pd(1)–N(2)	82.1(2)	82.5(3)	82.5(3)	82.2(3)	80.9(3)	82.0(3)
N(1)–Pd(1)–O(1)	92.6(2)	93.5(3)	93.9(3)	93.7(3)	92.0(3)	93.4(3)
N(2)–Pd(1)–Cl(1)	95.08(16)	95.4(2)	95.9(2)	95.7(3)	96.1(2)	95.7(2)
O(1)–Pd(1)–Cl(1)	90.18(13)	88.66(19)	87.7(2)	88.5(2)	90.73(19)	88.8(2)
N(1)–Pd(1)–Cl(1)	177.21(16)	175.3(2)	177.3(2)	177.6(2)	175.5(2)	175.6(2)
N(2)–Pd(1)–O(1)	173.4(2)	176.0(3)	176.0(3)	173.9(3)	172.1(3)	175.1(3)



Scheme 3 *Reagents and conditions*: (i) $Pd(OAc)_2$, toluene, 60 °C. Relative ratios determined by ^1H NMR spectroscopy.

Complexes **1a**, **1b**, **2a** and **2b**, all display molecular ion peaks in their FAB mass spectra along with fragmentation peaks corresponding to the loss of an acetate or a chloride, respectively. Their imine stretching frequencies shift by *ca.* 35 cm^{-1} to lower wavenumber on imine-coordination (in comparison with free **L1**-H) as is seen in related palladium(II) complexes.[17] In **1a** and **2a** two distinct doublets are seen for the isopropyl methyl groups in their ^1H NMR spectra consistent with some restricted rotation about the *N*-aryl bond in solution. The acetate methyl groups in **1** 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.* 176.7 in their ^{13}C NMR spectra. In addition strong bands assignable to the symmetric and asymmetric ν(COO) vibrations in **1**, are in agreement with those expected for monodentate acetate ligands.[18]

(c) Palladium(II) complexes of L2 and L3

Initially, the preparation of [{2-(3-$C_{12}H_8$-2-O)-6-(CH_2-NHAr)-C_5H_3N}Pd(OAc)] (Ar = 2,6-i-$Pr_2C_6H_3$ (**3a**), 2,4,6-$Me_3C_6H_2$ (**3b**)) was carried out using the conditions employed to synthesise **1** (*viz.* by reacting the pro-ligand with $Pd(OAc)_2$ in toluene at 60 °C). However, monitoring of the reactions using ^1H NMR spectroscopy revealed the presence of both **3** and aldimine-containing **1**, the relative ratio being dependent on the nature of the aryl group (relative ratio: **3a–1a** 47 : 53 and **3b–1b** 90 : 10) (Scheme 3). Similarly, the reaction of **L3**-H with $Pd(OAc)_2$ gave [{2-(3-$C_{12}H_8$-2-O)-6-(CMeH-NH(2,6-i-$Pr_2C_6H_3$))C_5H_3N}Pd(OAc)] (**4**) and ketimine-containing [{2-(3-$C_{12}H_8$-2-O)-6-(CMe=N(2,6-i-$Pr_2C_6H_3$))C_5H_3N}Pd(OAc)] (**5**) in a 81 : 19 ratio. To circumvent this apparent oxidation of **3** or **4**, the reaction of the corresponding pro-ligand with $Pd(OAc)_2$ was carried out at 0 °C in toluene affording, on work-up, almost exclusively **3a**, **3b** and **4**. The three new complexes have been characterised using a combination of FAB mass spectrometry, IR and NMR (^1H and ^{13}C) spectroscopy along with elemental analyses (see Experimental section). In addition, crystals of each complex have been the subject of single crystal X-ray diffraction studies.

The molecular structures of **3a**, **3b** and **4** are similar and will be discussed together. Views of **3a** and **5** are shown in Fig. 6 and 7; selected bond distances and angles are collected for all three structures in Tables 4 and 5. Each structure comprises two anti-parallel aligned square planar {2-(3-biphenyl-2-olate)-6-alkylamine-pyridine}Pd(OAc) monomeric units linked together by two $N_{amine}H\cdots O_{phenolate}$ hydrogen bonding interactions [N(2)···O(1A) 3.038 (**3a**), 2.929 (**3b**), 3.000 (**4**) Å][19] to form a dimeric assembly. Like **1** and **2**, the ONN-tridentate ligand in each monomer contain both 5- and 6-membered chelate rings with the bite angle for the 6-membered ring again being better matched with the geometrical requirements of the palladium(II) centre [O(1)–Pd(1)–$N(1)_{6\text{-membered}}$: 90.48(18) (**3a**), 92.2 (**3b**), 92.5° (**4**) *vs.* N(2)–Pd(1)–$N(1)_{5\text{-membered}}$ 84.59(19) (**3a**), 85.3(3) (**3b**), 83.4(3)° (**4**)]. The twisting of the phenolate unit with respect to the neighbouring pyridyl plane is, however, even more noticeable [tors. N(1)–C(13)–C(2)–C(1) 28.9 (9) (**3a**), 25.0(11) (**3b**), 31.3(12)° (**4**)] when compared to **1** and **2**, presumably to compensate for the puckering at the methylene (CH_2NHAr (**3**) or *C*HMeNHAr (**4**)) carbon atoms. There are no interactions of note between dimeric assemblies.

The palladium–palladium separations in **3b** (3.177(2) Å) and **4** (3.1409(15) Å) are shorter than the sum of the van der Waals radii (3.26 Å) while in **3a** (3.284 Å) the separation is slightly longer. In comparison with previously reported

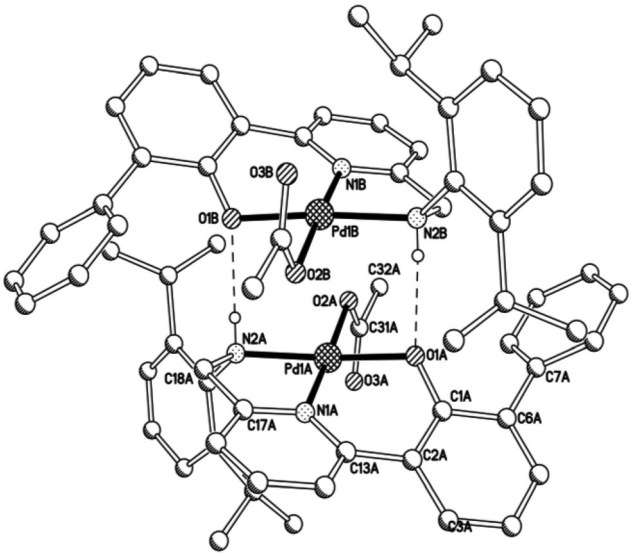


Fig. 6 Molecular structure of **3a** including a partial atom numbering scheme. All hydrogen atoms, apart from H2, have been omitted for clarity.

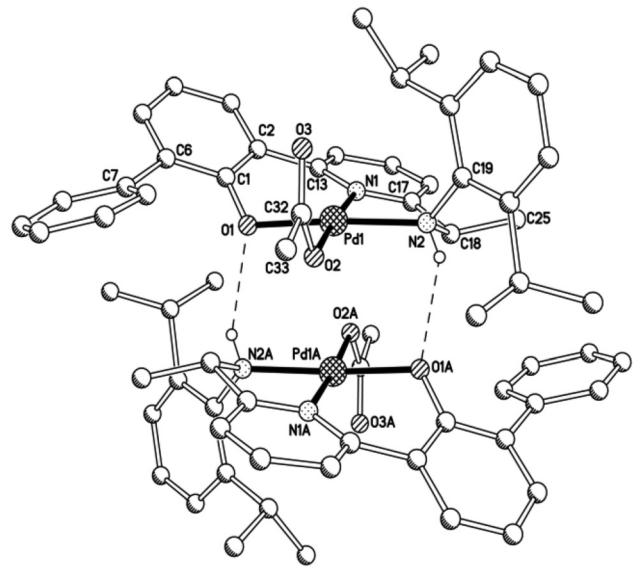


Fig. 7 Molecular structure of **4** including a partial atom numbering scheme. All hydrogen atoms, apart from H2, have been omitted for clarity.

covalently bridged palladium(II) dimers,[20] the Pd···Pd distances in **3a**, **3b** and **4** fall at the top end of the range (2.55–3.05 Å) but are comparable with that found in the related hydrogen-bonded dimer $[Pd(OPh)_2(pyrrolidine)_2]$ (3.0960(3) Å).[21] Interestingly, d^8–d^8 bonding interactions have been highlighted recently during a computational investigation on a range of palladium(II) dimers (Pd···Pd 2.55–3.05 Å)[22] and in the model compound $[Pd(CN)_2(PH_3)_2]_2$ (Pd···Pd 3.107 Å).[20b] Moreover, it has been suggested that the Pd–Pd bonding interaction is related to the separation between the palladium centres implying some interaction may be present in **3a**, **3b** and **4**, albeit weak.

Table 4 Selected bond lengths (Å) and angles (°) for **3a** and **3b**[a]

	3a	**3b**
Bond lengths		
Pd(1)–O(1)	1.990(4)	1.972(5)
Pd(1)–O(2)	2.019(4)	2.049(6)
Pd(1)–N(1)	1.955(5)	1.976(6)
Pd(1)–N(2)	2.078(4)	2.033(6)
C(18)–N(2)	1.505(6)	1.495(9)
C(6)–C(7)	1.477(8)	1.456(12)
C(31)–O(2)	1.257(7)	1.124(11)
C(31)–O(3)	1.221(7)	1.284(11)
Pd(1)···Pd(1A)	3.284	3.177(2)
Bond angles		
N(1)–Pd(1)–N(2)	84.59(19)	85.5(3)
N(1)–Pd(1)–O(1)	90.48(18)	92.2(3)
N(2)–Pd(1)–O(2)	94.99(17)	90.4(2)
O(1)–Pd(1)–O(2)	89.43(15)	91.6(2)
N(1)–Pd(1)–O(2)	176.25(19)	175.3(3)
N(2)–Pd(1)–O(2)	94.99(17)	90.4(2)

[a] The 'A' atoms denote the neighbouring palladium atom in the dimer; for **3b** it been generated by symmetry: symmetry operation $-x + 1$, $-y$, $-z$.

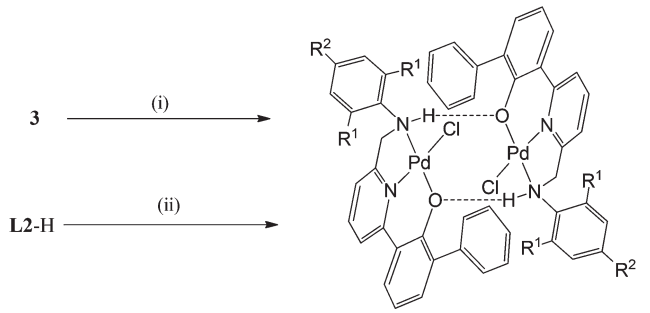
Table 5 Selected bond lengths (Å) and angles (°) for **4**[a]

Bond lengths	
Pd(1)–O(1)	1.959(5)
Pd(1)–O(2)	2.025(5)
Pd(1)–N(1)	1.971(6)
Pd(1)–N(2)	2.038(6)
C(18)–N(2)	1.557(10)
C(6)–C(7)	1.462(11)
C(32)–O(2)	1.260(9)
C(32)–O(3)	1.250(9)
Pd(1)···Pd(1A)	3.1409(15)
Bond angles	
N(1)–Pd(1)–N(2)	83.4(3)
N(1)–Pd(1)–O(1)	92.5(2)
N(2)–Pd(1)–O(2)	92.8(2)
O(1)–Pd(1)–O(2)	91.2(2)
N(1)–Pd(1)–O(2)	176.1(2)
N(2)–Pd(1)–O(2)	92.8(2)

[a] The 'A' atoms have been generated by symmetry: symmetry operation $-x + 1$, $-y$, $-z$.

Compounds **3a**, **3b** and **4** all show fragmentation peaks corresponding to the loss of an acetate group from both the dimeric and monomeric species in their ESI mass spectra. The methylene CH_2-NH protons in the ^{1}H NMR spectra of **3a** and **3b** are inequivalent and appear as two doublet of doublets [at δ 4.58 and 4.16 (**3a**); 4.76 and 4.02 (**3b**)], while in **4** the C*H*Me-NH proton appears as a doublet of quartets at δ 4.31. Each isopropyl-methyl proton in **3a** and **4** are inequivalent leading to four separate doublets. The NH proton in each complex is shifted by *ca.* 4 ppm downfield compared to that observed in the free pro-ligand, supportive of a hydrogen bonding interaction being maintained in solution.

It is uncertain as to the mechanism of oxidation that occurs during the formation of imines **1** and **5** on reaction of **L2**-H or **L3**-H with palladium acetate, respectively. Notably, palladium



Scheme 4 *Reagents and conditions*: (i) NaCl (aq.), $CHCl_3$, RT; (ii) $(MeCN)_2PdCl_2$, THF, RT.

acetate–pyridine mixtures have has been used as catalysts to promote the aerobic oxidation of secondary amines to imines (*e.g.*, Ar-CH_2NHPh to Ar-CH=N-Ph).[23] It would therefore seem plausible that adventitious amounts of oxygen may have contributed to the product distribution; we cannot however, rule out a mechanism involving metal–ligand cooperation *via* aromatisation–dearomatisation involving the pyridine core.[2]

The palladium chloride analogues of **3a** and **3b**, [{2-(3-$C_{12}H_8$-2-O)-6-(CH_2-NHAr)C_5H_3N}PdCl] (Ar = 2,6-i-$Pr_2C_6H_3$ (**6a**), 2,4,6-$Me_3C_6H_2$ (**6b**)), could be readily prepared by treatment of a chloroform solution of **3a** or **3b** with aqueous sodium chloride (Scheme 4). Attempts at reacting **L2**-H with $(MeCN)_2PdCl_2$ in tetrahydrofuran gave only modest yields of **6a** and **6b** and involved multiple crystallisations. Both **6a** and **6b** have been fully characterised including by single crystal X-ray diffraction studies.

Complexes **6a** and **6b** are isostructural; a view of **6a** is shown in Fig. 8 while selected bond distances and angles for both structures are given in Table 6. As with **3a** and **3b**, two square planar (2-(3-biphenyl-2-olate)-6-alkylamine-pyridine)PdCl monomeric units align in an anti-parallel fashion with intermolecular $N_{amine}H\cdots O_{phenolate}$ hydrogen bonding interactions [N(2)···O(1A) 2.955 (**6a**), 2.918 Å (**6b**)][19] supporting the dimeric assembly. Replacement of an acetate (**3**) with a chloride (**6**) appears to have little effect on the M···M separations with distances of 3.2412(10) and 3.291 Å in **6a** and **6b**, respectively. The spectroscopic properties of **6a** and **6b** are similar to those found in **3a** and **3b** with the N–H proton again shifted downfield (*ca.* 5.8) in comparison with **L2a**-H and **L2b**-H.

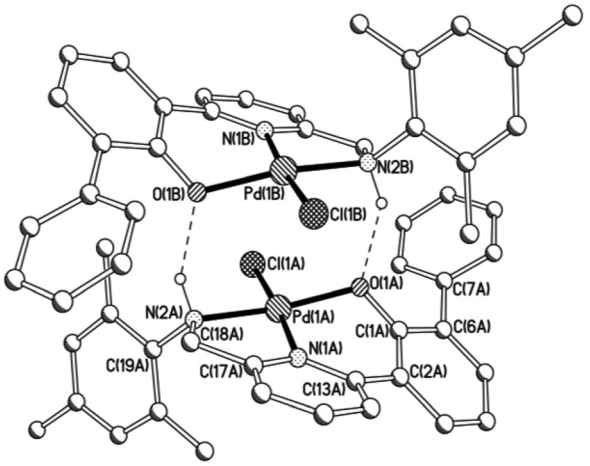


Fig. 8 Molecular structure of **6a** including a partial atom numbering scheme. All hydrogen atoms, apart from H2, have been omitted for clarity.

Table 6 Selected bond lengths (Å) and angles (°) for **6a** and **6b**[a]

	6a	6b
Bond lengths		
Pd(1)–O(1)	2.001(4)	1.999(10)
Pd(1)–N(1)	1.973(4)	1.966(12)
Pd(1)–N(2)	2.058(4)	2.049(12)
Pd(1)–Cl(1)	2.2982(14)	2.302(4)
C(18)–N(2)	1.510(7)	1.456(19)
C(6)–C(7)	1.485(8)	1.49(2)
Pd(1)···Pd(1A)	3.2412(10)	3.291
Bond angles		
N(1)–Pd(1)–N(2)	84.59(18)	83.6(5)
N(1)–Pd(1)–O(1)	90.92(17)	91.3(4)
N(2)–Pd(1)–Cl(1)	92.77(13)	93.6(4)
O(1)–Pd(1)–Cl(1)	92.07(11)	92.3(3)
N(1)–Pd(1)–Cl(1)	176.34(14)	174.4(3)
N(2)–Pd(1)–O(1)	170.17(16)	167.6(4)

[a] The 'A' atoms denote the neighbouring palladium atom in the dimer; for **6a** it been generated by symmetry: symmetry operation $-x + 2$, $-y + 2$, $-z + 1$.

Conclusions

Protonated forms of the new ONN pincer-type ligands, 2-(3-biphenyl-2-olates)-6-iminepyridines (**L1**) and 2-(3-biphenyl-2-olates)-6-(alkylamine)pyridines (**L2** and **L3**), have been successfully synthesised and provide convenient access to square planar complexes in which the ONN-ligand's substituents sterically shelter the metal-bound acetate or halide site. We have shown the presence of an amine donor in **L2** or **L3** to facilitate the self assembly of dimeric species through intermolecular hydrogen bonding. This synthetic chemistry sets the stage for an investigation of these and related systems in various applications. 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[24] 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 Kratos Concept spectrometer with NBA as matrix. 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) and 100.61 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, 2,4,6-trimethylaniline, lithium aluminium hydride, trimethylaluminium (2 M solution in toluene) and boron tribromide (1 M solution in dichloromethane) were purchased from Aldrich Chemical Co. and used without further purification. The compounds tetrakis(triphenylphosphine)palladium(0),[25] 2-methoxybiphenyl-3-ylboronic acid,[26] 2-bromo-6-formylpyridine[27] and bis(acetonitrile)dichloropalladium(II)[28] were prepared using literature procedures. All other chemicals were obtained commercially and used without further purification.

Synthesis of 2-(3-biphenyl-2-ol)-6-formylpyridine. The title compound was prepared in two steps. Step 1 (Suzuki coupling): a Schlenk flask equipped with stir bar was charged with 2-bromo-6-formylpyridine (2.180 g, 11.7 mmol), $Pd(PPh_3)_4$ (0.269 g, 0.23 mmol), toluene (30 mL) and an aqueous 2 M solution of potassium carbonate (12 mL, 23.4 mmol). The mixture was stirred at room temperature for 15 min. followed by the addition of 2-methoxybiphenyl-3-ylboronic acid (3.470 g, 15.2 mmol, 1.3 eq.) in ethanol (20 mL). The solution was heated to 90 °C and stirred at this temperature for 42 h. On cooling to room temperature hydrogen peroxide (10 mL, 30 wt% in water) was added and the solution left to stir for 1 h. Following extraction with diethyl ether (3–100 mL) and washing with a brine solution (1 × 50 mL), the combined organic extracts were dried over magnesium sulfate. Filtration followed by removal of the solvent on the rotary evaporator gave the crude product as a viscous brown oil. Catalyst residues were removed by a short silica column using a dichloromethane–hexane (80 : 20) solvent mixture as the eluent affording 2-(2-methoxybiphenyl-3-yl)-6-formylpyridine as a yellow oil (2.920 g, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.27 (s, 3H, OMe), 7.11–7.41 (m, 5H, Ar-H), 7.56–7.65 (m, 2H, Ar-H), 7.85 (dd, J_{HH} = 7.7, 1.8, 1H, Py-H), 7.92–7.96 (m, 2H, Py-H, Ar-H), 8.13 (dd, J_{HH} = 6.9, 1.4, 1H, Py-H), 10.16 (s, 1H, CH=O). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 61.0 (OCH_3), 118.8, 123.7, 125.9, 126.9, 127.3, 128.2, 129.8, 131.4, 132.2, 134.9, 136.0, 137.3, 151.7, 154.6, 156.0, 192.8 (CH=O). IR (cm^{-1}): 1712 (C=O), 1585 (C=$N_{pyridine}$). ESIMS: *m*/*z* 290 $[M + H]^+$. HRMS (FAB): Calcd for $C_{19}H_{15}NO_2$ $[M + H]^+$ 290.11770, found 290.11775.

Step 2 (deprotection): a Schlenk flask equipped with stir bar was initially evacuated and backfilled with nitrogen and then charged with 2-(2-methoxybiphenyl-3-yl)-6-formylpyridine (2.380 g, 8.24 mmol), dichloromethane (40 mL) and the solution cooled to −78 °C. A 1 M solution of boron tribromide (18 mL, 18 mmol) was added at −78 °C forming an orange solution. The solution was allowed to warm to room temperature and left to stir overnight. Water (40 mL) was added carefully and the mixture neutralised with potassium carbonate. The organic layer was separated and the aqueous phase washed repeatedly with chloroform (3 × 100 mL). All organic extracts were combined and the solvent removed on the rotary evaporator yielding 2-(3-biphenyl-2-ol)-6-formylpyridine as a green/gold foamy solid (1.830 g, 81%). Mp: 67–68 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.96 (t, J_{HH} = 6.8, 1H, Ar-H), 7.21–7.39 (m, 4H, Ar-H), 7.55 (d, J_{HH} = 6.8, 2H, Ar-H), 7.86 (d, J_{HH} = 7.7, 1H, Ar-H/Py-H), 7.92 (d, J_{HH} = 7.7, 1H, Ar-H/Py-H), 8.07 (t, J_{HH} = 7.7, 1H, Py-H), 8.13 (d, J_{HH} = 6.9, 1H, Py-H), 10.17 (s, 1H, CH=O), 14.22 (br s, 1H, OH). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 117.2, 118.1, 118.7, 119.6, 123.3, 125.0, 126.3, 127.1, 128.9, 133.5, 137.0, 149.0, 156.3, 158.2, 189.8 (CH=O). IR (cm^{-1}): 1712 (C=O), 1591 (C=$N_{pyridine}$). ESIMS (+ve): *m*/*z* 276 $[M + H]^+$. ESIMS (−ve): *m*/*z* 274 $[M - H]^+$. HRMS (FAB): Calcd for $C_{18}H_{14}NO_2$ $[M + H]^+$ 275.09463, found 275.09469.

Synthesis of 2-(3-$C_{12}H_8$-2-OH)-6-(CH=NAr)C_5H_3N (L1-H). (a) Ar = 2,6-i-$Pr_2C_6H_3$ (**L1a**-H). To a round bottomed flask equipped with stir bar was added 2-(3-biphenyl-2-ol)-6-formylpyridine (1.830 g, 6.65 mmol), 2,6-diisopropylaniline (1.760 g, 9.98 mmol) and absolute ethanol (13 mL). The suspension was stirred and heated to 40 °C and after 15 min. a catalytic amount of formic acid added. After further stirring at 40 °C overnight a yellow precipitate formed which was allowed to cool to room temperature. The precipitate was filtered, washed with ethanol and further dried under reduced pressure to give **L1a**-H as a yellow solid (1.990 g, 69%). Mp: 127–130 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.18 (d, J_{HH} = 6.9, 12H, $CH(CH_3)_2$), 2.95 (sept, J_{HH} = 6.9, 2H, $CH(CH_3)_2$), 7.04 (t, J_{HH} = 7.7, 1H, Ar-H), 7.09–7.14 (m, 3H, Ar-H), 7.35 (t, J_{HH} = 7.4, 1H, Ar-H), 7.35–7.45 (m, 3H, Ar-H), 7.66 (d, J_{HH} = 7.1, 2H, Ar-H), 7.88 (dd, J_{HH} = 8.1, 1.4, 1H, Ar-H), 8.03 (t, J_{HH} = 7.9, 1H, Py-H), 8.11 (d, J_{HH} = 7.7, 1H, Py-H), 8.24 (d, J_{HH} = 7.5, 1H, Py-H), 8.33 (s, 1H, N=CH), 14.20 (br s, 1H, OH). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 23.4 ($CH(CH_3)_2$), 27.9 ($CH(CH_3)_2$), 118.8, 118.9, 119.2, 121.3, 123.1, 124.7, 126.0, 127.0, 128.1, 129.5, 131.4, 133.0, 137.0, 138.4, 138.6, 148.2, 150.9, 157.0, 158.2, 161.0 (N=*C*–H). IR (cm^{-1}): 2962 (C-H), 2600 (br, OH), 1641 (C=N_{imine}), 1589 (C=$N_{pyridine}$). ESIMS: *m*/*z* 435 $[(M + H)]^+$, 457 $[(M + Na)]^+$. HRMS (FAB): Calcd. $C_{30}H_{31}N_2O$ $[M + H]^+$ 435.24286, found 435.24247.

(b) Ar = 2,4,6-$Me_3C_6H_2$ (**L1b**-H). Employing a similar procedure to that described for **L1a**-H with 2-(3-biphenyl-2-ol)-6-formylpyridine (2.734 g, 9.93 mmol), 2,4,6-trimethylaniline (2.014 g, 14.80 mmol) and absolute ethanol (20 mL) gave **L1b**-H as a yellow solid (2.729 g, 70%). Mp: 139–144 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.05 (s, 6H, Ar-*o*-Me), 2.21 (s, 3H, Ar-*p*-Me), 6.81 (s, 2H, Ar-H), 6.95 (t, J_{HH} = 7.7, 1H, Ar-H), 7.24–7.39 (m, 4H, Ar-H/Py-H), 7.56 (d, J_{HH} = 7.1, 2H, Py-*H*), 7.79 (dd, J_{HH} = 8.1, 1.6, 1H, Ar-H), 7.94 (t, J_{HH} = 7.9, 1H, Ar-*H*), 8.01 (d, J_{HH} =

7.3, 1H, Ar-*H*), 8.13 (d, J_{HH} = 7.5, 1H, Py-*H*), 8.25 (s, 1H, N=CH), 14.10 (br s, 1H, OH). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 18.3 (*o*-Me), 20.8 (*p*-Me), 118.8, 118.9, 119.1, 121.2, 126.0, 126.8, 127.1, 128.2, 129.0, 129.6, 131.4, 133.0, 133.8, 138.5, 138.6, 147.5, 151.1, 157.1, 158.1, 161.4 (N=*C*–H). IR (cm^{-1}): 2963 (CH), 2602 (br, OH), 1640 (C=N_{imine}), 1592 (C=$N_{pyridine}$). ESIMS: *m*/*z* 393 $[(M + H)]^+$. HRMS (FAB): Calcd. $C_{27}H_{25}N_2O$ $[M + H]^+$ 393.1967, found 393.1965.

Synthesis of 2-(3-$C_{12}H_8$-2-OH)-6-(CH_2-NHAr)C_5H_3N (L2-H). (a) Ar = 2,6-i-$Pr_2C_6H_3$ (**L2a**-H). Two Schlenk flasks equipped with stir bars were evacuated and backfilled with nitrogen. To one of the flasks was added lithium aluminium hydride (0.131 g, 3.46 mmol) and tetrahydrofuran (10 mL) and the resulting suspension stirred and cooled to 0 °C. To the second flask was added **L1a**-H (0.300 g, 0.69 mmol) and tetrahydrofuran (10 mL) and the contents stirred until dissolution. The solution of **L1a**-H was then transferred *via* cannular (dropwise) to the cooled $LiAlH_4$ suspension. The reaction mixture was allowed to warm to room temperature and stirred for 90 min. Water (2 mL) was carefully added followed by chloroform (30 mL) and more water (30 mL). The organic phase was separated and the aqueous layer extracted with chloroform (3 × 50 mL). All organic extracts were combined and dried over magnesium sulfate. Filtration followed by removal of the solvent under reduced pressure gave **L2a**-H as a yellow brown oil (0.230 g, 76%). ^1H NMR (300 MHz, $CDCl_3$): δ 1.21 (d, J_{HH} = 6.8, 12H, $CH(CH_3)_2$), 3.28 (sept, J_{HH} = 6.8, 2H, $CH(CH_3)_2$), 3.45 (s, 1H, N-H), 4.22 (s, 2H, NH-CH_2), 6.89 (t, J_{HH} = 7.7, 1H, Ar-H), 6.95–7.01 (m, 3H, Ar-H), 7.24 (t, J_{HH} = 8.1, 1H, Ar-H), 7.30–7.40 (m, 4H, Ar-H/Py-H), 7.57 (d, J_{HH} = 7.0, 2H, Ar-H), 7.80–7.70 (m, 3H, Ar-H), 15.2 (br s, 1H, OH). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 21.4 ($CH(CH_3)_2$), 23.2 ($CH(CH_3)_2$), 26.7 ($CH(CH_3)_2$), 55.4 ($NHCH_2$), 117.0, 117.5, 117.6, 118.0, 118.8, 121.7, 122.6, 123.4, 124.8, 125.9, 127.0, 128.5, 130.1, 131.4, 131.6, 137.4, 137.5, 139.2, 141.1, 141.9, 155.5, 155.3, 156.8. IR (cm^{-1}): 2962 (C-H), 2600 (br, OH), 1592 (C=$N_{pyridine}$), 1589. ESIMS (+ve): *m*/*z* 437 $[M + H]^+$. ESIMS (−ve): *m*/*z* 435 $[M - H]^+$. HRMS (FAB): Calcd for $C_{30}H_{33}N_2O$ $[M + H]^+$ 437.2593, found 437.2599.

(b) Ar = 2,4,6-$Me_3C_6H_2$ (**L2b**-H). Employing a similar procedure to that described for **L2a**-H with **L1b**-H (0.300 g, 0.76 mmol) and lithium aluminium hydride (0.145 g, 3.81 mmol) gave **L2b**-H as a pale yellow solid (0.141 g, 47%). Mp: 96–98 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 2.21 (s, 6H, Ar-*o*-Me), 2.22 (s, 3H, Ar-*p*-Me), 3.49 (br s, 1H, NH), 4.26 (s, 2H, NH-CH_2), 6.81 (s, 2H, Ar-H), 6.99 (t, J_{HH} = 7.7, 1H, Ar-H), 7.30–7.35 (m, 2H, Ar-H), 7.38 (dd, J_{HH} = 7.4, 1.3, 1H, Ar-H), 7.44 (t, J_{HH} = 7.6, 2H, Ar-H), 7.64 (d, J_{HH} = 7.4, 2H, Py-H), 7.79–7.88 (m, 3H, Ar-H/Py-H), 14.81 (br s, 1H, OH). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 17.2 (*o*-Me), 19.5 (*p*-Me), 52.6 ($NHCH_2$), 116.9, 117.6, 118.0, 118.9, 124.8, 125.9, 127.0, 128.5, 129.1, 130.1, 130.9, 131.6, 137.4, 137.5, 141.4, 155.8, 156.2, 156.7. IR (cm^{-1}): 2962 (C-H), 2599 (br, OH), 1596 (C=$N_{pyridine}$). ESIMS (+ve): *m*/*z* 395 $[M + H]^+$. HRMS (FAB): Calcd for $C_{27}H_{27}N_2O$ $[M + H]^+$ 395.2123, found 395.2119.

Synthesis of 2-(3-$C_{12}H_8$-2-OH)-6-{CMeH-NH(2,6-i-$Pr_2C_6H_3$)}-C_5H_3N (L3-H). A Schlenk flask equipped with stir bar was evacuated and backfilled with nitrogen and loaded with **L1a**-H (0.600 g, 1.38 mmol) and toluene (20 mL). A 2 M trimethylaluminium solution (2.1 mL, 4.15 mmol) was added dropwise and the reaction mixture stirred and heated to 100 °C overnight. On cooling to room temperature, all volatiles were removed under reduced pressure. Diethyl ether (20 mL) was added to the flask followed by careful dropwise addition of water (20 mL). After stirring for 3 h the organic layer was separated and the aqueous layer extracted with diethylether (3 × 30 mL). All organic extracts were combined and dried over magnesium sulfate. Following filtration, the solvent was removed under reduced pressure affording **L3**-H as yellow-brown solid (0.454 g, 73%). Mp: 95–98 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 1.00 (d, J_{HH} = 6.8, 6H, $CH(CH_3)_2$), 1.19 (d, J_{HH} = 6.8, 6H, $CH(CH_3)_2$), 1.63 (d, J_{HH} = 6.8, 3H, N-CH*Me*), 3.10 (sept, J_{HH} = 6.9, 2H, $CH(CH_3)_2$), 3.48 (br s, 1H, N-H), 4.23 (q, J_{HH} = 6.8, 1H, N-C*H*Me), 6.98–7.05 (m, 5H, Ar-H), 7.38 (m, 1H, Ar-H), 7.40 (dd, J_{HH} = 7.2, 1.2, 1H, Ar-H), 7.45 (t, J_{HH} = 7.4, 2H, Ar-H/Py-H), 7.68–7.71 (m, 3H, Ar-H), 7.80–7.90 (m, 2H, Ar-H/Py-H), 14.80 (br s, 1H, OH). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 19.7 (N-CH(CH_3)), 23.0 ($CH(CH_3)_2$), 23.2 ($CH(CH_3)_2$), 26.7 ($CH(CH_3)_2$), 59.5 (N-$CH(CH_3)$), 117.1, 117.6 , 118.2, 118.8, 122.5. 122.6, 124.8, 126.0, 127.0, 128.6, 130.0, 131.6, 137.0, 137.5, 139.9, 141.3, 156.3, 157.0, 159. 1 (C). IR (cm^{-1}): 2962 (C-H), 2581 (br, OH), 1594 (C=$N_{pyridine}$), 1567. ESIMS (+ve): *m*/*z* 451 $[M + H]^+$, 473 $[M + Na]^+$. ESIMS (−ve): *m*/*z* 449 $[M - H]^+$. HRMS (FAB): Calcd for $C_{31}H_{35}N_2O$ $[M + H]^+$ 451.2749, found 451.2760.

Synthesis of [{2-(3-$C_{12}H_8$-2-O)-6-(CH=NAr)C_5H_3N}Pd(OAc)] (1). (a) **1a**. A Schlenk flask equipped with stir bar was evacuated and backfilled with nitrogen and loaded with $Pd(OAc)_2$ (0.065 g, 0.29 mmol), **L1a**-H (0.126 g, 0.29 mmol) and toluene (10 mL). After stirring at 60 °C overnight, the reaction mixture was cooled to room temperature and filtered through celite and the celite cake washed thoroughly with dichloromethane. The filtrate was concentrated to *ca.* 1 mL whereupon diethyl ether (*ca.* 8 mL) was added. The resulting precipitate was filtered and dried under reduced pressure forming **1a** as a dark red powder (0.158 g, 91%). Red blocks suitable for an X-ray diffraction study could be grown by slow diffusion of hexane into a dichloromethane solution of the complex. Mp: >260 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 1.11 (d, J_{HH} = 6.9, 6H, $CH(CH_3)_2$), 1.33 (d, J_{HH} = 6.9, 6H, $CH(CH_3)_2$), 1.65 (s, 3H, CH_3CO_2), 3.43 (sept, J_{HH} = 6.7, 2H, $CH(CH_3)_2$), 6.83 (t, J_{HH} = 8.1, 1H, Ar-H), 7.18 (d, J_{HH} = 7.6, 1H, Ar-H), 7.22 (d, J_{HH} = 7.8, 2H, Ar-H), 7.30 (m, 3H, Ar-H), 7.40 (d, J_{HH} = 7.0, 1H, Ar-H), 7.64 (d, J_{HH} = 7.1, 1H, Ar-H), 7.76 (d, J_{HH} = 7.1, 2H, Ar-H), 7.88 (d, J_{HH} = 8.5, 1H, Py-H), 8.02 (s, 1H, N=C-H), 8.15 (t, J_{HH} = 8.3, 1H, Py-H), 8.52 (d, J_{HH} = 8.8, 1H, Py-H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 21.3 (H_3CCOO), 21.9 ($CH(CH_3)_2$), 24.2 ($CH(CH_3)_2$), 27.5 ($CH(CH_3)_2$), 114.9, 119.3, 122.4, 123.6, 125.5, 125.9, 126.5, 127.3, 127.6, 129.0, 132.5, 133.3, 136.6, 138.9, 140.2, 141.0, 151.1, 151.7, 160.4, 165.0 (N=*C*H), 176.5 (H_3CCOO). IR (cm^{-1}): 2961 (C-H), 1615 (C=N_{imine}), 1582 $(COO)_{asymm}$/C=$N_{pyridine}$), 1383 $(COO)_{symm}$. FABMS *m*/*z*: 599 $[M]^+$, 540 $[M - OAc]^+$. Anal Calc. for

($C_{32}H_{32}N_2O_3Pd$): C, 64.16; H, 5.38; N, 4.68. Found: C, 64.21; H, 5.21; N, 4.72%.

(b) **1b**. Employing a similar procedure to that described for **1a** using **L1b**-H (0.114 g, 0.29 mmol) and $Pd(OAc)_2$ (0.065 g, 0.29 mmol) gave **1b** as a red solid (0.126 g, 78%). Red blocks suitable for an X-ray diffraction study could be grown by slow diffusion of hexane into a dichloromethane solution of the complex. Mp: >260 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.58 (s, 3H, CH_3CO_2), 2.26 (s, 3H, Ar-*p*-Me), 2.31 (s, 6H, Ar-*o*-Me), 6.80 (td, J_{HH} = 7.8, 0.9, 1H, Ar-H), 6.85 (s, 2H, Ar-H), 7.19 (t, J_{HH} = 7.3, 1H, Ar-H), 7.29 (t, J_{HH} = 7.5, 2H, Ar-H), 7.39 (dd, J_{HH} = 7.2, 1.2, 1H, Ar-H), 7.55 (d, J_{HH} = 7.0, 1H, Ar-H), 7.70 (d, J_{HH} = 7.4, 2H, Ar-H/Py-H), 7.87 (dd, J_{HH} = 8.2, 1.2, 1H, Ar-H), 7.97 (s, 1H, N=C-H), 8.10 (t, J_{HH} = 7.9, 1H, Py-H), 8.52 (d, J_{HH} = 8.7, 1H, Py-H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 17.3 (*o*-Me), 19.97 (*p*-Me), 21.0 (H_3CCOO), 114.9, 119.0, 123.5, 125.4, 125.6, 126.4, 127.3, 127.7, 128.0, 128.9, 129.2, 132.4, 133.4, 136.2, 136.6, 138.8, 141.4, 151.6, 165.7 (N=CH), 176.9 (H_3CCOO). IR (cm^{-1}): 2963 (C-H), 1610 ($C{=}N_{imine}$), 1587 (COO_{asymm}/$C{=}N_{pyridine}$), 1381 (COO_{symm}). FABMS *m*/*z*: 556 $[M]^+$, 539 $[M - OAc]^+$. Anal Calc. for ($C_{29}H_{26}N_2O_3Pd$): C, 62.54; H, 4.71; N, 5.03. Found: C, 62.77; H, 4.69; N, 5.01%.

Synthesis of [{2-(3-$C_{12}H_8$-2-O)-6-(CH=NAr)C_5H_3N}PdCl] (2). (a) **2a**. A Schlenk flask equipped with stir bar was evacuated and backfilled with nitrogen and loaded with $(MeCN)_2PdCl_2$ (0.060 g, 0.231 mmol), **L1a**-H (0.110 g, 0.254 mmol) and tetrahydrofuran (25 mL). After stirring overnight at room temperature, the reaction mixture was concentrated to *ca.* 2 mL and hexane (15 mL) added. The precipitate was filtered, washed with hexane and dried under reduced pressure to give **2a** as dark red powder (0.071 g, 53%). Red blocks suitable for an X-ray diffraction study could be grown by slow diffusion of hexane into a dichloromethane solution of the complex. Mp: >260 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.00 (d, J_{HH} = 6.9, 6H, $CH(CH_3)_2$), 1.34 (d, J_{HH} = 6.6, 6H, $CH(CH_3)_2$), 3.22 (sept, J_{HH} = 7.0, 2H, $CH(CH_3)_2$), 6.83 (dd, J_{HH} = 8.4, 7.2, 1H, Ar-H), 7.20–7.28 (m, 3H, Ar-H), 7.33–7.40 (m, 3H, Ar-H), 7.53 (dd, J_{HH} = 7.2, 1.6, 1H, Ar-H), 7.77 (dd, J_{HH} = 7.2, 0.9, 1H, Ar-H), 7.86 (d, J_{HH} = 7.1, 2H, Py-H/Ar-H), 7.90 (dd, J_{HH} = 8.6, 1.6, 1H, Ar-H), 7.99 (s, 1H, N=C-H), 8.16 (dd, J_{HH} = 8.7, 7.2, 1H, Py-H), 8.51 (d, J_{HH} = 8.7, 1H, Py-H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 22.1 ($CH(CH_3)_2$), 22.6 ($CH(CH_3)_2$), 27.6 ($CH(CH_3)_2$), 115.4, 119.5, 122.4, 124.4, 125.6, 126.4, 126.6, 127.6, 127.7, 129.1, 132.9, 133.4, 137.0, 138.8, 139.6, 142.6, 151.1, 151.4, 159.9, 166.8 (N=CH). IR (cm^{-1}): 2961 (C-H), 1614 ($C{=}N_{imine}$), 1589 ($C{=}N_{pyridine}$). FABMS *m*/*z*: 575 $[M + H]^+$, 539 $[M - Cl]^+$. Anal Calc. for ($C_{30}H_{29}ClN_2OPd$): C, 62.62; H, 5.08; N, 4.87. Found: C, 62.61; H, 5.00; N, 4.81%.

(b) **2b**. Employing a similar procedure to that described for **2a** using **L1b**-H (0.100 g, 0.255 mmol) and $(MeCN)_2PdCl_2$ (0.060 g, 0.231 mmol) gave **2b** as a red solid (0.114 g, 93%). Red/orange blocks suitable for an X-ray diffraction study could be grown by slow diffusion of hexane into a dichloromethane solution of the complex. Mp: >260 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.23 (s, 3H, Ar-*p*-Me), 2.26 (s, 6H, Ar-*o*-Me), 6.79 (s, 2H, Ar-H), 6.86 (td, J_{HH} = 7.6, 1.2, 1H, Ar-H), 7.19 (t, J_{HH} = 7.4, 1H, Ar-H), 7.33 (t, J_{HH} = 7.6, 2H, Ar-H), 7.46 (dd, J_{HH} = 7.0, 1.4, 1H, Ar-H), 7.74 (d, J_{HH} = 7.2, 1H, Ar-H), 7.79 (d, J_{HH} = 7.2, 2H, Ar-H/Py-H), 7.86 (dd, J_{HH} = 8.0, 1.6, 1H, Ar-H), 7.91 (s, 1H, N=C-H), 8.15 (t, J_{HH} = 7.2, 1H, Py-H), 8.50 (d, J_{HH} = 8.8, 1H, Py-H). IR (cm^{-1}): 2963 (C-H), 1615 ($C{=}N_{imine}$), 1583 ($C{=}N_{pyridine}$). FABMS *m*/*z*: 533 $(M + H)^+$, 497 $(M - Cl)^+$. Anal Calc. for (For $C_{27}H_{23}ClN_2OPd$): C, 60.80; H, 4.35; N, 5.25. Found: C, 60.73; H, 4.23; N, 5.19%.

Conversion of 1 to 2

A round bottomed flask equipped with stir bar and open to the air was loaded with **1** (0.054 mmol), chloroform (10 mL) and brine (10 mL). After stirring vigorously at room temperature overnight the organic phase was separated and the aqueous phase washed with chloroform (3 × 10 mL). All organic extracts were combined and dried over magnesium sulfate. Following filtering, all volatiles were removed under reduced pressure affording **2** as red powders (0.031 g, 98% (**2a**), 0.026 g, 89% (**2b**)). The spectroscopic data obtained for **2a** and **2b** were consistent with that given above.

Synthesis of [{2-(3-$C_{12}H_8$-2-O)-6-(CH_2-NHAr)C_5H_3N}Pd(OAc)] (3). (a) **3a**. A Schlenk flask equipped with stir bar was evacuated and backfilled with nitrogen and loaded with $Pd(OAc)_2$ (0.065 g, 0.29 mmol), **L2a**-H (0.126 g, 0.29 mmol) and toluene (10 mL). After stirring at 0 °C overnight, the reaction mixture was filtered through celite and the celite cake washed thoroughly with dichloromethane. The filtrate was concentrated to *ca.* 1 mL whereupon diethyl ether (*ca.* 8 mL) was added. The resulting precipitate was filtered and dried under reduced pressure forming **3a** as a yellow powder (0.100 g, 58%). Yellow plates suitable for an X-ray diffraction study could be grown by slow diffusion of hexane into a dichloromethane solution of the complex. Mp: >260 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.16 (d, J_{HH} = 6.8, 3H, $CH(CH_3)_2$), 1.17 (d, J_{HH} = 6.4, 3H, $CH(CH_3)_2$), 1.33 (d, J_{HH} = 6.5, 3H, $CH(CH_3)_2$), 1.58 (s, 3H, CH_3CO_2), 1.68 (d, J_{HH} = 6.8, 3H, $CH(CH_3)_2$), 3.24 (sept, J_{HH} = 6.7, 1H, $CH(CH_3)_2$), 4.16 (dd, J_{HH} = 17.3, 9.2, 1H, HN-CH_aH_b), 4.58 (dd, J_{HH} = 17.2, 10.0, 1H, HN-CH_aH_b), 5.21 (sept, J_{HH} = 6.7, 1H, $CH(CH_3)_2$), 6.77 (t, J_{HH} = 7.8, 1H, Ar-H), 6.84 (t, J_{HH} = 7.6, 1H, Ar-H), 7.07 (dd, J_{HH} = 6.4, 3.2, 1H, Ar-H), 7.18 (t, J_{HH} = 7.2, 1H, Ar-H), 7.20–7.32 (m, 4H, Ar-H), 7.52 (dd, J_{HH} = 7.8, 1.6, 1H, Ar-H), 7.54 (br t, J_{HH} = 8.0, 1H, *H*N-CH_aH_b), 7.73–7.79 (m, 3H, Py-H/Ar-H), 7.89 (d, J_{HH} = 8.0, 1H, Py-H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 21.5 (H_3CCOO), 22.3 ($CH(CH_3)_2$), 23.5 ($CH(CH_3)_2$), 23.6 ($CH(CH_3)_2$), 24.9 ($CH(CH_3)_2$), 27.0 ($CH(CH_3)_2$), 27.7 ($CH(CH_3)_2$), 62.3 (HN-CH_2), 114.5, 114.9, 119.7, 122.6, 123.2, 125.1, 126.4, 126.5, 128.1, 128.9, 131.7, 132.5, 137.2, 137.8, 139.22, 140.0, 141.8, 152.8, 160.1, 161.2, 177.3 (H_3CCOO). IR (cm^{-1}): 3224 (NH), 2954 (C-H), 1585 (COO_{asymm}/$C{=}N_{pyridine}$), 1384 (COO_{symm}). ESIMS: *m*/*z* 1141 $[M_2 - OAc]$, 541 $[M - OAc]$. FABMS *m*/*z* 601 $[M + H]^+$, 540 $[M - OAc]^+$. Anal Calc. for ($C_{32}H_{34}N_2O_3Pd$): C, 63.95; H, 5.70; N, 4.66. Found: C, 64.01; H, 5.55; N, 4.89%.

(b) **3b**. Employing a similar procedure to that described for **3a** using **L2b**-H (0.114 g, 0.29 mmol) and $Pd(OAc)_2$ (0.065 g, 0.29 mmol) gave **3b** as a yellow solid (0.119 g, 74%).

Yellow needles suitable for an X-ray diffraction study could be grown by slow diffusion of hexane into a dichloromethane solution of the complex. Mp: >260 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.65 (s, 3H, CH_3CO_2), 2.20 (s, 3H, Ar-*p*-Me), 2.41 (br s, 3H, Ar-*o*-Me), 3.08 (br s, 3H, Ar-*o*-Me), 4.02 (dd, J_{HH} = 17.4, 6.4, 1H, HN-CH_aH$_b$), 4.76 (dd, J_{HH} = 17.3, 7.7, 1H, HN-CH$_a$$H_b$), 6.71 (t, J_{HH} = 7.7, 1H, Ar-H), 6.78 (br, 2H, Ar-H), 6.80–6.84 (m, 1H, Ar-H), 7.19 (t, J_{HH} = 7.3, 1H, Ar-H), 7.23–7.32 (m, 3H, Py-H/Ar-H), 7.40–7.52 (m, 2H, Ar-H/*H*N-CH$_a$H$_b$), 7.55–7.72 (m, 4H, Py-H/Ar-H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, low solubility) signals seen at δ 20.6 (*o*-Me), 22.7 (H$_3$*C*COO), 61.4 (HN-*C*H$_2$), 115.3, 115.8, 120.2, 123.4, 126.2, 127.4, 128.9, 129.9, 131.8, 132.8, 136.5, 137.8, 139.9. IR (cm^{-1}): 2924 (C-H), 1580 (COO_{asymm}/C=N$_{pyridine}$), 1382 (COO_{symm}). ESIMS: *m*/*z* 1057 [M$_2$ − OAc], 559 [M + H]$^+$, 499 [M − OAc]. FABMS *m*/*z*: 558 [M]$^+$, 499 [M − OAc]$^+$. Anal Calc. for ($C_{29}H_{28}N_2O_3Pd\cdot CH_2Cl_2$): C, 55.96; H, 4.70; N, 4.35. Found: C, 55.93; H, 4.51; N, 4.55%.

Synthesis of [{2-(3-C$_{12}$H$_8$-2-O)-6-(CMeH-NH(2,6-i-Pr$_2$C$_6$H$_3$))-C$_5$H$_3$N}Pd(OAc)] (4) and [{2-(3-C$_{12}$H$_8$-2-O)-6-(CMe=N(2,6-i-Pr$_2$C$_6$H$_3$))C$_5$H$_3$N}Pd(OAc)] (5). A Schlenk flask equipped with stir bar was evacuated and backfilled with nitrogen and loaded with $Pd(OAc)_2$ (0.065 g, 0.29 mmol), **L3**-H (0.130 g, 0.29 mmol) and toluene (10 mL). After stirring at 60 °C overnight, the reaction mixture was filtered through celite and the celite cake thoroughly washed with dichloromethane. The filtrate was concentrated to *ca.* 1 mL whereupon hexane (*ca.* 8 mL) was added. The resulting precipitate was filtered and dried under reduced pressure forming a mixture of **4** and **5** as a red powder (0.099 g, 56%). Complex **4** (83% of mixture): ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.99 (d, J_{HH} = 6.8, 3H, CH(CH_3)$_2$), 1.17 (d, J_{HH} = 6.4, 3H, CH(CH_3)$_2$), 1.28 (d, J_{HH} = 6.5, 3H, CH(CH_3)$_2$), 1.51 (d, J_{HH} = 6.5, 3H, HNCH(CH_3)), 1.58 (s, 3H, CH_3CO_2), 1.71 (d, J_{HH} = 6.8, 3H, CH(CH_3)$_2$), 3.21 (sept, J_{HH} = 6.7, 1H, C*H*(CH$_3$)$_2$), 4.31 (dq, J_{HH} = 8.8, 7.0, 1H, HN-C*H*Me), 5.25 (sept, J_{HH} = 6.7, 1H, C*H*(CH$_3$)$_2$), 6.67 (t, J_{HH} = 7.6, 1H, Ar-H), 6.81 (d, J_{HH} = 7.4, 1H, Ar-H), 7.04 (d, J_{HH} = 7.4, 1H, Ar-H), 7.09–7.24 (m, 6H, Ar-H), 7.44 (d, J_{HH} = 8.2, 1H, Py-H), 7.65 (d, J_{HH} = 8.0, 2H, Ar-H), 7.68 (br d, J_{HH} = 8.0, 1H, *H*N-CHMe), 7.72–7.82 (m, 2H, Py-H/Ar-H). Complex **5** (17% of mixture): ^{1}H NMR (400 MHz, $CDCl_3$): signals identifiable, δ 1.05 (d, J_{HH} = 6.9, 6H, CH(CH_3)$_2$), 1.37 (d, J_{HH} = 6.9, 6H, CH(CH_3)$_2$), 1.50 (s, 3H, CH_3CO_2), 2.21 (s, 3H, N=C*Me*), 3.22 (sept, J_{HH} = 6.7, 2H, CH(CH_3)$_2$), 6.83 (t, J_{HH} = 8.1, 1H, Ar-H), 8.05 (t, J_{HH} = 8.3, 1H, Py-H), 8.52 (d, J_{HH} = 8.8, 1H, Py-H). Orange blocks of **4** suitable for an X-ray diffraction study could be grown by slow diffusion of hexane into a dichloromethane solution of the mixture. Mp: >260 °C. IR (cm^{-1}): 2960 (C-H), 1589 ($COO)_{asymm}$/C=N$_{pyridine}$), 1385 ($COO)_{symm}$. ESIMS: *m*/*z* 1171 [M$_2$ − OAc], 555 [M − OAc]. FABMS *m*/*z* 615 [M + H]$^+$, 554 [M − OAc]$^+$. Anal Calc. for ($C_{33}H_{36}N_2O_3Pd$): C, 64.44; H, 5.90; N, 4.55. Found: C, 64.09; H, 5.75; N, 4.79%.

Synthesis of [{2-(3-C$_{12}$H$_8$-2-O)-6-(CH$_2$-NHAr)C$_5$H$_3$N)}PdCl] (6). (a) **6a**. A round bottomed flask equipped with stirrer bar and open to the air was loaded with **3a** (0.032 g, 0.054 mmol), chloroform (10 mL) and brine (10 mL). After stirring vigorously at room temperature overnight the organic phase was separated and the aqueous phase washed with chloroform (3 × 10 mL). All organic extracts were combined and dried over magnesium sulfate. Following filtering, all volatiles were removed under reduced pressure affording **6a** as yellowy brown powder (0.026 g, 87%). Yellow blocks suitable for an X-ray diffraction study could be grown by slow diffusion of hexane into a dichloromethane solution of the complex. Mp: >260 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.73 (d, J_{HH} = 6.8, 3H, CH(CH_3)$_2$), 1.02 (br s, 3H, CH(CH_3)$_2$), 1.20 (br s, 3H, CH(CH_3)$_2$), 1.48 (d, J_{HH} = 6.5, 3H, CH(CH_3)$_2$), 3.34 (dd, J_{HH} = 17.7, 1.8, 1H, HN-CH_aH$_b$), 3.72 (br s, 1H, C*H*(CH$_3$)$_2$), 4.21 (sept, J_{HH} = 6.5, 1H, C*H*(CH$_3$)$_2$), 4.99 (dd, J_{HH} = 17.7, 7.9, 1H, HN-CH$_a$$H_b$), 5.98 (br s, 1H, *H*N-CH$_2$), 6.60 (t, J_{HH} = 7.5, 1H, Ar-H), 7.05–7.24 (m, 7H, Py-H/Ar-H), 7.26 (t, J_{HH} = 7.5, 2H, Ar-H), 7.35 (br s, 2H, Py-H), 7.88 (d, J_{HH} = 8.1, 2H, Ar-H). IR (cm^{-1}): 3223 (NH), 2955 (CH), 1598 (C=N$_{pyridine}$). ESIMS *m*/*z* 1118 [M$_2$ − Cl]$^+$, 539 [M − Cl]$^+$. FABMS *m*/*z* 576 [M]$^+$, 539 [M − Cl]$^+$. Anal Calc. for ($C_{30}H_{31}ClN_2OPd$): C, 62.40; H, 5.41; N, 4.85. Found: C, 62.69; H, 5.25; N, 4.92%.

(b) **6b**. Employing a similar procedure to that described for **6a** using **3b** (0.030 g, 0.054 mmol) gave **6b** as a yellowy brown solid (0.020 g, 70%). Yellow plates suitable for an X-ray diffraction study could be grown by slow diffusion of hexane into a dichloromethane solution of the complex. Mp: >260 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.11 (s, 3H, Ar-*p*-Me), 2.48 (s, 3H, Ar-*o*-Me), 2.50 (br s, 3H, Ar-*o*-Me), 3.35 (d, J_{HH} = 17.7, 1H, HN-CH_aH$_b$), 5.21 (br s, 1H, HN-CH$_a$$H_b$), 5.71 (br s, 1H, *H*N-CH$_2$), 6.55 (t, J_{HH} = 7.5, 1H, Ar-H), 6.70 (s, 2H, Ar-H), 7.05–7.25 (m, 5H, Py-H/Ar-H), 7.26 (t, J_{HH} = 7.5, 2H, Ar-H), 7.48 (br s, 1H, Py-H), 7.81 (d, J_{HH} = 8.1, 2H, Ar-H). IR (cm^{-1}): 3224 (N-H), 2917 (C-H), 1582 (COO_{asymm}/C=N$_{pyridine}$), 1383 (COO_{symm}). ESIMS *m*/*z* 1035 [M$_2$ − Cl]$^+$, 535 [M + H]$^+$, 499 [M − Cl]$^+$. FABMS *m*/*z*: 535 [M]$^+$, 499 [M − Cl]$^+$, IR (cm^{-1}): 3224 (N-H), 2917 (C-H), 1582 (COO_{asymm}/C=N$_{pyridine}$), 1383 (COO_{symm}). Anal Calc. for ($C_{27}H_{25}ClN_2OPd$): C, 60.57; H, 4.71; N, 5.23. Found: C, 60.22; H, 4.51; N, 5.01%.

Crystallographic studies

Data for **L1a**-H, **L3**-H, **1a**, **1b**, **2a**, **2b**, **3a**, **3b**, **4**, **6a** and **6b** were collected on a Bruker APEX 2000 CCD diffractometer. Details of data collection, refinement and crystal data are listed in Table 7. 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.[29] Hydrogen atoms were included in calculated positions (C–H = 0.96–1.00 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 **L1a**-H, **1b**, **4** and **6a**.[30]

Table 7 Crystallographic and data processing parameters for **L1a**-H, **L3**-H, **1a**, **1b**, **2a**, **2b**, **3a**, **3b**, **4**, **6a** and **6b**[a]

Complex	**L1a**-H	**L3**-H	**1a**	**1b**	**2a**	**2b**
Formula	$C_{34}H_{40}N_2O_2$	$C_{31}H_{34}N_2O$	$C_{65}H_{66}ClN_4O_6Pd_2$	$C_{39}H_{49}Cl_2N_2O_3Pd$	$C_{30}H_{29}ClN_2OPd$	$C_{138}H_{121}Cl_{11}N_{10}O_5Pd_5$
M	508.68	450.60	1282.92	771.10	575.40	2921.40
Crystal size (mm^3)	0.25 × 0.23 × 0.12	0.21 × 0.15 × 0.14	0.14 × 0.10 × 0.09	0.16 × 0.15 × 0.12	0.33 × 0.27 × 0.18	0.20 × 0.15 × 0.08
Temperature (K)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
Crystal system	Triclinic	Monoclinic	Monoclinic	Tetragonal	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2(1)/c$	$P2(1)/c$	$I4(1)/a$	$P2(1)/c$	$P\bar{1}$
a (Å)	8.9542(16)	9.646712)	15.311(2)	20.075(8)	9.941(4)	13.427(8)
b (Å)	12.028(2)	24.689(3)	11.6253(17)	20.075(8)	12.678(5)	17.856(11)
c (Å)	14.082(3)	11.3413(15)	32.923(5)	28.842(17)	20.671(8)	26.730(16)
α (°)	89.451(3)	90	90	90	90	76.396(13)
β (°)	85.613(4)	110.409(3)	90.364(4)	90	97.076(7)	86.289(14)
γ (°)	81.432(4)	90	90	90	90	86.280(15)
U ($Å^3$)	1495.3(5)	2531.5(6)	5869.0(15)	11 624(10)	2585.3(17)	6208(6)
Z	2	4	4	16	4	2
D_c (Mg m^{-3})	1.130	1.182	1.454	1.763	1.478	1.563
F(000)	548	968	2632	6416	1176	2952
μ(Mo-K_α) (mm^{-1})	0.070	0.071	0.760	0.872	0.847	1.008
Reflections collected	10 849	18 269	45 009	41 787	19 633	48 941
Independent reflections	5210	4462	11 515	5124	5077	24 098
R_{int}	0.0850	0.1632	0.2017	0.2088	0.1370	0.1753
Restraints/parameters	0/303	0/313	0/720	0/320	679/429	1475/1536
Final R indices ($I > 2\sigma(I)$)	R_1 = 0.0613	R_1 = 0.0638	R_1 = 0.0699	R_1 = 0.0753	R_1 = 0.0697	R_1 = 0.0792
	wR_2 = 0.1362	wR_2 = 0.1102	wR_2 = 0.1035	wR_2 = 0.1631	wR_2 = 0.1413	wR_2 = 0.0993
All data	R_1 = 0.1155	R_1 = 0.1604	R_1 = 0.1671	R_1 = 0.1453	R_1 = 0.1204	R_1 = 0.2329
	wR_2 = 0.1513	wR_2 = 0.1375	wR_2 = 0.1271	wR_2 = 0.1854	wR_2 = 0.1608	wR_2 = 0.1346
Goodness of fit on F^2 (all data)	0.825	0.808	0.841	0.966	0.958	0.797

Complex	**3a**	**3b**	**4**	**6a**	**6b**
Formula	$C_{33}H_{36}Cl_2N_2O_3Pd$	$C_{30}H_{29}Cl_3N_2O_3Pd$	$C_{52}H_{79}Cl_3N_2O_3Pd$	$C_{39}H_{54}ClN_2O_2Pd$	$C_{28}H_{27}Cl_3N_2OPd$
M	685.94	678.3	992.92	724.69	629.27
Crystal size (mm^3)	0.15 × 0.13 × 0.04	0.24 × 0.08 × 0.05	0.17 × 0.11 × 0.10	0.18 × 0.13 × 0.12	0.17 × 0.11 × 0.04
Temperature (K)	150(2)	150(2)	150(2)	150(2)	150(2)
Crystal system	Monoclinic	Monoclinic	Rhombohedral	Triclinic	Triclinic
Space group	$P2(1)/c$	$P2(1)/c$	$R\bar{3}$	$P\bar{1}$	$P\bar{1}$
a (Å)	13.471(3)	13.216(10)	22.469(7)	10.5900(16)	9.632(9)
b (Å)	14.913(3)	18.856(14)	22.469(7)	10.9142(16)	11.597(11)
c (Å)	16.595(4)	11.977(9)	22.469(7)	14.160(2)	13.229(12)
α (°)	90	90	115.655(6)	92.595(3)	90.597(19)
β (°)	108.732(4)	100.468(17)	115.655(6)	95.184(3)	108.415(19)
γ (°)	90	90	115.655(6)	105.297(3)	112.533(18)
U ($Å^3$)	3157.1(12)	2935(4)	5952(3)	1568.1(4)	1280(2)
Z	4	4	6	2	2
D_c (Mg m^{-3})	1.443	1.535	1.662	1.535	1.609
F(000)	1408	1376	3156	762	628
μ(Mo-K_α) (mm^{-1})	0.792	0.939	0.724	0.717	1.063
Reflections collected	24 097	22 755	46 610	12 345	10 113
Independent reflections	6204	5773	7800	6069	4967
R_{int}	0.1722	0.1950	0.3336	0.0958	0.1186
Restraints/parameters	0/357	0/356	351/358	0/320	0/319
Final R indices ($I > 2\sigma(I)$)	R_1 = 0.0644	R_1 = 0.0785	R_1 = 0.0781	R_1 = 0.0584	R_1 = 0.1151
	wR_2 = 0.0905	wR_2 = 0.1467	wR_2 = 0.1533	wR_2 = 0.1216	wR_2 = 0.3053
All data	R_1 = 0.1428	R_1 = 0.1792	R_1 = 0.1881	R_1 = 0.0849	R_1 = 0.1526
	wR_2 = 0.1070	wR_2 = 0.1757	wR_2 = 0.1769	wR_2 = 0.1289	wR_2 = 0.3219
Goodness of fit on F^2 (all data)	0.860	0.937	0.819	0.873	1.100

[a] Data in common: graphite-monochromated Mo-K_α radiation, λ = 0.71073 Å; $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$, $w^{-1} = [\sigma^2(F_o)^2 + (aP)^2]$, $P = [\max(F_o^2,0) + 2(F_c^2)]/3$, where a is a constant adjusted by the program; goodness of fit = $[\Sigma(F_o^2 - F_c^2)2/(n-p)]^{1/2}$ where n is the number of reflections and p the number of parameters.

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