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N-Triisopropylphenyl-substituted N,N_{py},O pincers as supports for mononuclear palladium(II) complexes and hydrogen-bonded dimeric assemblies

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ABSTRACT

Treatment of the sterically bulky 2-(3-biphenyl-2-ol)-6-iminepyridine, 2-(3-$C_{12}H_8$-2-OH)-6-(CH=N(2,4,6-*i*-$Pr_3C_6H_2$))C_5H_3N (H**L1**$_{tripp}$), with $Pd(OAc)_2$ or $(MeCN)_2PdCl_2$ results in deprotonation of H**L1**$_{tripp}$ to afford the discrete square planar O,N_{py},N-pincer complexes, [(**L1**$_{tripp}$)Pd(OAc)] (**1**) and [(**L1**$_{tripp}$)PdCl] (**2**) respectively, in good yield; conversion of **1** directly to **2** using aqueous sodium chloride or to [(**L1**$_{tripp}$)PdI] (**3**) using aqueous sodium iodide has been demonstrated. Selective reduction of the imino unit in H**L1**$_{tripp}$ with $LiAlH_4$ proceeds smoothly to yield the 2-(3-biphenyl-2-ol)-6-methylaminepyridine, 2-(3-$C_{12}H_8$-2-OH)-6-(CH_2-NH(2,4,6-*i*-$Pr_3C_6H_2$))C_5H_3N (H**L2**$_{tripp}$), which on reaction with $Pd(OAc)_2$ at low temperature gives [(**L2**$_{tripp}$)Pd(OAc)] (**4**) as the sole product. Complex **4** exists as a dimeric species in the solid state in which two square planar monomers are linked together by two intermolecular $NH_{amine}\cdots O_{acetate}$ interactions resulting in a Pd···Pd separation of 6.255 Å. The corresponding chloride complex, [(**L2**$_{tripp}$)PdCl] (**5**), formed by reaction of **4** with aqueous sodium chloride, also exists as a dimeric assembly in the solid state but in this case the presence of two intermolecular $NH_{amine}\cdots O_{phenolate}$ interactions has the effect of compressing the palladium–palladium separation to 3.2580(11) Å. Single crystal X-ray diffraction studies have been performed on **1**, **2**·CH_2Cl_2, **2**·C_6H_6, **3**, **4** and **5**.

1. Introduction

Recent years have seen a surge of interest in pyridine-based pincer-type complexes due, in large measure, to their applications in a variety of fields including organic synthesis, homogeneous catalysis, bond activation, and design of new materials [1–3]. The electronic and steric flexibility offered by the exterior donor atoms of the terdentate ligand coupled with an appreciation of the aromatisation-dearomatisation processes that can occur at the pyridine core during certain bond activations has no doubt lent further impetus to the area [4–8].

As part of a general study directed towards developing new sterically encumbered N,N_{py},O pincer ligands that can support a range of metal-mediated catalytic processes [9–12], we have recently been interested in adding a hydrogen bonding capacity to the role of the pincer [13]. It was envisaged that by introducing suitably positioned hydrogen bond donor (D) and acceptor (A) moieties within a sterically sheltered N,N_{py},O-metal pocket, self-dimerisation or non-covalent substrate binding could be promoted. As a preliminary investigation into the palladium(II) chemistry of monoanionic **L1** and **L2** (Fig. 1, Ar = 2,4,6-$Me_3C_6H_2$, 2,6-*i*-$Pr_2C_6H_3$), it was found that the coordinated secondary amine in **L2** could indeed serve as a directional hydrogen bond donor in this case generating dimeric palladium(II) assemblies linked by two intermolecular $N_{amine}H\cdots O_{phenolate}$ interactions [12].

To probe the scope of this chemistry and to potentially improve the solubility of the resultant dimeric assemblies, we are concerned in this note with the synthesis of palladium(II) acetate and chloride complexes bound by the *N*-2,4,6-triisopropylphenyl (tripp) derivative of **L2**. For purposes of comparison we also report the corresponding coordination chemistry of imine-containing **L1**$_{tripp}$ along with full details of the synthetic procedures employed to prepare H**L1**$_{tripp}$ and H**L2**$_{tripp}$.

2. Results and discussion

The 2-(3-biphenyl-2-ol)-6-iminepyridine, 2-(3-$C_{12}H_8$-2-OH)-6-(CH=N(2,4,6-*i*-$Pr_3C_6H_2$))C_5H_3N (H**L1**$_{tripp}$), has been prepared in reasonable yield by the condensation reaction of 2-(3-biphenyl-2-ol)-6-formylpyridine with 2,4,6-triisopropylaniline (Scheme 1). 2-(3-Biphenyl-2-ol)-6-formylpyridine is accessible *via* sequential Suzuki coupling and deprotection reactions from 2-methoxybiphenyl-3-ylboronic acid and 2-bromo-6-formylpyridine using general methodologies we have described elsewhere [9,12]. The imino unit in H**L1**$_{tripp}$ could be readily reduced by addition of lithium

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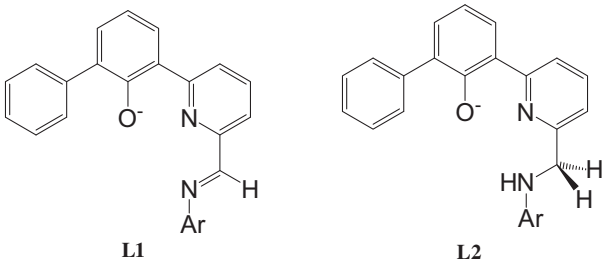


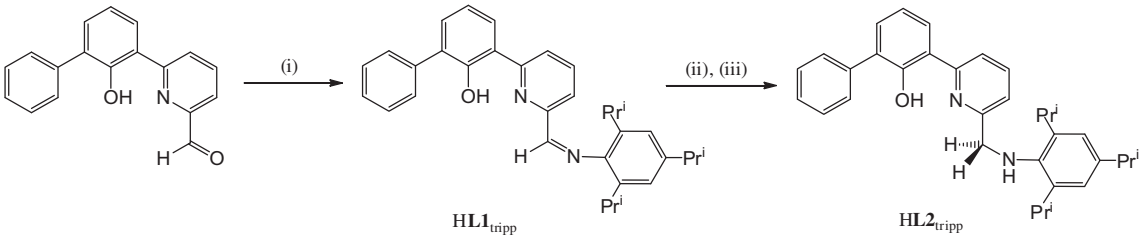
Fig. 1. Monoanionic 2-(3-biphenyl-2-olate)-6-iminepyridine (**L1**) and 2-(3-biphenyl-2-olate)-6-methylaminepyridine (**L2**).

aluminium hydride to yield the 2-(3-biphenyl-2-ol)-6-methylaminepyridine, 2-($C_{12}H_8$-2-OH)-6-(CH_2-NH(2,4,6-*i*-$Pr_3C_6H_2$))C_5H_3N (H**L2**$_{tripp}$). Both H**L1**$_{tripp}$ and H**L2**$_{tripp}$ have been characterised using a combination of electrospray mass spectrometry, IR, ^{1}H NMR and ^{13}C NMR spectroscopy (see experimental section).

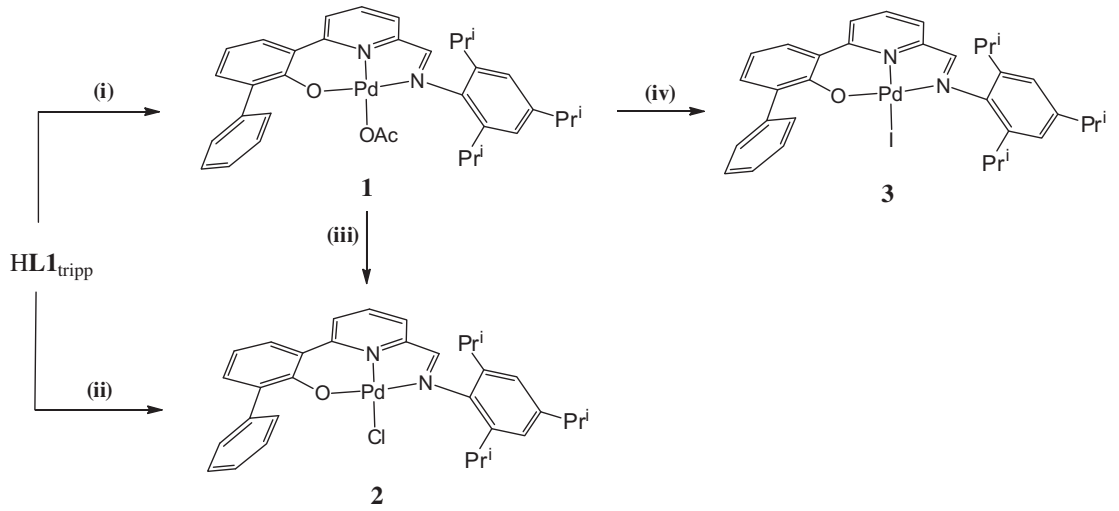
Compounds, H**L1**$_{tripp}$ and H**L2**$_{tripp}$, either display protonated molecular ions or peaks corresponding to their sodium adduct ions, $(M+Na)^+$, in their electrospray mass spectra. The phenolic hydrogen atoms in both compounds undergo strong hydrogen bonding interactions as evidenced by downfield shifted signals for the OH protons (range: δ 14.2–14.8) in their ^{1}H NMR spectra and broad ν(OH) absorption bands centred at *ca.* 2600 cm^{-1} in their IR spectra. Crystal structures of a series of related compounds support these observations highlighting the presence of intramolecular OH$\cdots$N$_{pyridine}$ hydrogen bond interactions in the solid state [9,12,14]. In the ^{1}H NMR spectrum of imine-based H**L1**$_{tripp}$, the *CH*=N proton is seen as a singlet at δ 8.35 with the corresponding imino carbon atom appearing at δ 161.0 in its ^{13}C NMR spectrum; the $\nu(CN)_{imine}$ stretch is observable at 1649 cm^{-1}. The CH_2–NH moiety in reduced H**L2**$_{tripp}$ can be seen as singlet for the methylene protons (δ 4.20) and a broad singlet for the NH proton at δ 3.41 in the ^{1}H NMR spectrum.

Reaction of H**L1**$_{tripp}$ with either $Pd(OAc)_2$ at 60 °C in toluene or $(MeCN)_2PdCl_2$ in tetrahydrofuran at room temperature gave, on work-up, [(**L1**$_{tripp}$)Pd(OAc)] (**1**) and [(**L1**$_{tripp}$)PdCl] (**2**), respectively, in good yield (Scheme 2). Alternatively, **1** can be converted to **2** in near quantitative yield by treatment of **1** with aqueous sodium chloride followed by extraction into chloroform. Similarly, reaction of **1** with aqueous sodium iodide gives [(**L1**$_{tripp}$)PdI] (**3**). Complexes **1**–**3** are all air stable and have been characterised using a combination of FAB mass spectrometry, IR and ^{1}H NMR spectroscopy and elemental analyses (see experimental section). In addition, crystals of each complex have been the subject of single crystal X-ray diffraction studies.

A perspective view of **1** is given in Fig. 2; selected bond distances and angles are collected in Table 1. There are two *pseudo* "non-superimposable" mirror images (molecules A and B) within the asymmetric unit with the most noticeable structural difference between the two molecules being the relative inclination of the 3-phenyl groups (*vide infra*). The structure consists of a single palladium centre bound by a monoanionic 2-(3-biphenyl-2-olate)-6-iminepyridine ligand which binds in a tridentate fashion along with a monodentate O-bound acetate to complete a distorted square planar geometry. Within the N,N,O-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)$_{6\text{-membered}}$ 93.8(3)$_A$, 94.0(3)$_B$° versus N(2)–Pd(1)–N(1)$_{5\text{-membered}}$ 82.6(4)$_A$, 83.4(4)$_B$°]. Some twisting within the backbone of the N,N,O-ligand is apparent which is most noticeable on inspection of the relative inclination of the neighbouring phenolate and



Scheme 1. *Reagents and conditions*: (i) 2,4,6-*i*-$Pr_3C_6H_2NH_2$, ethanol, 40 °C, (ii) $LiAlH_4$, THF, −78 °C; (iii) H_2O.



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

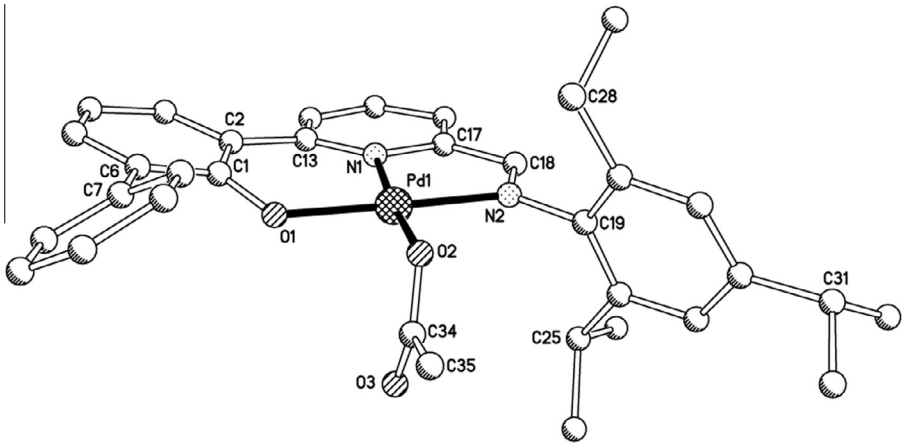


Fig. 2. Molecular structure of **1** (*molecule A*) including a partial atom numbering scheme. All hydrogen atoms have been omitted for clarity.

Table 1
Selected bond distances (Å) and angles (°) for **1**.

	Molecule A	Molecule B
Bond lengths		
Pd(1)–O(1)	1.948(8)	1.946(7)
Pd(1)–O(2)	1.985(7)	1.994(7)
Pd(1)–N(1)	1.970(9)	1.947(9)
Pd(1)–N(2)	1.980(9)	1.978(9)
C(18)–N(2)	1.263(14)	1.279(14)
C(6)–C(7)	1.470(18)	1.476(18)
C(34)–O(2)	1.256(14)	1.262(14)
C(34)–O(3)	1.211(15)	1.222(13)
Bond angles		
N(1)–Pd(1)–N(2)	82.6(4)	83.4(4)
N(1)–Pd(1)–O(1)	93.8(3)	94.0(3)
O(1)–Pd(1)–O(2)	88.7(3)	87.6(3)
N(1)–Pd(1)–O(2)	175.1(3)	177.8(3)
N(2)–Pd(1)–O(2)	95.0(3)	95.0(3)

pyridine planes [tors. N(1)–C(13)–C(2)–C(1) 10.2(17)$_A$, 9.6(17)$_B$°]. Of the four bonds to palladium, the Pd(1)–O(2)$_{acetate}$ distance is among the longest [1.985(7)$_A$, 1.994(7)$_B$ Å] while the Pd(1)–O(1)$_{phenolate}$ distance [1.948(8)$_A$, 1.946(7)$_B$ Å] the shortest. The *N*-tripp group is inclined up to 15.3° away from orthogonality with regard to the neighbouring C=N$_{imine}$ vector presumably, in part, to avoid any steric interaction with the pendant acetate group. Likewise the plane of the 3-phenyl group is tilted [tors. C(1)–C(6)–C(7)–C(12) 44.0(17)$_A$, 39.9(19)$_B$°] with respect to the adjacent phenolate unit in a manner similar to that observed in complexes containing coordinated *o*-phenylphenolates [15]. There are no intermolecular contacts of note. Similar structural features can be seen in the analogues [{2-(3-$C_{12}H_8$-2-O)-6-CH=N(Ar)C_5H_3-N}Pd(OAc)] (Ar = 2,4,6-$Me_3C_6H_2$, 2,6-*i*-$Pr_2C_6H_3$) [12].

The molecular structures of halide-containing **2** [as both the dichloromethane (**2**·CH_2Cl_2) and benzene (**2**·C_6H_6) solvates] and **3** are closely related and will be discussed together. In **2**·C_6H_6 there are two independent molecules in the unit cell (molecules A and B) while in **3** there are three (molecules A, B and C); the main differences between A, B and C can be attributed to a combination of factors including the relative inclination of the *N*-aryl groups, the 3-phenyl groups and the inter-pyridine-phenolate plane angle. Perspective views of **2**·CH_2Cl_2 and **3** are given in Figs. 3 and 4; selected bond distances and angles are collected for all structures in Tables 2 and 3. Like **1** each structure consists of single palladium centre bound by a tridentate 2-(3-biphenyl-2-olate)-6-iminepyridine ligand but differs in that a halide [**2** (Cl), **3** (I)] now fills the site that was occupied by an acetate oxygen atom to complete a distorted square planar geometry. The bite angle displayed by the 6-membered chelate ring formed by the N,N,O ligand is again better matched to the geometrical requirements of the palladium(II) centre [O(1)–Pd(1)–N(1)$_{6\text{-membered}}$ 92.71(11) (**2**·CH_2Cl_2), 93.0(4)$_A$, 91.6(3)$_B$ (**2**·C_6H_6), 90.1(3)$_A$, 90.9(3)$_B$, 92.0(3)$_C$° (**3**) versus N(2)–Pd(1)–N(1)$_{5\text{-membered}}$ 82.28(12) (**2**·CH_2Cl_2), 83.5(4)$_A$, 80.6(4)$_B$ (**2**·C_6H_6), 82.6(3)$_A$, 81.3(3)$_B$, 81.4(4)$_C$° (**3**)]. The flexibility of the N,N,O ligand backbone is again evident with the relative inclination of the neighbouring phenolate and pyridine planes varying anywhere between 2.6(19) and 28.4(17)° [tors. N(1)–C(13)–C(2)–C(1) 17.5(5) (**2**·CH_2Cl_2), 2.6(19)$_A$, 28.4(17)$_B$ (**2**·C_6H_6), 24.9(16)$_A$, 21.3(15)$_B$, 23.3(14)$_C$° (**3**)]. Replacing an O-bound acetate in **1** for

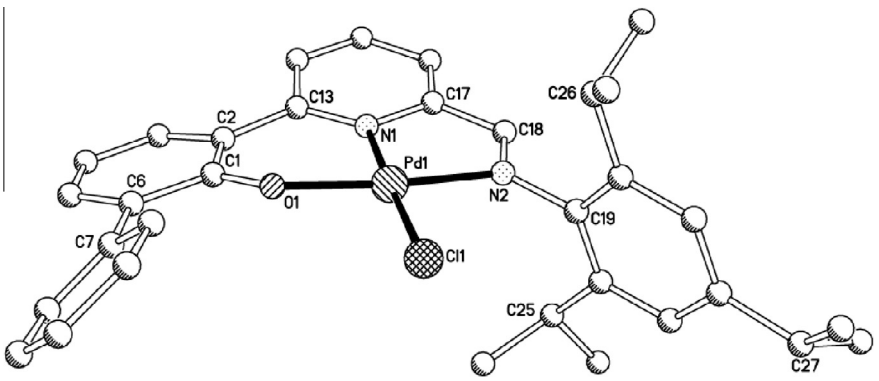


Fig. 3. Molecular structure of **2**·CH_2Cl_2 including a partial atom numbering scheme. All hydrogen atoms have been omitted for clarity.

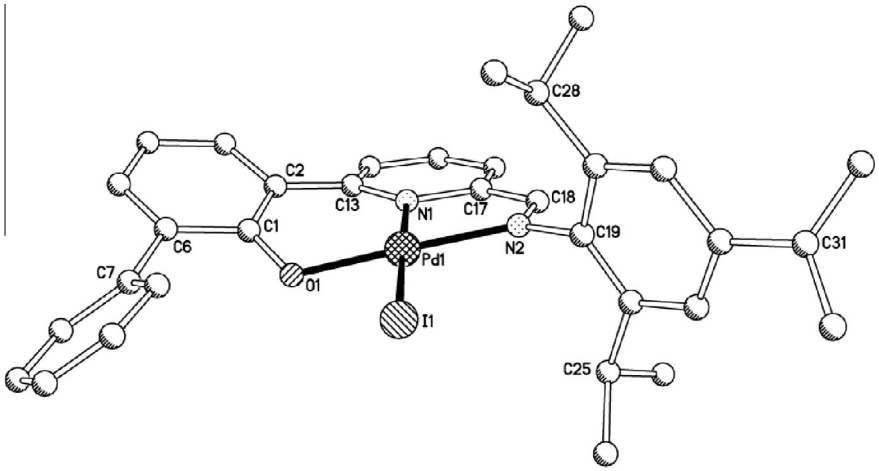


Fig. 4. Molecular structure of **3** (*molecule A*) including a partial atom numbering scheme. All hydrogen atoms have been omitted for clarity.

Table 2
Selected bond distances (Å) and angles (°) for **2**·CH_2Cl_2 and **2**·C_6H_6.

	2·CH_2Cl_2	**2**·C_6H_6	
		Molecule A	Molecule B
Bond lengths			
Pd(1)–O(1)	1.958(2)	1.961(7)	1.965(7)
Pd(1)–N(1)	1.973(3)	1.949(8)	1.953(8)
Pd(1)–N(2)	2.007(3)	1.992(8)	2.012(9)
Pd(1)–Cl(1)	2.2975(10)	2.290(3)	2.290(3)
C(18)–N(2)	1.280(5)	1.283(13)	1.250(12)
C(6)–C(7)	1.478(5)	1.479(15)	1.442(16)
Bond angles			
N(1)–Pd(1)–N(2)	82.28(12)	83.5(4)	80.6(4)
N(1)–Pd(1)–O(1)	92.71(11)	93.0(4)	91.6(3)
N(2)–Pd(1)–Cl(1)	96.03(9)	94.0(3)	97.3(3)
O(1)–Pd(1)–Cl(1)	88.98(7)	89.9(2)	90.6(2)
N(1)–Pd(1)–Cl(1)	178.31(9)	173.9(2)	177.5(3)
N(2)–Pd(1)–O(1)	174.57(11)	175.2(4)	170.4(3)

Table 3
Selected bond distances (Å) and angles (°) for **3**.

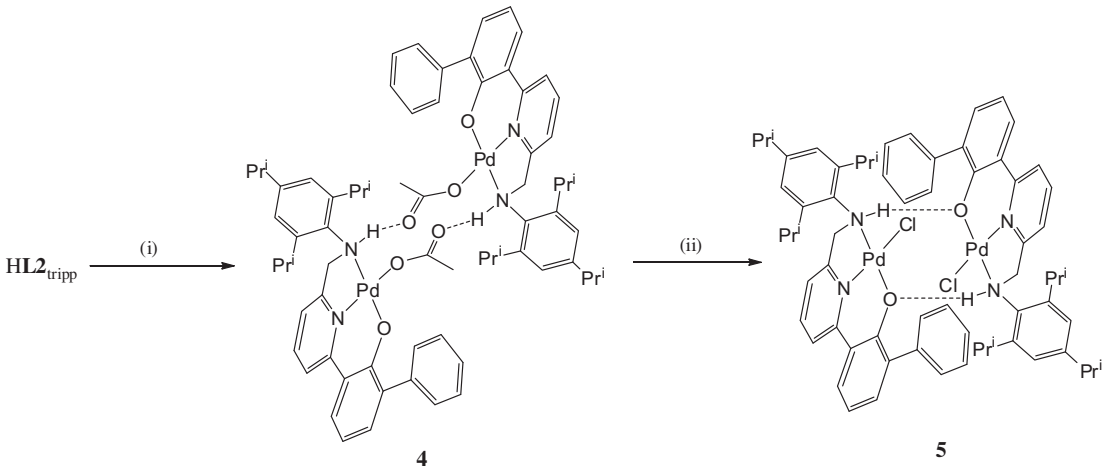
	Molecule A	Molecule B	Molecule C
Bond lengths			
Pd(1)–O(1)	1.963(7)	1.964(6)	1.997(6)
Pd(1)–N(1)	1.992(8)	1.982(8)	1.986(9)
Pd(1)–N(2)	2.013(8)	2.015(8)	2.016(8)
Pd(1)–I(1)	2.5807(12)	2.5852(12)	2.5861(12)
C(18)–N(2)	1.302(11)	1.254(11)	1.289(12)
C(6)–C(7)	1.527(18)	1.431(14)	1.469(16)
Bond angles			
N(1)–Pd(1)–N(2)	82.6(3)	81.3(3)	81.4(4)
N(1)–Pd(1)–O(1)	90.1(3)	90.9(3)	92.0(3)
N(2)–Pd(1)–I(1)	96.4(2)	97.0(2)	96.8(3)
O(1)–Pd(1)–I(1)	90.9(2)	90.7(2)	89.6(2)
N(1)–Pd(1)–I(1)	179.0(3)	178.1(2)	174.9(3)
N(2)–Pd(1)–O(1)	171.0(3)	170.8(3)	173.0(3)

a chloride in **2** appears to have little effect on the *trans* Pd–$N(1)_{pyridine}$ distance [$1.970(9)_A$, $1.947(9)_B$ Å (**1**) versus 1.973(3) (**2**·CH_2Cl_2), $1.949(8)_A$, $1.953(8)_B$ Å (**2**·C_6H_6)], although a modest elongation is apparent for iodide-containing **3** [$1.992(8)_A$, $1.982(8)_B$, $1.986(9)_C$ Å]. Despite the absence of a more sterically bulky acetate ligand (**1**), the *N*-aryl groups in chloride **2** and iodide **3** can be inclined up to 19.2° away from orthogonality [tors. C(18)–N(2)–C(19)–C(20) 79.0(5) (**2**·CH_2Cl_2), $75.7(13)_A$, $70.5(16)_B$ (**2**·C_6H_6), $82.1(13)_A$, $86.9(12)_B$, $70.8(12)_C$° (**3**)]; the 3-phenyl groups also show some variation in the degree of tilting with respect to the adjacent phenolate groups [tors. C(1)–C(6)–C(7)–C(12) 33.9(6) (**2**·CH_2Cl_2), $55.7(19)_A$, $31.0(19)_B$ (**2**·C_6H_6), $50.9(16)_A$, $46.2(14)_B$, $42.6(15)_C$° (**3**)]. There are no intermolecular contacts of note. The closest structural comparators to **2** and **3** are [{2-(3-$C_{12}H_8$-2-O)-6-CH=N(Ar)C_5H_3N}PdCl] (Ar = 2,4,6-$Me_3C_6H_2$, 2,6-*i*-$Pr_2C_6H_3$) in which similar features are apparent [12].

The halide complexes, **2** and **3**, both display molecular ion peaks in their FAB mass spectra along with fragmentation peaks corresponding to the loss of a chloride or an iodide, while acetate-containing **1** instead displays a M-OAc fragmentation peak but no parent peak. The imine stretching frequencies for **1**–**3** all shift by *ca.* 30 cm^{-1} to lower wavenumber on imine-coordination (in comparison with free H**L1**$_{tripp}$) as is seen in related palladium(II) complexes [16]. In all three complexes, three distinct doublets of equal intensity (6:6:6) are seen for the isopropyl methyl groups in their ^{1}H NMR spectra implying free rotation for the *para*-isopropyl group while the inequivalency of the *ortho*-isopropyl methyl groups suggests restricted rotation about the *N*-aryl bond in solution. The acetate methyl group in **1** can be seen at δ 1.56 in its ^{1}H NMR spectrum with the Me*C*(O)O carbon atoms observable at δ 176.4 in the ^{13}C NMR spectrum. 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 [17].

Complex [(**L2**$_{tripp}$)Pd(OAc)] (**4**) could be prepared in good yield by treating H**L2**$_{tripp}$ with $Pd(OAc)_2$ at 0 °C (Scheme 3). Notably, if the reaction was conducted at higher temperature the yield of **4** was found to significantly drop with imine **1** proving a competitive side product [18]. Conversion of **4** to [(**L2**$_{tripp}$)PdCl] (**5**) could be readily achieved by treatment with aqueous sodium chloride at room temperature. Complexes **4** and **5** proved highly soluble in aromatic and chlorinated organic solvents and have been characterised using a combination of FAB mass spectrometry, IR and ^{1}H NMR spectroscopy and elemental analyses (see experimental section).

In the electrospray mass spectra of **4** and **5** fragmentation peaks corresponding to the loss of an acetate or chloride group from both dimeric and monomeric species are evident, respectively. The NH proton in each complex takes the form of a broad triplet (**4**) or singlet (**5**) resonance in the ^{1}H NMR spectra and is markedly shifted downfield compared to that observed in free H**L2**$_{tripp}$ (from δ 3.41 to δ 7.58 (**4**) or δ 5.91 (**5**)), supportive of both metal coordination and the probable onset of hydrogen bonding interactions. The PyCH_2 protons in the ^{1}H NMR spectra for **4** and **5** are inequivalent and appear as two doublet of doublets attributable to mutual



Scheme 3. *Reagents and conditions*: (i) $Pd(OAc)_2$, toluene, 0 °C; (ii) NaCl(aq), $CHCl_3$, RT.

coupling ($^2J_{HH}$ 17.0–17.8 Hz) and coupling to the NH proton ($^3J_{HH}$ 1.9–8.3 Hz). Each *ortho*-isopropyl-methyl group in **4** and **5** are also inequivalent leading to four separate doublets consistent with restricted rotation around a pyramidal NH–Pd bond. To identify the nature of the NH hydrogen bonding interactions and likely dimeric structure adopted in **4** and **5**, single crystals of each complex were the subject of X-ray determinations.

Views of **4** and **5** are shown in Figs. 5 and 6; selected bond distances and angles are listed in Tables 4 and 5. The structure of **4** comprises two square planar (**L2**$_{tripp}$)Pd(OAc) monomeric units linked together by two $N_{amine}H\cdots O_{acetate}$ hydrogen bonding interactions [N(2)···O(3A) 2.919 Å] [19] to form a dimeric assembly in which the palladium centres are separated by a distance of 6.255 Å. Within each monomeric unit, **L2**$_{tripp}$ adopts a tridentate bonding mode and the acetate binds as a monodentate O-bound ligand. As with **1**–**3**, the phenolate and pyridyl units within the N,N,O ligand are not co-planar [tors. N(1)–C(13)–C(2)–C(1) 15.5(5)°] but are nevertheless closer to co-planarity than that found in the previously reported dimeric species [{2-(3-$C_{12}H_8$-2-O)-6-(CH_2-NH(Ar)C_5H_3N}Pd(OAc)] [Ar = 2,6-*i*-$Pr_2C_6H_3$ (28.9(9)°), 2,4,6-$Me_3C_6H_2$ (25.0(11)°)] [12]. Indeed, in these latter complexes it is the phenolate oxygen atom rather than the acetate oxygen that acts as the hydrogen bond acceptor. It is unclear as to the origin of this variation in intermolecular O···HN interaction but crystal packing effects may play a role. It is worthy of note, that numerous crystals of **4** have been subject to single crystal X-ray diffraction studies each revealing the structure described.

In the structure of **5**, which contains only one type of potential O-based hydrogen bond acceptor, dimerisation does indeed occur but in this case makes use of two intermolecular $N_{amine}H\cdots O_{phenolate}$ interactions [N(2)···O(1A) 3.008 Å] to link the monomeric units. Moreover, these (**L2**$_{tripp}$)PdCl units align in an anti-parallel fashion allowing two metal centres to approach to a distance of 3.2580(11) Å; a separation close to the sum of the van der Waals radii (3.26 Å) and similar to that found in the mesityl and 2,6-diisopropylphenyl analogues [12], but longer than that observed in dimeric [$Pd(OPh)_2$(pyrrolidine)$_2$] (Pd···Pd 3.0960(3) Å) in which four intermolecular NH···O interactions exist [20]. The structural features within the monomeric unit in **5** resemble that in **4** but it is evident that the increased twisting of the phenolate unit with respect to the adjacent pyridine [tors. N(1)–C(13)–C(2)–C(1) 15.5(5) (**4**), 27.6(6)° (**5**)] makes the phenolate oxygen atom more accessible to undergo the observed intermolecular $NH\cdots O_{phenolate}$ interaction.

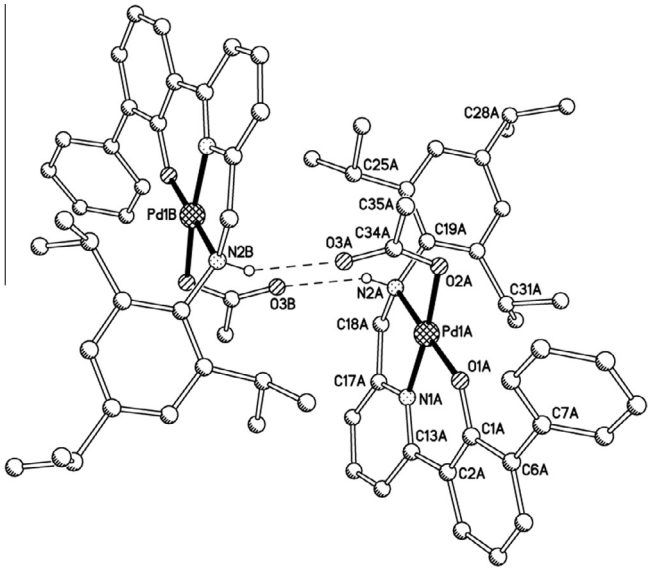


Fig. 5. Molecular structure of **4** including a partial atom numbering scheme. All hydrogen atoms, apart from H2, have been omitted for clarity.

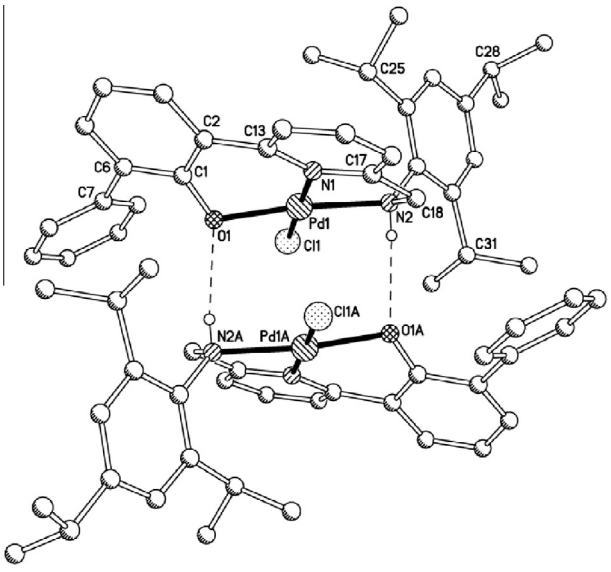


Fig. 6. Molecular structure of **5** including a partial atom numbering scheme. All hydrogen atoms, apart from H2, have been omitted for clarity.

Table 4
Selected bond distances (Å) and angles (°) for **4.**

Bond lengths	
Pd(1)–O(1)	1.951(2)
Pd(1)–O(2)	2.013(2)
Pd(1)–N(1)	1.970(3)
Pd(1)–N(2)	2.041(3)
C(18)–N(2)	1.492(4)
C(6)–C(7)	1.486(5)
C(34)–O(2)	1.276(4)
C(34)–O(3)	1.225(4)
Pd(1)···Pd(1A)	6.225
Bond angles	
N(1)–Pd(1)–N(2)	85.61(10)
N(1)–Pd(1)–O(1)	94.71(10)
N(2)–Pd(1)–O(2)	94.18(9)
O(1)–Pd(1)–O(2)	85.62(9)
N(1)–Pd(1)–O(2)	173.92(9)
N(2)–Pd(1)–O(2)	94.18(9)

The 'A' atoms denote the neighbouring palladium atom in the dimer.

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

Bond lengths	
Pd(1)–O(1)	1.985(3)
Pd(1)–Cl(1)	2.2962(14)
Pd(1)–N(1)	1.980(3)
Pd(1)–N(2)	2.068(3)
C(18)–N(2)	1.507(5)
C(6)–C(7)	1.479(6)
Pd(1)···Pd(1A)	3.2580(11)
Bond angles	
N(1)–Pd(1)–N(2)	84.72(13)
N(1)–Pd(1)–O(1)	91.03(12)
N(2)–Pd(1)–Cl(1)	93.53(9)
O(1)–Pd(1)–Cl(1)	91.00(8)
N(1)–Pd(1)–Cl(1)	177.28(10)
N(2)–Pd(1)–Cl(1)	93.52(9)

The 'A' atoms have been generated by symmetry: symmetry operation $-x+2$, $-y+1$, $-z$.

Like **1**–**3** the 3-phenyl groups in **4** and **5** are tilted with respect the phenolate unit [tors. C(1)–C(6)–C(7)–C(12) 44.0(4) (**4**), 48.8(6)° (**5**)].

3. Conclusions

Protonated forms of the tripp-substituted pincer-type ligand **L1** and its reduced derivative **L2**, have been successfully synthesised and provide a straightforward route to square planar palladium complexes in which the O,N,N-ligand's substituents sterically protect the metal-bound acetate or halide site. The presence of a secondary amine donor in $\mathbf{L2}_{tripp}$ has been shown to promote the self-assembly of highly soluble dimeric species through either intermolecular NH···$O_{phenolate}$ or, for the first time, NH···$O_{acetate}$ hydrogen bonding interactions. Work is in progress to potentially exploit the coordinated amine donor in **L2** as a directional hydrogen bond donor for a range of small organic acceptors.

4. Experimental

4.1. General

All operations, unless otherwise stated, were carried out under an inert atmosphere of dry, oxygen-free nitrogen using standard Schlenk and cannula techniques or in a nitrogen purged glove box. Solvents were distilled under nitrogen from appropriate drying agents [21] 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 methanol as the matrix while FAB mass spectra 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 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 reagent lithium aluminium hydride was purchased from Aldrich Chemical Co. and used without further purification. The compounds tetrakis(triphenylphosphine)palladium(0) [22], 2-(3-biphenyl-2-ol)-6-formylpyridine [12], 2,4,6-triisopropylaniline [23] and $(MeCN)_2PdCl_2$ [24] were prepared using literature procedures. All other chemicals were obtained commercially and used without further purification.

4.2. Synthesis of 2-(3-$C_{12}H_8$-2-OH)-6-(CH=N(2,4,6-i-$Pr_3C_6H_2$))C_5H_3N (H$\mathbf{L1}_{tripp}$)

To a round bottomed flask equipped with stir bar was added 2-(3-biphenyl-2-ol)-6-formylpyridine (1.207 g, 4.38 mmol), 2,4,6-triisopropylaniline (1.450 g, 6.62 mmol) and ethanol (15 ml). The suspension was stirred and heated to 40 °C and after 15 min a catalytic amount of formic acid was added. After further stirring at 40 °C overnight the solution was allowed to cool to room temperature and then left to stand overnight to form a yellow precipitate. The precipitate was filtered, washed with ethanol and further dried under reduced pressure to give H$\mathbf{L1}_{tripp}$ as a yellow solid (0.750 g, 42%). Mp: 114–117 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.16 (d, J_{HH} 6.8, 12H, CH(CH_3)$_2$), 1.28 (d, J_{HH} 6.9, 6H, CH(CH_3)$_2$), 2.80–2.99 (m, 3H, C*H*(CH$_3$)$_2$), 7.00 (s, 2H, Ar-*H*), 7.02 (t, J_{HH} 7.7, 1H, Ar-*H*), 7.32 (t, J_{HH} 7.4, 1H, Ar-*H*), 7.40 (dd, J_{HH} 7.4, 1.7, 1H, Ar-*H*), 7.42 (t, J_{HH} 7.3, 1H, Ar-*H*), 7.63 (d, J_{HH} 1.4, 2H, Ar-*H*), 7.85 (dd, J_{HH} 8.1, 1.4, 1H, Py-*H*), 8.00 (t, J_{HH} 8.1, 1H, Py-*H*), 8.09 (d, J_{HH} 7.6, 1H, Py-*H*), 8.19 (dd, J_{HH} 7.6, 0.9, 1H, Ar-*H*), 8.35 (s, 1H, N=C*H*), 14.2 (br s, 1H, OH). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 23.5 (CH(*C*H$_3$)$_2$), 24.2 (CH(*C*H$_3$)$_2$), 28.1 (*C*H(CH$_3$)$_2$), 34.1 (*C*H(CH$_3$)$_2$), 118.9, 119.2, 120.8, 121.0, 121.2, 126.0, 127.0, 128.1, 129.5 (CH), 131.3 (C), 133.0 (CH), 136.8, 138.4 (C), 138.6 (CH),144.9, 146.0, 151.1, 157.1, 158.2 (C), 161.0 (N=*C*–H). IR (cm^{-1}): 2957 (C–H), 2627 (br, OH), 1649 (C=N_{imine}), 1591 (C=$N_{pyridine}$). ESIMS: *m/z* 477 [M+H]$^+$. HRMS (TOFMS ES+): Calc. $C_{33}H_{37}N_2O$ [M+H]$^+$ 477.2906, found 477.2903.

4.3. Synthesis of 2-(3-$C_{12}H_8$-2-OH)-6-(CH_2-NH(2,4,6-i-$Pr_3C_6H_2$))C_5H_3N (H$\mathbf{L2}_{tripp}$)

Two Schlenk flasks equipped with stir bars were evacuated and backfilled with nitrogen. To one of the flasks was added lithium aluminium hydride (0.219 g, 5.77 mmol) and dry tetrahydrofuran (10 ml) and the resulting suspension stirred and cooled to 0 °C. To the second flask was added H$\mathbf{L1}_{tripp}$ (0.550 g, 1.15 mmol) and dry tetrahydrofuran (10 ml) and the contents stirred until dissolution. The solution of H$\mathbf{L1}_{tripp}$ 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 60 min. Water (1 ml) was carefully added followed by chloroform (30 ml) and more water (20 ml). The organic phase was separated and the aqueous layer extracted with chloroform (3 × 10 ml). All

organic extracts were combined and dried over magnesium sulfate. Filtration followed by removal of the solvent under reduced pressure gave a yellow brown oil which was then dissolved in a small amount of methanol. On standing at room temperature a cream precipitate formed which was filtered and dried affording H**L2**$_{tripp}$ as a white solid (0.349 g, 63%). Mp: 132–135 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.23 (d, J_{HH} 6.9, 12H, CH(CH_3)$_2$), 1.25 (d, J_{HH} 7.1, 6H, CH(CH_3)$_2$), 2.86 (sept, J_{HH} 7.1, 1H, CH(CH$_3$)$_2$), 3.29 (sept, J_{HH} 7.1, 2H, CH(CH$_3$)$_2$), 3.41 (br s, 1H, HNCH$_2$), 4.20 (s, 2H, HNCH_2), 6.96 (s, 2H, Ar-H), 6.99 (t, J_{HH} 7.8, 1H, Ar-H), 7.39–7.48 (m, 5H, Ar-H/Py-H), 7.66 (dd, J_{HH} 7.4, 0.8, 2H, Ar-H), 7.80–7.90 (m, 3H, Ar-H/Py-H), 14.8 (br s, 1H, OH). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 23.1 (CH(CH_3)$_2$), 23.3 (CH(CH_3)$_2$), 29.4 (CH(CH$_3$)$_2$), 33.0 (CH(CH$_3$)$_2$), 55.6 (HNCH$_2$), 116.9, 117.5 (CH), 118.0 (C), 118.8, 120.5, 125.9, 126.9, 128.5 (CH), 130.1 (C), 131.4, 137.4 (CH), 137.5, 138.8, 141.8, 143.5, 155.7, 156.3, 156.7 (C). IR (cm^{-1}): 2957 (C–H), 2601 (br, OH), 1595 (C=N$_{pyridine}$). ESIMS (+ve): m/z 501 [M+Na]$^+$. ESIMS (−ve): m/z 477 [M−H]$^-$. HRMS (TOFMS ES+): Calc. for $C_{33}H_{39}N_2O$ [M+H]$^+$ 479.3062, found 479.3055.

4.4. Synthesis of [(*L1*$_{tripp}$)Pd(OAc)] (*1*)

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), H**L1**$_{tripp}$ (0.137 g, 0.28 mmol) and dry 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 thoroughly washed with dichloromethane. All volatiles were removed from the filtrate under reduced pressure and the resultant solid dissolved in the minimum quantity of dichloromethane (*ca.* 1 ml) at which point hexane (*ca.* 8 ml) was added. The resulting precipitate was filtered and dried under reduced pressure forming **1** as a red powder (0.179 g, 96%). 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 (400 MHz, $CDCl_3$): δ 1.11 (d, J_{HH} 6.9, 6H, CH(CH_3)$_2$), 1.26 (d, J_{HH} 6.9, 6H, CH(CH_3)$_2$), 1.40 (d, J_{HH} 6.7, 6H, CH(CH_3)$_2$), 1.56 (s, 3H, O_2C-CH_3), 2.91 (sept, J_{HH} 6.7, 1H, CH(CH$_3$)$_2$), 3.40 (sept, J_{HH} 6.7, 2H, CH(CH$_3$)$_2$), 6.85 (t, J_{HH} 8.1, 1H, Ar-H), 7.05 (s, 2H, Ar-H), 7.19 (tt J_{HH} 7.3, 1H, Ar-H), 7.30 (t, J_{HH} 7.6, 2H, Ar-H), 7.45 (dd, J_{HH} 7.0, 1.6, 1H, Ar-H), 7.71 (dd, J_{HH} 7.2, 1.0, 1H, Ar-H), 7.75 (d, J_{HH} 1.3, 1H, Ar-H), 7.79 (d, J_{HH} 1.3, 1H, Py-H), 7.91 (dd, J_{HH} 8.7, 1.3, 1H, Py-H), 8.07 (s, 1H, N=C$_{imine}$-H), 8.18 (t, J_{HH} 8.4, 1H, Py-H), 8.55 (d, J_{HH} 8.4, 1H, Py-H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 22.1 (O_2C-CH$_3$), 22.9 (CH(CH_3)$_2$), 24.0 (CH(CH_3)$_2$), 25.4 (CH(CH_3)$_2$), 29.7 (CH(CH$_3$)$_2$), 34.4 (CH(CH$_3$)$_2$), 115.9 (CH), 120.3 (C), 121.3, 124.5, 126.5, 126.8, 127.5, 128.4, 130.1, 133.4 (CH), 134.5 (C), 137.4 (CH), 139.9, 141.0, 149.2, 152.2, 152.7, 161.5 (C), 166.0 (N$_{imine}$-=CH), 177.4 (O_2C-CH$_3$). IR (cm^{-1}): 2958 (C–H), 1619 (C=N$_{imine}$), 1589 (COO)$_{asymm}$/C=N$_{pyridine}$), 1380 (COO)$_{symm}$. FABMS: m/z 581 [M−OAc]$^+$. *Anal.* Calc. for ($C_{35}H_{38}N_2O_3Pd$): C, 65.57; H, 5.97; N, 4.37. Found: C, 65.24; H, 6.01; N, 4.18%.

4.5. Synthesis of [(*L1*$_{tripp}$)PdCl] (*2*)

A Schlenk flask equipped with stir bar was evacuated and backfilled with nitrogen and loaded with $(MeCN)_2PdCl_2$ (0.062 g, 0.23 mmol), H**L1**$_{tripp}$ (0.126 g, 0.254 mmol) and tetrahydrofuran (25 ml). After stirring overnight at room temperature, the solution was concentrated to *ca.* 2 ml and hexane (15 ml) added. The resultant precipitate was filtered, washed with hexane and dried under reduced pressure to give **2** as a red solid (0.124 g, 88%). Orange/red plates of **2**·CH_2Cl_2 suitable for an X-ray diffraction study could be grown by slow diffusion of hexane into a dichloromethane solution of the complex. Alternatively, red needles of **2**·C_6H_6 could be grown by prolonged standing in benzene at room temperature. Mp: >260 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05 (d, J_{HH} 6.9, 6H, CH(CH_3)$_2$), 1.19 (d, J_{HH} 6.9, 6H, CH(CH_3)$_2$), 1.33 (d, J_{HH} 6.7, 6H, CH(CH_3)$_2$), 2.83 (sept, J_{HH} 7.0, 1H, CH(CH$_3$)$_2$), 3.20 (sept, J_{HH} 7.0, 2H, CH(CH$_3$)$_2$), 6.81 (dd, J_{HH} 8.4, 7.2, 1H, Ar-H), 6.95 (s, 2H, Ar-H), 7.14 (dd, J_{HH} 7.4, 1.2, 1H, Ar-H), 7.28 (t, J_{HH} 7.4, 2H, Ar-H), 7.45 (dd, J_{HH} 7.2, 1.6, 1H, Ar-H), 7.67 (dd, J_{HH} 7.2, 1.0, 1H, Ar-H), 7.79 (d, J_{HH} 1.4, 1H, Ar-H), 7.81 (d, J_{HH} 1.4, 1H, Ar-H), 7.82 (d, J_{HH} 7.6, 1H, Py-H), 7.97 (s, 1H, N=C-H), 8.12 (dd, J_{HH} 8.7, 7.3, 1H, Py-H), 8.47 (d, J_{HH} 8.4, 1H, Py-H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 22.2 (CH(CH_3)$_2$), 22.9 (CH(CH_3)$_2$), 23.5 (CH(CH_3)$_2$), 27.7 (CH(CH$_3$)$_2$), 33.2 (CH(CH$_3$)$_2$), 115.3 (CH), 119.3 (C), 120.3, 123.7, 125.6, 126.1, 126.6, 127.4, 129.2, 132.9 (CH), 133.5 (C), 136.7 (CH), 138.4, 139.3, 140.6, 147.8, 151.1, 151.5, 160.1 (C), 166.5 (N=CH). IR (cm^{-1}): 2958 (C–H), 1619 (C=N$_{imine}$), 1596 (C=N$_{pyridine}$). FABMS: m/z 616 [M]$^+$, 581 [M−Cl]$^+$. *Anal.* Calc. for ($C_{33}H_{35}N_2OPdCl$): C, 64.18; H, 5.71; N, 4.54. Found: C, 64.01; H, 5.72; N, 4.32%.

4.6. Conversion of *1* to [(*L1*$_{tripp}$)PdX] (*2* X = Cl, *3* X = I)

(a) **2** (X = Cl). A round bottomed flask equipped with stirrer bar, and open to the air, was loaded with **1** (0.048 g, 0.07 mmol), chloroform (5 ml) and a saturated solution of brine (25 ml) added. After stirring vigorously at room temperature overnight the red solution was extracted 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 a red solid (0.046 g, 99%). The spectroscopic data were consistent with that given above.

(b) **3** (X = I). A round bottomed flask equipped with stirrer bar was loaded with **1** (0.103 g, 0.16 mmol), chloroform (5 ml) and a saturated solution of sodium iodide (25 ml) added. After stirring vigorously at room temperature overnight the red solution was extracted 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 **3** as a red solid (0.111 g, 97%). Orange/red plates of **3** 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 1.09 (d, J_{HH} 6.9, 6H, CH(CH_3)$_2$), 1.27 (d, J_{HH} 6.9, 6H, CH(CH_3)$_2$), 1.40 (d, J_{HH} 6.8, 6H, CH(CH_3)$_2$), 2.92 (sept, J_{HH} 7.0, 1H, CH(CH$_3$)$_2$), 3.20 (sept, J_{HH} 7.0, 2H, CH(CH$_3$)$_2$), 6.89 (dd, J_{HH} 8.4, 7.2, 1H, Ar-H), 7.02 (s, 2H, Ar-H), 7.24 (dd, J_{HH} 7.4, 1.8, 1H, Ar-H), 7.37 (t, J_{HH} 7.7, 2H, Ar-H), 7.48 (dd, J_{HH} 7.1, 1.7, 1H, Ar-H), 7.72 (dd, J_{HH} 7.2, 1.0, 1H, Ar-H), 7.82 (d, J_{HH} 1.4, 1H, Ar-H), 7.84 (d, J_{HH} 1.3, 1H, Ar-H), 7.92 (d, J_{HH} 8.7, 1H, Py-H), 8.05 (s, 1H, N=C-H), 8.24 (dd, J_{HH} 8.7, 7.2, 1H, Py-H), 8.61 (d, J_{HH} 8.2, 1H, Py-H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 21.5 (CH(CH_3)$_2$), 23.0 (CH(CH_3)$_2$), 23.9 (CH(CH_3)$_2$), 28.7 (CH(CH$_3$)$_2$), 33.1 (CH(CH$_3$)$_2$), 115.4, 118.8, 120.8, 123.3, 125.6, 126.3, 126.5, 127.6, 129.4, 132.8 (CH), 134.0 (C), 137.1 (CH), 138.3, 138.7, 143.7, 147.9, 150.6, 150.9, 159.6 (C), 167.1 (N=CH). IR (cm^{-1}): 2961 (C–H), 1611 (C=N$_{imine}$), 1589 (C=N$_{pyridine}$). FABMS: m/z 709 [M]$^+$, 581 [M−I]$^+$. *Anal.* Calc. for ($C_{33}H_{35}N_2OPdI$): C, 55.91; H, 4.98; N, 3.95. Found: C, 56.01; H, 4.77; N, 4.21%.

4.7. Reaction of H*L2*$_{tripp}$ with $Pd(OAc)_2$

A Schlenk flask equipped with stir bar was evacuated and backfilled with nitrogen and loaded with $Pd(OAc)_2$ (0.066 g, 0.29 mmol), H**L2**$_{tripp}$ (0.136 g, 0.28 mmol) and dry toluene (10 ml). After stirring at 0 °C (cryostatically controlled) overnight, the reaction mixture was concentrated to *ca.* 1 ml at which point hexane (*ca.* 8 ml) was added. The resulting precipitate was filtered and dried under reduced pressure forming **4** as a yellow powder (0.108 g, 46%). Yellow plates suitable for an X-ray diffraction study could be grown by slow diffusion of hexane into a dichlorometh-

ane solution of the complex. Mp: >260 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.20 (d, J_{HH} 6.8, 3H, CH(CH_3)$_2$), 1.21 (d, J_{HH} 7.0, 3H, CH(CH_3)$_2$), 1.22 (d, J_{HH} 6.9, 6H, CH(CH_3)$_2$), 1.38 (d, J_{HH} 6.5, 3H, CH(CH_3)$_2$), 1.59 (s, 3H, O_2CCH_3), 1.70 (d, J_{HH} 6.6, 3H, CH(CH_3)$_2$), 2.85 (sept, J_{HH} 6.7, 1H, CH(CH$_3$)$_2$), 3.23 (sept, J_{HH} 6.7, 1H, CH(CH$_3$)$_2$), 4.29 (dd, J_{HH} 17.1, 8.3, 1H, HN-CH_aH_b), 4.54 (dd, J_{HH} 17.0, 6.9, 1H, HN-CH_aH_b), 5.33 (sept, J_{HH} 6.7, 1H, CH(CH$_3$)$_2$), 6.77 (dd, J_{HH} 8.2, 7.3, 1H, Ar-*H*), 6.91 (d, J_{HH} 2.1, 1H, Ar-*H*), 6.94 (d, J_{HH} 7.5, 1H, Py-*H*), 7.07 (d, J_{HH} 2.0, 1H, Ar-H), 7.19 (tt, J_{HH} 7.3, 2.0, 1H, Ar-H), 7.29 (t, J_{HH} 7.6, 2H, Ar-H), 7.33 (dd, J_{HH} 7.2, 1.7, 1H, Ar-H), 7.54 (dd, J_{HH} 8.5, 1.6,1H, Ar-H), 7.58 (br t, J_{HH} 7.5, 1H, *H*N-CH_aH_b), 7.73 (dd, J_{HH} 8.0, 1.4, 2H, Py-H), 7.80 (dd, J_{HH} 8.4,7.4, 1H, Py-H), 7.89 (d, J_{HH} 8.4, 1H, Py-H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 21.4 (H_3C–CO_2), 22.4 (CH(CH_3)$_2$), 22.8 (CH(CH_3)$_2$), 23.7 (CH(CH_3)$_2$), 23.9 (CH(CH_3)$_2$), 25.1 (CH(CH_3)$_2$), 27.2 (CH(CH$_3$)$_2$), 27.8 (CH(CH$_3$)$_2$), 33.0 (CH(CH$_3$)$_2$), 62.4 (HN-CH_2), 114.3, 114.9, 120.0, 122.7, 122.9, 125.2, 126.4, 128.0, 128.8, 132.1 (CH), 132.7, 134.9 (C), 137.1 (CH), 139.1, 140.0, 141.9, 146.9, 153.4, 159.3, 161.5 (C), 177.8 (H_3C–CO_2). IR (cm^{-1}): 3224 (NH), 2954 (C–H), 1585 (COO_{asymm}/C=$N_{pyridine}$), 1384 (COO_{symm}). ESIMS (MeOH): *m/z* 1196 [M_2−2OAc+MeOH], 583 [M−OAc]. FABMS: *m/z* 643 [M+H]$^+$, 583 [M−OAc]$^+$. *Anal.* Calc. for ($C_{35}H_{40}N_2O_3Pd$): C, 65.38; H, 6.23; N, 4.36. Found: C, 65.13; H, 6.18; N, 4.42%.

4.8. Conversion of **4** to [(**L2**$_{tripp}$)PdCl] (**5**)

A round bottomed flask equipped with stirrer bar, and open to the air, was loaded with **4** (0.045 g, 0.07 mmol), chloroform (5 ml) and a saturated solution of brine (25 ml) added. After stirring vigorously at room temperature overnight the yellow solution was extracted 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 **5** as a yellowy brown solid (0.043 g, 99%). 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 0.72 (d, J_{HH} 6.8, 3H, CH(CH_3)$_2$), 1.01 (br s, 3H, CH(CH_3)$_2$), 1.11 (d, J_{HH} 6.8, 6H, CH(CH_3)$_2$), 1.22 (br s, 3H, CH(CH_3)$_2$), 1.46 (d, J_{HH} 6.4, 3H, CH(CH_3)$_2$), 2.71 (sept, J_{HH} 6.5, 1H, CH(CH$_3$)$_2$), 3.33 (dd, J_{HH} 17.8, 1.9, 1H, HN-CH_aH_b), 3.73 (br s, 1H, CH(CH$_3$)$_2$), 4.23 (sept, J_{HH} 6.5, 1H, CH(CH$_3$)$_2$), 5.00 (dd, J_{HH} 17.7, 9.0, 1H, HN-CH_aH_b), 5.91 (br s, 1H, *H*N-CH_2), 6.54 (t, J_{HH} 7.5, 1H, Ar-H), 6.82 (s, 1H, Ar-H), 6.87 (s, 1H, Ar-H), 7.08 (app t, J_{HH} 7.3, 2H, Ar-H), 7.16 (d, J_{HH} 6.9, 1H, Ar-H), 7.24 (app t, J_{HH} 7.4, 3H, Ar-H), 7.35 (br s, 2H, Py-H), 7.87 (d, J_{HH} 8.3, 2H, Ar-H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 22.2 (CH(CH_3)$_2$), 22.6 (CH(CH_3)$_2$), 22.9 (CH(CH_3)$_2$), 23.7 (CH(CH_3)$_2$), 24.5 (CH(CH_3)$_2$), 27.0 (CH(CH$_3$)$_2$), 27.2 (CH(CH$_3$)$_2$), 32.9 (CH(CH$_3$)$_2$), 64.2 (HN-CH_2), 114.3, 114.7 (CH), 117.5 (C), 120.7, 122.4, 125.0, 126.3, 127.7, 129.5, 130.5, 135.9 (CH), 138.7, 138.8, 140.3, 140.5, 145.9, 146.4, 151.5, 164.3 (C). IR (cm^{-1}): 3183 (NH), 2955 (CH), 1596 (C=$N_{pyridine}$). ESIMS (MeOH): *m/z* 1196 [M_2−2Cl+MeOH], 583 [M−Cl]. FABMS: *m/z* 1202 [M_2−Cl]$^+$, 618 [M]$^+$, 583 [M−Cl]$^+$. *Anal.* Calc. for ($C_{33}H_{37}N_2$OPdCl): C, 63.98; H, 6.02; N, 4.52. Found: C, 64.12; H, 5.77; N, 4.41%.

4.9. Crystallographic studies

Data for **1**, **2**·CH_2Cl_2, **2**·C_6H_6, **3**, **4** and **5** 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 [25] Hydrogen atoms were included in calculated positions (C–H = 0.95–1.00 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

Table 6
Crystallographic and data processing parameters for **1**, **2**·CH_2Cl_2, **2**·C_6H_6, **3**, **4** and **5**.

Complex	1	**2**·CH_2Cl_2	**2**·C_6H_6	**3**	**4**	**5**
Formula	$C_{71}H_{78}Cl_2N_2O_6Pd_2$	$C_{33}H_{35}ClN_2OPd\cdot CH_2Cl_2$	$C_{33}H_{35}ClN_4O_6Pd\cdot 2C_6H_6$	$C_{106}H_{123}Cl_2I_3N_6O_4Pd_3$	$C_{35}H_{40}N_2O_3Pd$	$C_{34}H_{39}Cl_3N_2OPd$
M	1367.07	702.41	773.70	2315.90	643.09	704.42
Crystal size (mm^3)	0.39 × 0.30 × 0.05	0.43 × 0.16 × 0.06	0.32 × 0.12 × 0.06	0.20 × 0.13 × 0.07	0.46 × 0.15 × 0.08	0.41 × 0.12 × 0.03
Temperature (K)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
Crystal system	triclinic	monoclinic	monoclinic	triclinic	orthorhombic	monoclinic
Space group	$P\bar{1}$	*P*2(1)/*c*	*P*2(1)/*c*	$P\bar{1}$	Pbca	*P*2(1)/*c*
a (Å)	12.354(9)	24.959(5)	33.260(10)	14.135(3)	16.473(12)	11.897(4)
b (Å)	14.641(11)	9.2993(19)	21.331(6)	20.227(5)	13.926(11)	10.402(4)
c (Å)	18.486(13)	14.127(3)	22.821(7)	20.772(6)	26.98(2)	29.135(8)
α (o)	75.561(14)	90	90	60.961(4)	90	90
β (o)	89.887(14)	99.082(4)	124.524(6)	84.879(6)	90	113.491(11)
γ (o)	86.015(15)	90	90	71.216(4)	90	90
U (Å^3)	3230(4)	3237.8(11)	13340(7)	4900(2)	6189(8)	3306.7(19)
Z	2	4	16	2	8	4
D_{calc} (Mg m^{-3})	1.406	1.441	1.541	1.570	1.380	1.415
F(000)	1412	1440	6432	2328	2672	1448
μ (Mo Kα) (mm^{-1})	0.694	0.850	0.678	1.599	0.636	0.832
Reflections collected	27423	24529	51534	38282	45864	25179
Independent reflections	13852	6361	13086	18976	6089	6494
R_{int}	0.2089	0.0744	0.2631	0.2088	0.0918	0.10971
Restraints/parameters	0/780	0/376	0/695	0/1045	0/377	0/376
Final *R* indices ($I > 2\sigma(I)$)	R_1 = 0.1262	R_1 = 0.0468	R_1 = 0.0880	R_1 = 0.0758	R_1 = 0.0410	R_1 = 0.0515
	wR_2 = 0.2656	wR_2 = 0.1170	wR_2 = 0.1898	wR_2 = 0.1447	wR_2 = 0.0871	wR_2 = 0.0829
All data	R_1 = 0.2128	R_1 = 0.0597	R_1 = 0.2300	R_1 = 0.1621	R_1 = 0.0597	R_1 = 0.0904
	wR_2 = 0.3016	wR_2 = 0.1228	wR_2 = 0.2243	wR_2 = 0.1670	wR_2 = 0.0935	wR_2 = 0.0921
Goodness-of-fit (GOF) on F^2 (all data)	1.006	1.037	0.806	0.824	0.999	0.923

Data in common: graphite-monochromated Mo Kα radiation, λ = 0.71073 Å; $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w^{-1} = [\sigma^2(F_o)^2 + (aP)^2]$, $P = [\max(F_o^2,0) + 2(F_c^2)]/3$, 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.

parameters. Disordered solvent was omitted using the SQUEEZE option in PLATON for **3** and the benzene solvate of **2** [26].

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Appendix A. Supplementary data

CCDC 932354–932359–contain the supplementary crystallographic data for **1**, **2**·CH_2Cl_2, **2**·C_6H_6, **3**, **4** and **5**. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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