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Cyclometallated imine complexes with oxygen-functionalised side-chains: Effect of the nature of the functional group, chain length and charge on coordination of the oxygen

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Abstract

Imines **1a–e** derived from benzaldehyde or 3,4-dimethoxy benzaldehyde and ether- or alcohol-functionalised amines H_2NR ($R = C_2H_4OMe$, C_3H_6OMe, C_2H_4OH, C_3H_6OH,) all undergo cyclometallation with $[Pd(OAc)_2]_3$ (in some cases the dimeric products **2** were isolated) and subsequently react with lithium chloride to give chloride complexes, which are dimeric **3a–c**, or monomeric for the C_3H_6OH-functionalised complexes **4d,e** which have a C,N,O tridentate imine. The chloride complexes subsequently react with triphenylphosphine, and in some cases pyridine, to give mononuclear complexes **5** and **6**, respectively with bidentate C,N imines. Treatment of **5** with silver salts leads to cations, the length of the tether (C2 or C3) and nature of the donor (ether or alcohol) and the counterion all effect whether or not the oxygen is coordinated.

Keywords: Cyclometallated; Hemilabile; Imines; Palladium

1. Introduction

Cyclometallated complexes of palladium are well-known and have been applied in several different areas [1,2]. The vast majority of cyclometallated complexes involve ligands which are only bidentate, complexes with tri- or tetradentate cyclometallated ligands are much rarer [3]. In addition, the majority of tridentate cyclometallated complexes are symmetrical pincer ligands with the carbon as the central atom, PCP and NCN ligands being particularly common [2,4]. Unsymmetrical C,N-bidentate cyclometallated ligands with pendant donor atoms can in principle act as tridentate ligands, examples with C,N,N [5–7], C,N,S [8,9], and C,N,O [10–15] ligands have all been reported, some specific examples are shown in Fig. 1 [6,8,10].

It is notable that in the case of a C_2H_4 tether the thioether and amine-functionalised arms will coordinate to form neutral tridentate complexes however with the oxygen-functionalised ligands coordination of the oxygen usually only occurs in cationic complexes unless the ligand can be deprotonated to give a C,N,O^{2-} ligand. As regards C,N cyclopalladated complexes with pendant O-donor ligands there are examples of alcohol [10,13,14], ether [12], amide [15] and hydrazone and related groups [16] but so far there has been little systematic attempt to evaluate the effect of length of the tether and nature of the functional group on coordination of the oxygen functionality. The aim of this work is to assess what factors control coordination of an ether or alcohol ligand tethered to a C,N-chelate and to establish whether this interaction can be hemilabile [17].

2. Results and discussion

2.1. Synthesis of neutral cyclometallated complexes (Scheme 1)

The imines **1a–e** were synthesised by stirring equimolar amounts of an amine and the appropriately substituted

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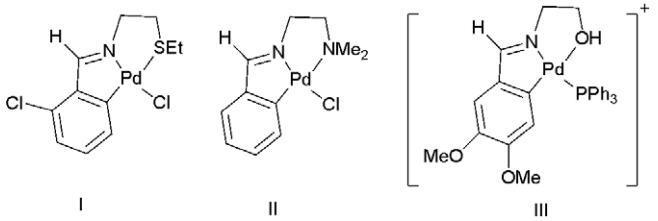


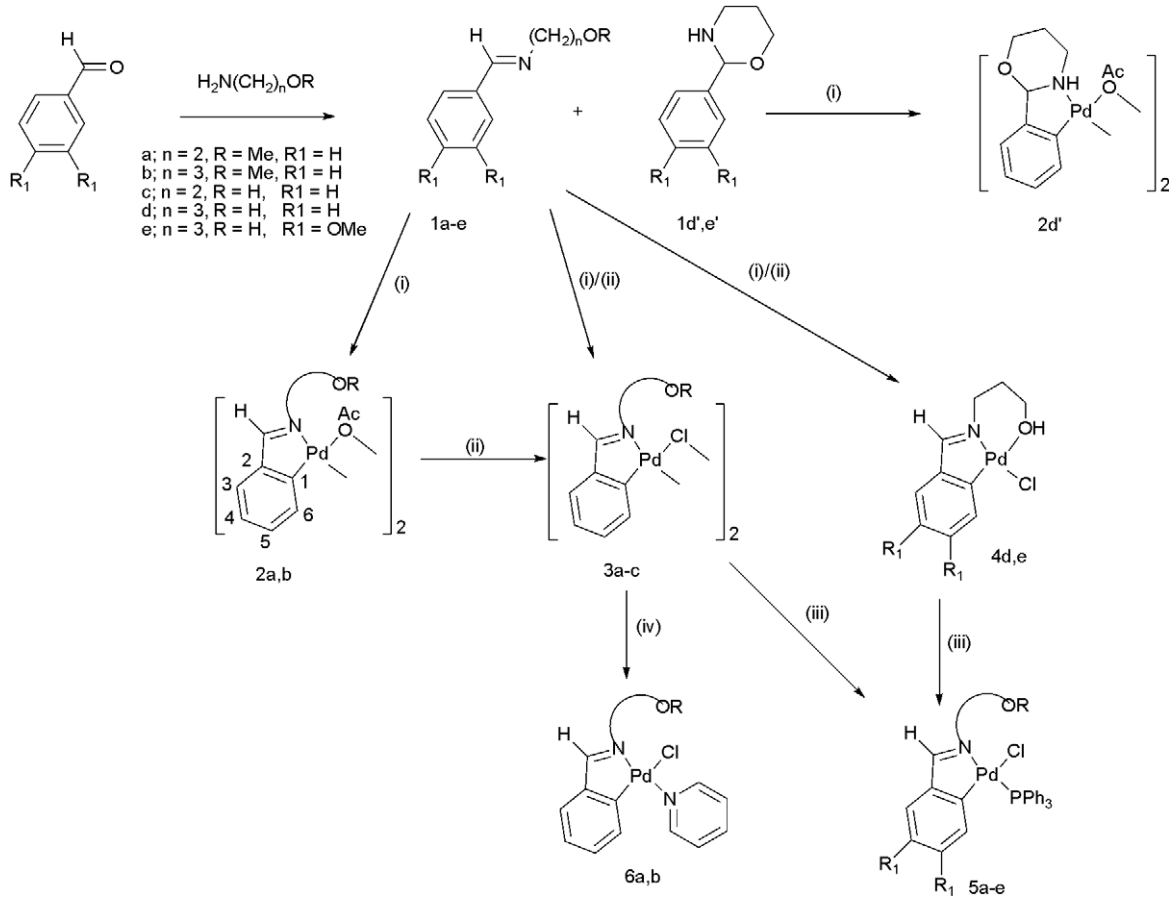
Fig. 1. Examples of tridentate (C,N,X) (X = S, N, O) cyclopalladated complexes.

benzaldehyde at room temperature in dichloromethane or ethanol as described by Navarro et al. [10]. For **1c–e** which have an OH group, anhydrous $MgSO_4$ was added to remove the water produced. In all cases ^1H and ^{13}C–$\{^1H\}$ NMR spectroscopy proved that the imines were pure, with the exception of **1d** and **e** (see below). The ^1H NMR spectra of the imines showed a characteristic singlet at δ 8.10–8.70 due to the imine proton. Imines **1a,b**, and **e** containing OMe groups, also gave rise to singlets in the range δ 3.26–4.00; the OH group gave a broad peak at 3.92 for (**c**) but was not observed in **1d** or **e**. The imine carbon was observed at δ 161–164 in the ^{13}C–$\{^1H\}$ NMR spectra and the IR spectra showed the υ(C=N) at 1644–1648 cm^{-1}.

The ^1H NMR spectra of **1d** and **e** each showed the presence of two species in a ratio 2:1 for **d** and 6:1 for **e**. In each case, the major species showed a signal characteristic of the imine proton, at δ 8.20 for **1d** and δ 8.16 for **1e**, however, this signal was absent from the minor isomer. The presence of isomers was also detected in the ^{13}C–$\{^1H\}$ NMR spectra. For **1d**, which is an oil, the mixture could not be separated by crystallisation. Hence the mixture was used in reaction with $[Pd(OAc)_2]_3$ subsequent identification of some of the products by X-ray diffraction (see below) has allowed us to identify the mixture as being composed of the expected imine **1d** as the major component and its aminal isomer **1d′** as the minor component. With this information it has been possible to assign peaks for both isomers (see Section 3).

Ligand **1e** is a solid and crystallisation gave a crystal that was suitable for X-ray crystallography. The structure, shown in Fig. 2, shows that the crystal is the imine isomer which was proved by ^1H NMR spectroscopy to be the major isomer in the mixture.

The synthesis of neutral cyclopalladated complexes is shown in Scheme 1 and the NMR labelling scheme is illustrated for complexes **2a,b**. The imines **1a,b** were easily cyclopalladated by reaction with $[Pd(OAc)_2]_3$ at room temperature for 2 h in methanol. These mild conditions contrast to previous work which reported refluxing for a similar period of time [10]. We have recently carried out DFT calculations on acetate-assisted cyclometallation with



Scheme 1. (i) $[Pd(OAc)_2]_3$ in MeOH, (ii) LiCl, (iii) PPh_3 (CH_2Cl_2), (iv) pyridine (CH_2Cl_2).

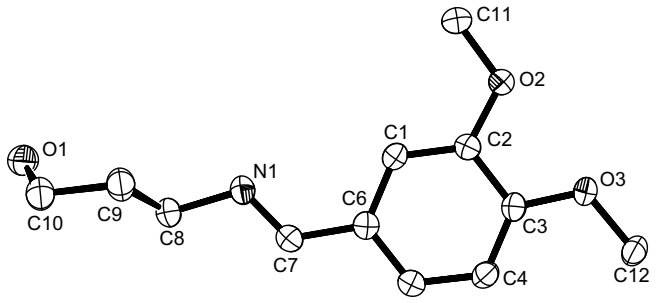


Fig. 2. Ortep diagram showing atom numbering scheme for **1e** with 50% displacement ellipsoids. H atoms have been omitted for clarity.

palladium [18] and iridium [19] and shown that intramolecular hydrogen bonding to the acetate plays a key role in providing a low energy pathway to cyclometallation.

The cyclopalladated acetate complexes **2a**,**b** were isolated and fully characterised. The ^{1}H NMR spectrum of **2a** showed singlets at ca. δ 3.30 and 7.29 due to the methoxy group and imine proton respectively, the latter is shifted upfield 0.9 ppm compared with the free ligand consistent with the imine being the *E*-isomer as expected for cyclometallation to occur. The two acetate groups were observed as a 6H singlet at δ 2.13 and the C_2H_4 tether gave rise to four multiplets between δ 2.7 and 3.7, the aromatic protons were not well resolved giving a broad multiplet at about δ 7.1. The ^{13}C–{^{1}H} NMR spectrum of **2a** showed four CH carbons and two quaternary carbons in the aromatic region which confirmed that cyclometallation had occurred, other peaks were as expected with the OMe at ca. δ 59 ppm and the imine carbon at δ 173.8. and two signals for acetate at δ 24.67 and 181.36. The equivalence of the acetate groups means either that the complex is an *anti*-isomer rather than *syn* or that the isomers are exchanging fast on the NMR timescale. Fast exchange, at room temperature, of *syn* and *anti* isomers of a cyclometallated oxazoline has been reported by Balavoine et al. [20] though for other cyclometallated complexes exchange was slow on the NMR timescale and both isomers were observed [13,21].

The IR spectrum of **2a** showed a strong absorption at 1610 cm^{-1} due to the C=N stretch which is at lower energy than the free ligand (1646 cm^{-1}), consistent with coordination of nitrogen to the metal. Strong absorption bands at 1565 and 1413 cm^{-1} confirmed the presence of bridging acetates as found in related complexes [22]. FAB mass spectrometry also confirmed that **2a** is a dimer, ions being observed at *m*/*z* 655 due to $[M-H]^+$ and at *m*/*z* 597 $[M-(OAc)]^+$.

The acetate bridged dimer **2a** was easily converted into the chloride bridged dimer **3a** by stirring with LiCl. Complex **3a** showed similar spectroscopic features to **2a** however the planar nature of **3a**, means that the C_2H_4 tether should give rise to only two signals rather than four, in fact the two signals were coincident. The IR spectrum showed a strong absorption at 1613 cm^{-1} due to the C=N stretch (cf. 1610 cm^{-1} in **2a**). FAB mass spectrometry showed a molecular ion at *m*/*z* 608 and a fragment ion at *m*/*z* 573 $[Pd_2L_2Cl]^+$. The electrospray mass spectrum in MeCN showed a large peak at *m*/*z* 309 due to [Pd(L)(NCMe)] consistent with easy cleavage of the dimer by donor ligands.

The ^{1}H NMR spectrum of **2b** showed similar features to **2a**, with singlets at δ 3.24 and 7.19 due to the OMe group and imine proton respectively, a singlet due to the OAc at δ 2.13 and the C_3H_6 linker giving rise to multiplets at δ 3.25, 2.75 and 1.91. The presence of four signals due to CH carbons and two signals for quaternary carbons in the aromatic region in the ^{13}C–{^{1}H} NMR spectrum clearly demonstrated that cyclometallation had occurred. The IR spectrum showed υ(C=N) at ca. 1610 cm^{-1} and bands due to bridging acetate at 1570 and 1410 cm^{-1}. FAB mass spectrometry showed a molecular ion at *m*/*z* 684 and fragment ions at *m*/*z* 601 $[Pd_2L_2Cl]^+$. As for **2a**, **2b** was easily converted into the chloride bridged dimer **3b** by stirring with LiCl. Complex **3b** showed similar spectroscopic features to **2b** and was additionally characterised by X-ray crystallography (see below).

The structure of **3b** is shown in Fig. 3 with selected bond distances and angles. The palladium atom adopts a distorted square-planar geometry with the distortion most noticeable in the cyclometallated chelate angle C(1)–Pd(1)–N(1) of 81.27°, the sum of angles about the palladium atom is 360°. The Pd–Cl bond *trans* to C is about 0.13 Å longer than that *trans* to nitrogen in accordance with the relative *trans* influences of C and N [23]. The bond lengths are similar to those reported previously for chloride-bridged dimer complexes, e.g the Pd–C and Pd–N bond distances in $[Pd\{C_6H_4C(H)=NPh\}(\mu\text{-}Cl)]_2$ are 1.965(2) Å and 2.022(1) Å, respectively [24] compared with 1.979(4) and 2.028(3) Å in **3b**. There is no evidence for any interaction of the OMe group with the metal.

The hydroxy-functionalised imines **1c**–**e** were cyclopalladated in a similar manner to **1a**,**b**. Thus, **1c** was reacted

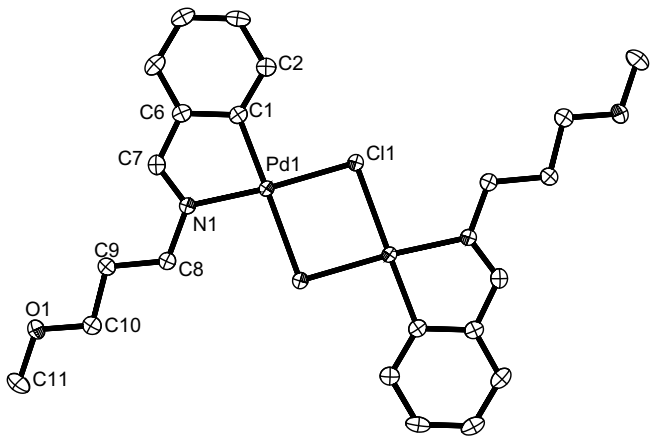


Fig. 3. Ortep diagram showing atom numbering scheme for **3b** with 50% displacement ellipsoids. H atoms have been omitted for clarity. Selected bond distances (Å) and bond angles (°): Pd(1)–C(1) 1.979(4), Pd(1)–N(1) 2.028(3), Pd(1)–Cl(1) 2.3237(9), Pd(1)–Cl(1′) 2.4549(9); N(1)–Pd(1)–C(1) 81.27(13).

with $[Pd(OAc)_2]_3$ followed by LiCl leading to formation of **3c**. The corresponding complex made using the imine derived from 3,4-dimethoxybenzaldehyde has been reported by Navarro et al. [10]. Complex **3c** is insoluble in chlorinated solvents, so the ^{1}H NMR spectrum was recorded in d^6-DMSO however even then some peaks were broad. The ^{1}H NMR spectrum showed four inequivalent protons in the aromatic region as expected for the ortho-metallated product. The imine proton was observed at δ 7.90, approximately 0.3 ppm upfield from the free ligand, with the OH proton at δ 4.55, close to that (δ 4.77) observed by Navarro et al. [10] in which the OH group is not coordinated. The υ(C=N) stretch was observed at 1613 cm^{-1}, about 30 cm^{-1} less than the free ligand, as expected for coordination of the imine. The FAB mass spectrum of **3c** showed a cluster of ions with a maximum at m/z 545 corresponding to $[Pd_2L_2Cl]^+$ and fragment ions at m/z 254 due to $[PdL]^+$. The elemental analysis was also consistent with the formulation.

As mentioned previously, imine **1d** exists as a mixture with the aminal isomer **1d′**. This mixture was reacted with $[Pd(OAc)_2]_3$ to give a green crystalline precipitate, which was insoluble in chlorinated solvents, and we failed to obtain an ^{1}H NMR spectrum even in d^6-DMSO. FAB mass spectrometry showed ions at m/z 596 corresponding to the dimeric species $[Pd_2L_2(OAc)]^+$ and another cluster at 268 corresponding to the monomeric fragment $[PdL]^+$. The IR spectrum of the product showed bands at 1563 and 1413 cm^{-1}, suggesting a bridging acetate, and bands at 1605 cm^{-1}and 3396 cm^{-1} assigned to (C=N) and (OH) respectively, suggesting the presence of the imine isomer **2d**. However, the precise identity of the compound(s) formed cannot be ascertained from this data. Fortunately, a few crystals were obtained which were suitable for X-ray diffraction. The X-ray structure is shown in Fig. 4 with selected bond distances and angles. The structure shows an acetate-bridged dimer **2d′**, containing a cyclometallated aminal. The complex adopts the *anti* geometry, and the coordination geometry around each palladium atom is approximately square-planar. The Pd(1)–C(1) and Pd(1)–N(1) bond distances [1.952(5) and 2.047(4) Å] are similar to the values [1.96(2) and 2.022(12) Å] in [Pd(μ-OAc)-(C_6H_4-^{i}Pr-oxaz)]$_2$ [25]. The *trans* influence of the σ-bonded carbon is illustrated by the lengthening of the Pd–O bond *trans* to carbon [2.143(3) and 2.130(3) Å] relative to those *trans* to nitrogen atoms [2.049(3) and 2.053(3) Å]. The long distance between both palladium atoms [3.123(3) Å] confirms that these is no interaction between them.

To try and gain further information, the mixture of isomers **1d**,**d′** was reacted with $[Pd(OAc)_2]_3$ in MeOH, then after stirring for 2 h, LiCl was added. The solution was concentrated and hexane was added to give a green crystalline precipitate. Again this precipitate was very insoluble and we failed to get NMR data. The FAB mass spectrum only showed ions at m/z 268 $[Pd(L)]^+$, with no dimeric species. The IR spectrum showed a band at 1585 cm^{-1} assigned to coordinated C=N, and a band at 3118 cm^{-1} possibly due to a coordinated O–H. Fortunately, a crystal was suitable for X-ray diffraction, and the structure showed that the crystal was derived from the imine isomer with the oxygen coordinated to palladium to form a mononuclear (C,N,O) tridentate complex **4d**. The structure is shown in Fig. 5 with selected bond distances and angles. Hence, for the imine isomer the coordination of the oxygen tether occurred to form **4d** rather than dimerisation through chloride bridges to form **3d**. The fate of the minor aminal isomer in this reaction is not known.

In an attempt to form more soluble complexes the dimethoxy-substituted ligand **1e**,**e′** was reacted with $[Pd(OAc)_2]_3$ followed by LiCl. In this case the precipitate formed was

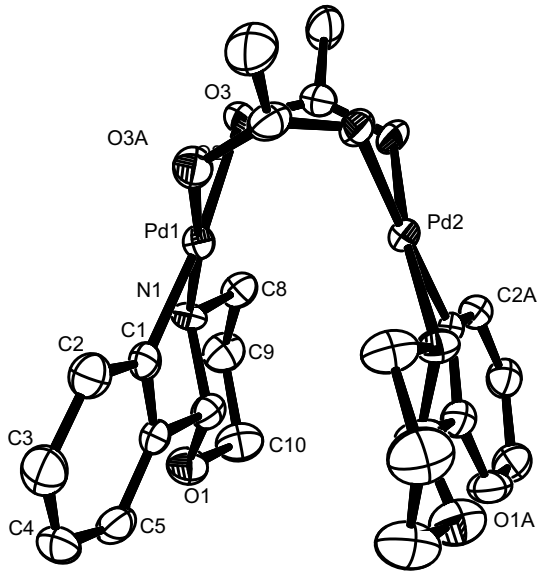


Fig. 4. Ortep diagram showing atom numbering scheme for **2d′** with 50% displacement ellipsoids. H atoms have been omitted for clarity. Selected bond distances (Å) and bond angles (°): Pd(1)–C(1) 1.952(5), Pd(1)–N(1) 2.047(4), Pd(1)–O(3) 2.143(3), Pd(1)–O(3A) 2.049(3); N(1)–Pd(1)–C(1) 80.78(17).

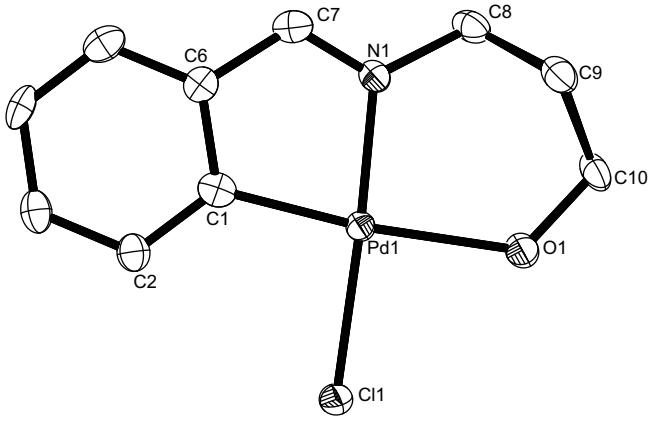


Fig. 5. Ortep diagram showing atom numbering scheme for **4d** with 50% displacement ellipsoids. H atoms have been omitted for clarity. Selected bond distances (Å) and bond angles (°): Pd(1)–C(1) 1.963(5), Pd(1)–N(1) 2.008(3), Pd(1)–O(1) 2.168(3), Pd(1)–Cl(1) 2.320(2), N(1)–Pd(1)–C(1) 81.03(16); N(1)–Pd(1)–O(1) 93.35(13).

soluble in chlorinated solvents and the ^{1}H NMR spectrum showed a mixture of products. The FAB mass spectrum showed ions at *m*/*z* 728 and 693 corresponding to dimeric species $[Pd_2L_2Cl_2]^+$ and $[Pd_2L_2Cl]^+$ and another cluster at *m*/*z* 365 corresponding to the monomeric fragment $[Pd(L)Cl]^+$. Attempted separation of the mixture by column chromatography led to isolation of only one product. The ^{1}H NMR spectrum of the isolated product showed two singlets, at δ 3.81 and 3.90, due to two methoxy groups a singlet at δ 7.72 due to the imine, and a broad singlet at δ 4.53 assigned to the OH group. In addition, there were only two singlets in the aromatic region at δ 6.76 (H^3) and δ 7.18 (H^6) consistent with the *ortho* proton being replaced by the palladium. The υ(C=N) stretch was observed at 1633 cm^{-1}, about 15 cm^{-1} less than the free ligand, as expected for coordination of the imine. The structure was determined by X-ray crystallography (see Supplementary Material) and showed a tridentate (C,N,O) bound cyclometallated imine ligand, i.e. complex **4e** rather than a chloride bridged dimer **3e**.

The palladium atoms in (**4d**,**e**) adopt a distorted square-planar geometry. In both structures, the N(1)–Pd(1)–O(1) chelate bite angle [93.35(13)° and 93.04(8)°, respectively] is larger than that for the C(1)–Pd(1)–N(1) [81.03(16)° and 81.48(10)°], which is expected because of the larger chelate ring size (six-membered ring rather than five-membered ring). The Pd–C(1) bond distances [1.963(5) and 1.983(3) Å, respectively] and Pd–N(1) bond distances [2.008(3) and 2.014(2) Å] are similar in both complexes.

It can be seen that chelate ring size and nature of the oxygen containing functional group both affect the tendency of the oxygen to coordinate. Thus, with a C_2H_4 chain neither the ether- nor alcohol-functionalised ligands **1a**,**c** respectively, gave tridentate complexes, acetate- and chloride-bridged dimers **2a** and **3a**,**c** being formed instead. However with the C_3H_6 tether the ether-functionalised ligand **1b** formed bidentate acetate- and chloride-bridged dimers **2b** and **3b** respectively, whereas the alcohol-functionalised ligands **1d,e** formed tridentate C,N,O chloride complexes **4d**,**e**. The exact nature of the acetate complexes with **d** and **e** cannot be established because they are very insoluble.

Chloride-bridged dimers **3a**–**c** react as expected [10] with two equivalents of PPh_3 to give mononuclear derivatives **5a**–**c**. The products were obtained in high yield and were characterised by ^{1}H, ^{13}C–{^{1}H} and ^{31}P–{^{1}H} NMR spectroscopy, FAB mass spectrometry, IR spectroscopy and microanalysis.

The ^{31}P–{^{1}H} NMR spectra of **5a**–**c** each showed a singlet, at δ 39.5, 42.5 and 41.1, respectively. The ^{1}H NMR spectra each showed four (1H) multiplets in the aromatic region due to the cyclometallated ligand, and one PPh_3 ligand. The imine protons were observed as doublets due to coupling to phosphorus ($J_{PH} = 8$ Hz) [26] indicating the *trans* arrangement of the phosphine ligand and imine nitrogen, [10] and adjacent to the cyclometallated phenyl group. As a result, the ring-current of the PPh_3 ligand causes the resonances for (H^6) and (H^5) to shift upfield compared to the starting dimers, (0.74–1 ppm for H^6 and 0.37 to 0.52 ppm H^5). Complexes **5a**,**b** also gave rise to a singlet at ca. δ 3.36 due to the OMe group. Complex **5c** showed a broad singlet at δ 2.59 due to the hydroxyl proton consistent with no coordination of the hydroxyl as found in the analogue made by Navarro [10]. The ^{13}C–{^{1}H} NMR spectra of **5a**–**c** showed signals corresponding to all the expected carbons, in particular the imine carbon was observed at δ 177.25 (**5a**), 175.91 (**5b**) and 177.1 (**5c**). The FAB mass spectra of **5a**–**c** all showed ions corresponding to $[M-Cl]^+$ at *m*/*z* 530, 544 and 516 respectively, **5b**,**c** also showed a molecular ion at *m*/*z* 579 and 551, respectively.

Careful recrystallisation of **5b** from dichloromethane/ether gave crystals suitable for X-ray diffraction. The X-ray structure is shown in Fig. 6. The structure, confirms the coordination of PPh_3 *trans* to N and the bidentate nature of the cyclometallated imine.

The reaction of the C,N,O-tridentate complexes, **4d**,**e** with PPh_3 was also investigated. In these cases, the reaction could in principle proceed by substitution of the alcohol, the orthometallated ligand being converted to bidentate coordination (two isomers possible), or by substitution of the chloride to form a cationic species. Since **4e** was more easily obtained as a pure compound this is explained first. The ^{31}P–{^{1}H} NMR spectrum of the product showed a singlet, at δ 43.14, indicating a single product. The ^{1}H NMR spectrum is similar to those for **5a,b**. Thus, the imine proton was observed at δ 8.06 as a doublet due to coupling to phosphorus, suggesting the imine is *trans* to the PPh_3. The resonances due to (H^6) and the 5-OMe were both shifted upfield 1.5 and 1.09 ppm, respectively compared to the starting material due to shielding by the PPh_3 providing further confirmation that the PPh_3 is adjacent to the metallated carbon and *trans* to the nitrogen. The OH proton was observed at δ 2.99, compared to δ 4.53 in **4e** consistent with cleavage of the Pd–OH bond. The ^{13}C–{^{1}H} NMR

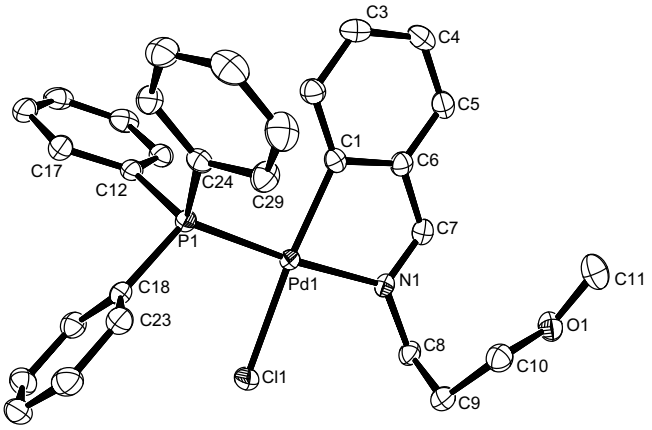


Fig. 6. Ortep diagram showing atom numbering scheme for **5b** with 50% displacement ellipsoids. H atoms have been omitted for clarity. Selected bond distances (Å) and bond angles (°): Pd(1)–C(1) 2.032(2), Pd(1)–N(1) 2.102(2), Pd(1)–P(1) 2.2493(6), Pd(1)–Cl(1) 2.3691(6); N(1)–Pd(1)–C(1) 81.35(7).

spectrum shows the imine carbon resonance at δ 175.45 and the metallated carbon (C^1) at δ 151.08, 3 ppm downfield from the starting compound. The FAB mass spectrum showed ions at m/z 590 due to $[M-Cl]^+$. The IR spectrum showed the imine stretch at 1620 cm^{-1}, with the OH stretch at 3436 cm^{-1}, the shift to higher wavenumber consistent with displacement of the OH from the Pd atom. A crystal of **5e** was suitable for X-ray diffraction and the structure is shown in Fig. 7 with selected bond distances and angles. The structure confirms that displacement of the OH group from palladium has occurred and that the PPh_3 is *trans* to nitrogen. The crystal structure shows that the Pd has a slightly distorted square-planar coordination geometry. The Pd(1)–C(1) and Pd(1)–N(1) bond distances [2.017(3) and 2.096(3) Å, respectively] are similar to those in **5b** [2.032(2) and 2.102(2) Å].

Complex **5e** arises from cleavage of the Pd–O bond and coordination of PPh_3. However, simple substitution of the chelated oxygen would leave the PPh_3 *cis* to nitrogen whereas the product isolated has PPh_3 *trans* to nitrogen hence isomerisation occurs at some stage. The displacement of the O-donor by PPh_3 is not surprising given that Pd^{II} has a preference for coordination of relatively soft nucleophiles and is consistent with previous observations of displacement of stronger donor NMe_2 [5,6] and SEt-functionalised [27] tethers by PPh_3.

The chloride complex derived from ligand **d**,**d′** was also reacted with PPh_3. The product showed one singlet at δ 42.67 in the $^{31}P-\{^1H\}$ NMR spectrum. The ^1H NMR spectrum showed a doublet at δ 8.17 due to the imine proton, the coupling indicating a P *trans* to N arrangement. The OH proton was observed at δ 2.97, and the OH stretch was observed at 3436 cm^{-1} in the IR spectrum, both consistent with the OH not being coordinated to the palladium atom. The other spectroscopic features were similar to **5e** hence the product was assigned as **5d**. The isolation of only the imine isomer in 81% yield, may suggest that during the reactions of the mixture conversion of aminal **1d′** to imine isomer **1d** had occurred.

Mononuclear complexes **6a**,**b** were synthesised in good yield from **3a**,**b**, respectively by reaction with pyridine. The ^1H NMR spectra of **6a**,**b** both showed singlets at δ 7.90 due to the imine protons and doublets due to (H^6) at δ 6.16, upfield about 1.2 ppm from **3a**,**b** respectively, consistent with a ring current effect of the pyridine. In the aromatic region (in each case), there were four multiplets each integrating to 1H assigned to the cyclometallated phenyl group. The pyridine protons were observed as multiplets in a 2:1:2 ratio at ca. δ 7.44 (H_m), δ 7.88 (H_p) and δ 8.90 (H_o) for both complexes. This confirms either rapid rotation of the pyridine group or that it is oriented perpendicular to the square plane of the palladium.

The $^{13}C-\{^1H\}$ NMR spectra of **6a**,**b** show the expected signals, the imine carbons being observed at δ 177.17, and 176.05 and the metallated carbon (C^1) at δ 158.15, and 158.11, respectively. The pyridine carbons were observed as three singlets at ca. δ 125, 132 (C_o, C_m) and 154 (C_p). The FAB mass spectra showed ions at m/z 347 **6a** and 361 **6b**, due to $[M-Cl]^+$. Crystallisation of **6a** from CH_2Cl_2/hexane gave X-ray quality crystals. The structure is shown in Fig. 8 with selected bond distances and angles.

2.2. Attempted preparation of cationic complexes

The preparation of cationic complexes is shown in Scheme 2. To promote coordination of the oxygen, complexes **5a**,**b**,**d**,**e** were treated with silver salts to remove chloride. After removal of AgCl, the products were recrystallised and characterised by ^1H, $^{13}C-\{^1H\}$ and $^{31}P-\{^1H\}$ NMR spectroscopy, FAB mass spectrometry and microanalysis, and in some cases X-ray diffraction.

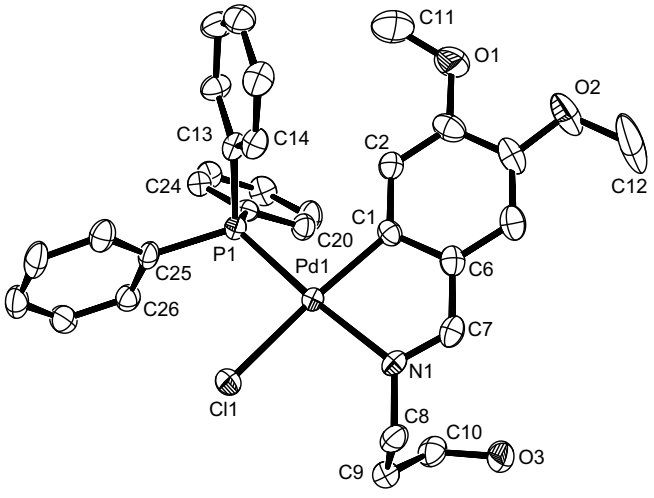


Fig. 7. Ortep diagram showing atom numbering scheme for **5e** with 50% displacement ellipsoids. H atoms have been omitted for clarity. Selected bond distances (Å) and bond angles (°): Pd(1)–C(1) 2.017(3), Pd(1)–N(1) 2.096(3), Pd(1)–P(1) 2.2583(9), Pd(1)–Cl(1) 2.3766(9); N(1)–Pd(1)–C(1) 81.01(13).

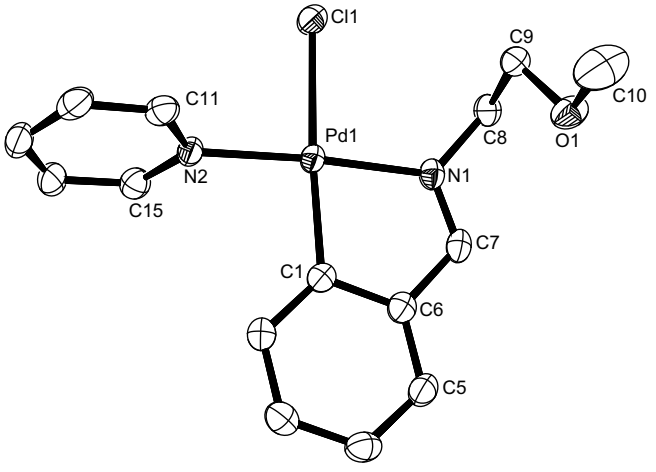
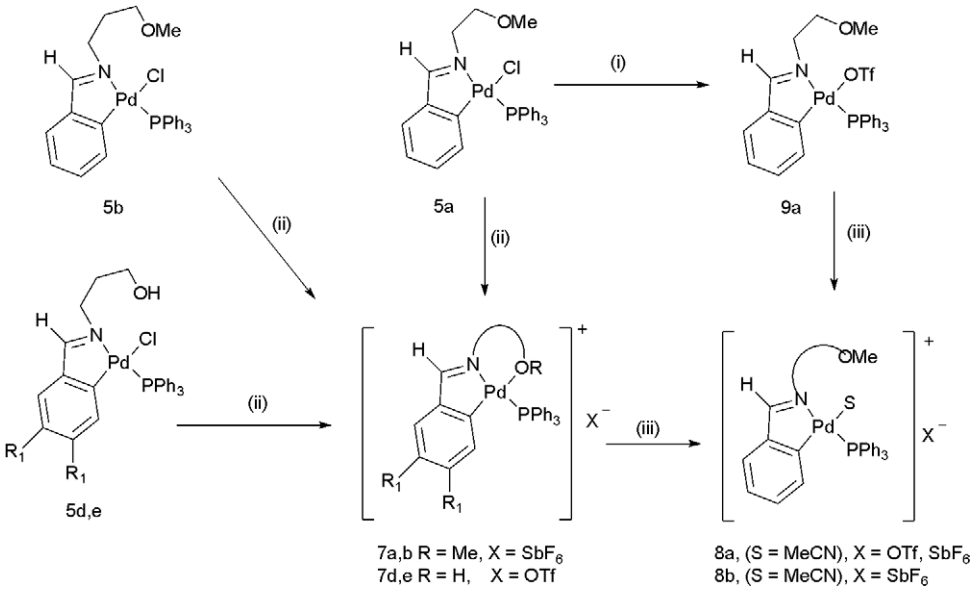


Fig. 8. Ortep diagram showing atom numbering scheme for **6a** with 50% displacement ellipsoids. H atoms have been omitted for clarity. Selected bond distances (Å) and bond angles (°): Pd(1)–C(1) 1.992(2), Pd(1)–N(1) 2.025(2), Pd(1)–N(2) 2.042(2), Pd(1)–Cl(1) 2.387(1); N(1)–Pd(1)–C(1) 80.85(8).



Scheme 2. Preparation of cationic complexes (i) AgOTf, (ii) $AgSbF_6$, (iii) MeCN.

Treatment of **5a** with AgOTf in acetone at room temperature led to the precipitation of AgCl. The $^{31}P–\{^1H\}$ spectrum of the product showed a sharp singlet at δ 39.9, suggesting the formation of only one phosphorus-containing product or rapid interconversion of complexes on the NMR timescale. The ^1H NMR spectrum showed a doublet due to the imine proton at δ 8.17, the coupling confirming that the PPh_3 is still *trans* to the imine. This is also supported by the signal for (H^6) which was observed at δ 6.35, i.e. still shielded by the PPh_3. A singlet at δ 3.34 and multiplets at δ 3.78 and 4.02 were assigned to the OMe, CH_2–O and N–CH_2 protons respectively, very slightly upfield ca. 0.04 ppm, in each case, from the starting complex; these changes are not large enough to confirm coordination of the OMe. A broad peak integrating to less than two protons was observed at δ 3.35 assigned to water. The $^{13}C–\{^1H\}$ NMR spectrum of the product showed the imine carbon at δ 176.39 and the OMe at δ 59.50, again very similar shifts to the starting complex δ 177.25 and 59.05 respectively. The metallated carbon (C^1) was observed at δ 150.13, 8.2 ppm upfield from the starting complex. This is consistent with changing the nature of ligand *trans* to (C^1), however it does not clarify whether this ligand is solvent (acetone or water), triflate or coordinated OMe. The FAB mass spectrum of the product showed ions at *m*/*z* 530 due to $[PdLPPh_3]^+$, as expected for coordination of OMe, however, the same ion would be formed by loss of solvent or OTf which may be facile. Microanalysis of the product suggested the absence of water therefore we assign the complex as **9a** with coordinated triflate.

It seems that OTf is a better ligand than the OMe tether hence the reaction was tried using the much less coordinating $AgSbF_6$ in place of AgOTf. The $^{31}P–\{^1H\}$ NMR spectrum of the product from **5a** and $AgSbF_6$ showed a singlet at δ 40.10, cf. 39.9 for the OTf product. The ^1H NMR spectrum showed resonances corresponding to all the expected protons and is similar to the species formed from AgOTf except for the C_2H_4OMe signals. The OMe signal was observed at δ 3.19, 0.2 ppm upfield from **5a** and 0.15 ppm upfield of the OTf product, possibly indicating shielding of the OMe by PPh_3, which would be close if the OMe coordinates. A similar upfield shift has been observed for coordination of an NMe_2 tether [5]. Two multiplets due to the OCH_2 and NCH_2 protons were observed at δ 3.84 and 3.94. Whilst the absolute change in chemical shift for each of those signals is small, the separation of the signals has been reduced from almost 0.25 to only 0.1 ppm. This is consistent with a significant change in orientation of the C_2H_4OMe chain hence we assign the complex as **7a** ($\mathbf{X = SbF_6}$) with OMe-coordinated. A small amount of free water (less than one equivalent) was observed as a singlet at δ 2.66. The $^{13}C–\{^1H\}$ NMR spectrum was very similar to that for the OTf complex, the metallated carbon was at δ 151 (cf. δ 150.13 in the OTf complex). At 253 K, the ^1H NMR signals for the OMe and –CH_2CH_2-protons became broader with a small downfield shift of 0.1 ppm for the OMe resonance and the peak due to water shifted downfield to δ 3.65. However there was no evidence for coordinated water. Microanalysis was also in agreement with this formulation with no water present. In conclusion, with the non-coordinating anion SbF_6 coordination of the OMe group occurs whereas anion coordination is preferred in the case of OTf.

To further investigate the strength of the Pd–OMe interaction two equivalents of NCMe were added to the NMR sample of **7a** ($\mathbf{X = SbF_6}$). After addition of NCMe, the CH_2O and NCH_2 signals shifted upfield and their separation increased to 0.17 ppm, in contrast, the OMe resonance shifted downfield 0.21 ppm, all of which are consistent with

displacement of OMe by MeCN and the OMe no longer being affected by the ring current of the PPh_3. The NCMe protons are observed at δ 1.88, 0.12 ppm upfield from free NCMe due to a ring current effect (Note at room temperature only one signal was observed for NCMe even though two equivalents were present hence there was fast exchange of free and coordinated NCMe). Therefore, NCMe is a better ligand than the ether and displaced the OMe to form **8a** (**S = NCMe**). The same species was also formed if NCMe was added to the OTf product **9a**.

Crystallisation of **8a** (**S = NCMe**, **X = SbF_6**) from CH_2Cl_2/hexane gave X-ray quality crystals. The structure of the cation is shown in Fig. 9 with selected bond distances and angles. The geometry is as expected with PPh_3 *trans* to the imine, and NCMe *trans* to the metallated carbon atom.

To investigate the effect of the length of the tether on coordination of the OMe, complex **5b** was reacted with $AgSbF_6$. The ^{31}P–{^1H} NMR spectrum of the product from the reaction of **5b** with $AgSbF_6$, showed a singlet at δ 39.79. The ^1H NMR spectrum showed the imine and (H^6) protons at δ 8.23 and 6.29, respectively, indicating that the imine is still *trans* to the PPh_3. The OMe signal was observed at δ 2.95, 0.38 ppm upfield from **5b**, this large shift strongly suggesting that the OMe group is shielded by PPh_3 and hence is coordinated. Water was observed as a singlet at δ 1.82, which integrated to less than two protons, suggesting the water was not coordinated. Thus, the complex is identified as **7b** (**X = SbF_6**) with OMe-coordinated. Microanalysis was also in agreement with this formulation with no water present. To investigate possible fluxional processes a ^1H NMR spectrum was obtained at low temperature. At 253 K the signal for water resolved into two broad singlets at δ 2.75 (free water) and δ 5.3 (coordinated water) the coordinated water only corresponded to ca. 25% of the complex. The signals of the OMe, CH_2–O, N–CH_2 and H^6 protons became broader but did not resolve into separate signals. Thus, at 253 K there were two species present, which were interconverting and the average chemical shifts were seen. The major species (ca. 75%) was still OMe coordinated **7b** (**X = SbF_6**), the minor species (ca. 25%) had water coordinated **8b** (**S = H_2O**).

The strength of the Pd–OMe interaction was probed by addition of NCMe to the NMR sample of **7b** (**X = SbF_6**). After addition of NCMe, the OMe protons shifted downfield 0.35 ppm to δ 3.30, consistent with displacement of OMe by NCMe and the OMe no longer being affected by the ring current of the PPh_3. The reaction of **5b** with AgOTf was also attempted. In this case the ^1H NMR spectrum showed the OMe signal at δ 3.14 which is intermediate between that (δ 2.95) of **7b** (**X = SbF_6**) containing coordinated OMe, and that (δ 3.30) in **8b** (**S = NCMe**) formed after addition of NCMe. Thus, we conclude that in the triflate reaction the complex with the coordinated OMe **7b** (**X = OTf**) must be in fast exchange with coordinated water **8b** (**S = H_2O**) and/or coordinated OTf **9b**. This fluxionality has not been investigated further. A few crystals were obtained that were suitable for X-ray diffraction. Surprisingly these turned out to contain a mixture of **7b** (**X = OTf**) and **8b** (**S = H_2O**) (the structures are shown in the Supplementary information).

The structure of 7**b** (**X = SbF_6**) has been determined by X-ray crystallography. There are two independent molecules in the unit cell and the structure of one of the cations is shown in Fig. 10 with selected bond distances and angles. The cations adopt the expected square planar geometry with PPh_3 *trans* to the imine and confirms the coordination

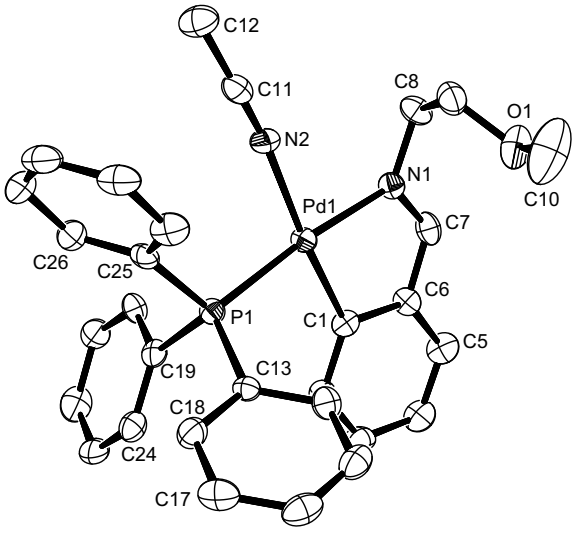


Fig. 9. Ortep diagram showing atom numbering scheme for the cation of **8a** (**S = NCMe**) with 50% displacement ellipsoids. H atoms have been omitted for clarity. Selected bond distances (Å) and bond angles (°): Pd(1)–C(1) 2.011(5), Pd(1)–N(1) 2.095(4), Pd(1)–P(1) 2.271(3), Pd(1)–N(2) 2.087(4); N(1)–Pd(1)–C(1) 81.31(19).

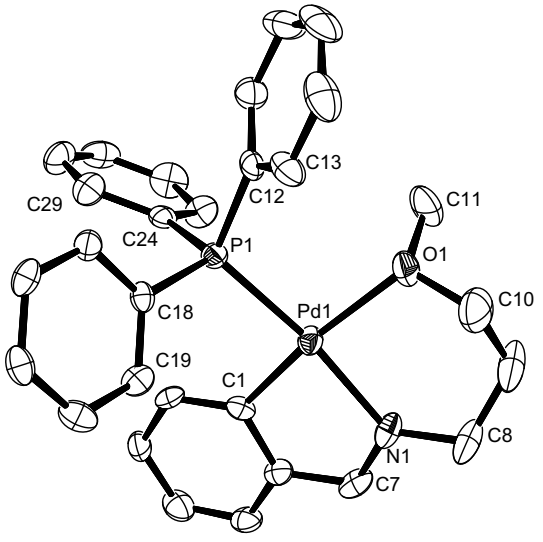


Fig. 10. Ortep diagram showing atom numbering scheme for the cation of **7b** (**X = SbF_6**) with 50% displacement ellipsoids. H atoms have been omitted for clarity. Selected bond distances (Å) and bond angles (°) for molecule 1: Pd(1)–C(1) 2.014(5), Pd(1)–N(1) 2.097(4), Pd(1)–O(1) 2.187(3), Pd(1)–P(1) 2.257(2), N(1)–Pd(1)–C(1) 82.25(18); N(1)–Pd(1)–O(1) 90.03(15).

of OMe and the C,N,O-tridentate nature of the cyclometallated imine. The Pd(1)–C(1) and Pd(1)–N(1) bond distances of molecule 1 (**7b**, $\mathbf{X = SbF_6}$) [2.014(5) and 2.097(4) Å, respectively] are slightly longer than the corresponding bond distances Pd(2)–C(30) and Pd(2)–N(2) of molecule 2 [1.991(5) and 2.063(4) Å, respectively] however, they are statistically the same as those [1.997(8) and 2.096(6) Å, respectively] in (**7b**, $\mathbf{X = OTf}$).

The influence of coordination of the side-chain in cationic complexes was also examined for alcohol-substituted ligands. Navarro has previously shown that for a cyclometallated imine with a C_2H_4OH side-arm, the alcohol does coordinate in cationic complexes [10]. The complexes **5d**,**e** containing a C_3H_6OH side-arm were treated with AgOTf in dichloromethane at room temperature. The $^{31}P–\{^1H\}$ NMR spectra of the products each showed a single resonance at δ 39.90 and 39.85, respectively, suggesting the formation of only one phosphorus-containing product or rapid interconversion on the NMR timescale. The ^1H NMR spectra showed the imine proton at δ 8.09 and δ 8.07 as doublets, and the proton (H^6) at δ 6.40 and δ 5.86, respectively, confirming that the PPh_3 is still *trans* to the imine. The hydroxy proton was observed at δ 5.72 and 5.75, a downfield shift of ca. 2.75 ppm from the starting complexes, consistent with coordination of the OH group to palladium to form **7d**,**e** ($\mathbf{X = OTf}$). In both complexes, a singlet was observed at ca. δ 1.5 assigned to free water integrating to less than two protons. Thus, in these cases water does not displace OH from coordination.

The $^{13}C–\{^1H\}$ NMR spectra of **7d**,**e** showed no significant changes compared with the starting neutral complexes, hence did not help to confirm the coordination of OH. The FAB mass spectra showed ions with maxima at *m*/*z* 530 **7d** and 590 **7e** respectively, due to $[PdLPPh_3]^+$ and the microanalyses were consistent with the expected products. Coordination of the OH has been confirmed by X-ray diffraction for **7e**. There are two independent molecules in the unit cell with a mole of water which is hydrogen bonded to the coordinated alcohol proton. There are other hydrogen bonds with the triflate counterions. The X-ray structure of molecule of one cation is shown in Fig. 11 with selected bond distances and angles.

The structure confirms that OH coordination has occurred on formation of a cationic complex. The palladium has square-planar geometry. The Pd(1)–C(1) [1.992(4) Å] and Pd(1)–N(1) [2.056(4) Å] bond distances are similar to those found in the tridentate OMe complex **7b** ($\mathbf{X = SbF_6}$) [1.991(5) and 2.063(4) Å respectively]. The Pd–O(1) bond distance [2.138(3) Å] is shorter than that [2.216(8) Å] in the related complex with a C_2H_4OH side chain[10] (see III, Fig 1) this might be expected in that the 6-membered ring allows a stronger interaction with the metal. The Pd–OH bond is also shorter than the Pd–OMe [2.187(3) Å] in complex **7b** ($\mathbf{X = SbF_6}$) with the same length tether.

In conclusion, coordination of the pendant arm in cationic complexes depends on the length of the chain, the

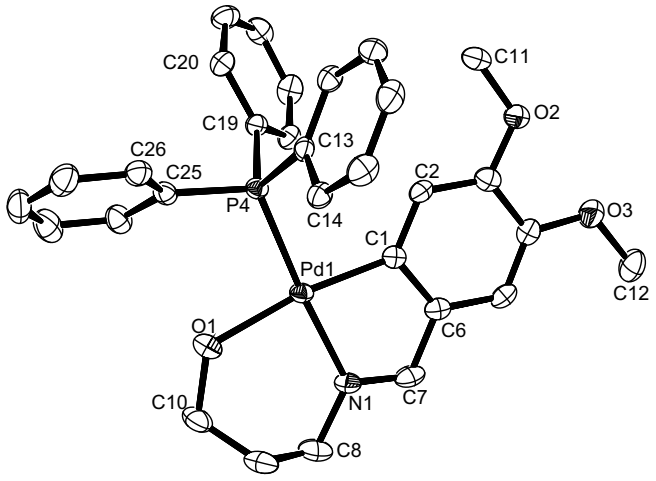


Fig. 11. Ortep diagram showing atom numbering scheme for the cation of **7e** ($\mathbf{X = OTf}$) with 50% displacement ellipsoids. H atoms have been omitted for clarity. Selected bond distances (Å) and bond angles (°): Pd(1)–C(1) 1.992(4), Pd(1)–N(1) 2.056(4), Pd(1)–O(1) 2.138(3), Pd(1)–P(4) 2.259(2); N(1)–Pd(1)–C(1) 81.32(16), N(1)–Pd(1)–O(1) 91.24(13).

nature of the O-donor (ether or alcohol) and on the anion used. In the case of ether complexes, **5a**,**b** reaction with $AgSbF_6$ leads to C,N,O-tridentate cationic complexes **7a,b** ($\mathbf{X = SbF_6}$). However, with AgOTf, coordination of OTf is favoured with the C_2H_4OMe complex (and some H_2O coordination at low temperature), with the C_3H_6OMe complex OMe coordination is in fast exchange with either H_2O and/or OTf. Addition of NCMe to **7a**,**b** ($\mathbf{X = SbF_6}$); causes displacement of the OMe chelate arm giving C,N-bidentate complexes **8a,b** ($\mathbf{S = NCMe}$). Thus, NCMe is a better ligand than an ether for these cations. In this case pendant ether functionality would be useful as a hemilabile donor since it is only weakly coordinating. In the alcohol complexes, **5d**,**e** reaction with AgOTf forms C,N,O-tridentate cationic complexes **7d**,**e** ($\mathbf{X = OTf}$).

Overall, a pendant ether only coordinates to the metal centre in cationic complexes, not neutral ones. Coordination of a pendant alcohol can occur in a neutral complex if the ligand has a $(CH_2)_3$ spacer but can occur for either a $(CH_2)_2$ or $(CH_2)_3$ spacer in cationic complexes. This is consistent with an alcohol being a better ligand than an ether and that there is less strain in a bicyclic system containing fused five and six-membered rings than in a bicyclic system containing both fused five-membered ring. The weaker coordination of an ether is further evidenced by its displacement by water and or OTf in some cases.

3. Experimental

All reactions were carried out at room temperature under nitrogen using dry solvents. ^1H, $^{13}C–\{^1H\}$ and $^{31}P–\{^1H\}$ NMR spectra were obtained using a Bruker ARX250 or 300 MHz spectrometer, with $CDCl_3$ as solvent, unless otherwise stated. Chemical shifts were recorded in ppm (with tetramethylsilane as internal reference). FAB mass spectra were obtained on a Kratos concept mass

spectrometer using NOBA as matrix. The electrospray (ES) mass spectra were recorded using a micromass Quattra LC mass spectrometer with dichloromethane or methanol as the matrix. Infrared spectra were run as solids in a diamond ATR cell using a Perkin Elmer Spectrum 1 instrument. Microanalyses were performed by the Elemental Analysis Service (University of North London). All starting materials were obtained from Aldrich, with the exception of $[PdCl_2(PhCN)_2]$ which was prepared according to literature method[28] and $[Pd(OAc)_2]_3$ which was provided by Johnson Matthey. The imines **1a**–**e** were synthesised by stirring equimolar amounts of an amine and the appropriately substituted benzaldehyde at room temperature in dichloromethane or ethanol as described by Navarro et al. [10].

3.1. Preparation of *[Pd(μ-OAc){C_6H_4-2-C(H)=NCH_2-CH_2OMe-$_K$-C_1,N}]$_2$ (**2a**)*

To a suspension of $[Pd(OAc)_2]_3$ (200 mg, 0.89 mmol) in MeOH (35 ml), imine **1a** (146 mg, 0.92 mmol) was added. The mixture was stirred at room temperature for 2 h, and then filtered over celite to remove (Pd^0). The filtrate was evaporated to dryness and the yellow oil was dissolved in dichloromethane. Addition of hexane gave **2a** as a yellow solid. (245 mg, 84%): Anal. Calc. for $C_{24}H_{30}O_6N_2Pd_2$: C, 43.99; H, 4.61; N, 4.27. Found: C, 44.08; H, 4.60; N, 4.26%. ^{1}H NMR: δ 2.13 (s, 3H, OAc), 2.75 (m, 1H, C*H*HO) 3.26 (s, 3H, OMe), 3.40 (m, 2H, NC*H*H–CH*H*–O), 3.65 (m, 1H, N–CH*H*), 7.00 (m, 4H, Ar–H), 7.29 (s, 1H, HC=N); ^{13}C NMR: δ 24.67 (OAc), 58.79 (CH_2), 59.09 (OMe), 70.04 (CH_2), 124.16, 126.78, 129.26, 132.07 (Ar–C^3, C^4, C^5, C^6), 146.17 (C^2), 155.51 (C^1), 173.82 (HC=N), 181.36 (OAc). MS (FAB) *m/z* 655 $[M-H]^+$, 597 $[Pd_2L_2(OAc)]^+$, 268 $[PdL]^+$. IR: υ(C=N) 1610 cm^{-1}. υ(COO) 1565 and 1413 cm^{-1}

3.2. Preparation of *[Pd(μ-OAc){C_6H_4-2-C(H)=NCH_2-CH_2CH_2OMe-$_K$-C_1,N}]$_2$ (**2b**)*

To a suspension of $[Pd(OAc)_2]_3$ (200 mg, 0.89 mmol) in MeOH (35 ml), the imine **1 b** (158 mg, 0.89 mmol) was added. The mixture was stirred at room temperature for 2 h, and then filtered over celite to remove (Pd^0). The filtrate was evaporated to dryness and the yellow oil was dissolved in dichloromethane. Addition of hexane gave **2b** as a yellow solid. (240 mg, 87%): Anal. Calc. for $C_{26}H_{38}O_6N_2Pd_2$: C, 45.69; H, 5.01; N, 4.1. Found: C, 45.74; H, 5.00; N, 4.02%. ^{1}H NMR: δ 1.91 (m, 2H, –CH_2–), 2.13 (s, 3H, OAc), 2.75 (m, 1H, CH*H*–O), 3.24 (s, 3H, OMe), 3.25 (m, 3H, C*H*H–O, N–CH_2), 7.00 (m, 4H, Ar–H), 7.19 (s, 1H, HC=N); ^{13}C NMR: δ 24.64 (OAc), 28.96 (–CH_2–), 56.14 (CH_2). 58.63 (OMe), 69.13 (CH_2), 124.09, 126.41, 129.10, 132.14 (Ar=C^3, C^4, C^5, C^6), 145.92 (C^2), 155.43 (C^1), 172.54 (HC=N), 181.23 (OAc). MS (FAB) m/s: 684 [M[$^+$, 625 $[M-OAc]^+$. IR: υ(C=N) 1610 cm^{-1}. υ(COO) 1570 and 1410 cm^{-1}.

3.3. Reaction of **1d**,**d′** with $Pd(OAc)_2$

To a suspension of $[Pd(OAc)_2]_3$ (200 mg, 0.89 mmol) in MeOH (35 ml), a mixture of **1d**,**d′** (145 mg, 0.89 mmol) was added. The mixture was stirred at room temperature for 2 h, and then filtered over celite to remove (Pd^0). The filtrate was concentrated to a small volume, hexane was added and the solution was left overnight to precipitate. Green crystals were formed (60 mg, 22%), however, the crystals were insoluble in most solvents so the crystal was identified by X-ray diffraction to be **2d′**. Anal. Calc. for $C_{24}H_{30}O_6N_2Pd_2$: C, 43.99; H, 4.61; N, 4.27. Found: C, 43.93; H, 4.56; N, 4.39%. MS (FAB) *m/z* 596 $[Pd_2L_2OAc]^+$, 535 $[Pd_2L_2]^+$, 268 $[PdL]^+$. IR: υ(C=N) 1605 cm^{-1}. υ(COO) 1563 and 1413 cm^{-1}. υ(OH) 3396 cm^{-1}.

3.4. Preparation of *[Pd(μ-Cl){C_6H_4-2-C(H)=NCH_2-CH_2OMe-$_K$-C_1,N}]$_2$ (**3a**)*

To a suspension of $[Pd(OAc)_2]_3$ (206 mg, 0.92 mmol) in MeOH (30 ml), the imine **1a** (150 mg, 0.92 mmol) was added. The mixture was stirred at room temperature for 2 h, and then filtered over celite to remove (Pd^0). The resulting orange solution was treated with LiCl (150 mg, 3.5 mmol) to give a green precipitate which was filtered, washed with hexane and dried to give **3a** (181 mg, 76%): Anal. Calc. for $C_{20}H_{24}O_2N_2Pd_2$: C, 40. 30; H, 2.03; N, 4.70. Found: C, 40.25; H, 2.09; N, 4.64%. ^{1}H NMR: δ 3.37 (s, 3H, OMe), 3.76 (s, 4H, N–CH_2–CH_2–O), 7.05 (m, 2H, H^4, H^5), 7.22 (m, 1H, H^3), 7.37 (m, 1H, H^6), 7.83 (s, 1H, HC=N); ^{13}C NMR: δ 59.3 (OMe), 59.3 (CH_2), 70.23 (CH_2), 125.0, 127.69, 130.22, 133.42 (Ar-C^3, C^4, C^5, C^6), 146.33 (C^2), 154.68 (C^1), 176.21 (HC=N). MS (FAB) *m/z* 608 $[M]^+$, 573 $[M-Cl]^+$. IR: υ(C=N) 1613 cm^{-1}.

3.5. Preparation of *[Pd(μ-Cl){C_6H_4-2-C(H)=NCH_2CH_2-CH_2OMe-$_K$-C_1,N}]$_2$ (**3b**)*

To a suspension of $[Pd(OAc)_2]_3$ (200 mg, 0.89 mmol) in MeOH (35 ml), the imine **1b** (158 mg, 0.89 mmol) was added. The mixture was stirred at room temperature for 2 h, and then filtered over celite to remove (Pd^0). The resulting orange solution was treated with LiCl (0.15 g, 3.5 mmol) to give **3b** as a green precipitate. The solid was filtered, washed with hexane and air dried. (270 mg, 95%): Anal. Calc. for $C_{22}H_{28}O_2N_2Pd_2$: C, 41.53; H, 4.44; N, 4.40. Found: C, 41.53; H, 4.52; N, 4.45%. ^{1}H NMR: δ 2.12 (q, 2H, *J* 6, –CH_2–), 3.32 (s, 3H, OMe), 3.44 (t, 2H, *J* 6, CH_2O), 3.70 (t, 2H, *J* 6.5, NCH_2), 7.04 (m, 2H, H^4, H^5), 7.20 (m, 1H, H^3), 7.38(m, 1H, H^6), 7.81 (s, 1H, HC=N). ^{13}C NMR: δ 29.71 (–CH_2–), 57.02 (CH_2), 58.77 (OMe), 69.08 (CH_2), 124.95, 127.46, 130.25, 133.46 (Ar–C^3, C^4, C^5, C^6), 146.09 (C^2), 154.44 (C^1), 174.97(HC=N). MS (FAB) *m/z* 636 $[M]^+$, 601 $[M-Cl]^+$. IR: υ(C=N) 1611 cm^{-1}.

3.6. Preparation of [Pd(μ-Cl){C_6H_4-2-C(H)=NCH_2-CH_2OH-$_K$-C_1,N}]$_2$ (**3c**)

To a suspension of $[Pd(OAc)_2]_3$ (200 mg, 0.89 mmol) in MeOH (35 ml), the imine **1 c** (132 mg, 0.89 mmol) was added. The mixture was stirred for 2 h, and then filtered over celite to remove (Pd^0). The filtrate was treated with LiCl (0.15 g, 3.5 mmol) to give **3c** as a white precipitate. The solid was filtered, washed with hexane and dried under vacuum. (165 mg, 65%): Anal. Calc. for $C_{18}H_{20}O_2N_2Cl_2Pd_2$ (1 equiv. H_2O): C, 36.18; H, 3.69; N, 4.69. Found: C, 35.86; H, 3.12; N, 4.41%. ^{1}H NMR: δ (d_6-DMSO, RT) 3.52 (br, 4H, –CH_2–CH_2–), 4.55 (m, 1H, OH), 6.90 (br, 2H, H^4, H^5), 7.20 (br, 1H, H^3), 7.75 (br, 1H, H^6), 7.90 (s, 1H, HC=N). MS (FAB) *m*/*z* 545 $[2M-Cl]^+$, 254 $[M-Cl]^+$. IR: υ(C=N) 1613 cm^{-1}.

3.7. Reaction of **1d,d′** with $Pd(OAc)_2$ followed by LiCl

To a suspension of $[Pd(OAc)_2]_3$ (200 mg, 0.89 mmol) in MeOH (35 ml), a mixture of **1d**,**d′** (150 mg, 0.89 mmol) was added. The mixture was stirred at room temperature for 2 h, and then filtered over celite to remove (Pd^0). The filtrate was treated with LiCl (150 mg, 3.5 mmol) to give a green precipitate. The precipitate was filtered and washed with hexane. A further amount was obtained by concentration of the filtrate and precipitation with hexane. The total yield was 240 mg (89%). No meaningful NMR spectra could be obtained. An X-ray structure determination on one crystal showed it to be a monomer **4d**. Anal. Calc. for $C_{10}H_{12}OClNPd$: C, 39.50; H, 3.98; N, 4.61. Found: C, 39.56; H, 3.81; N, 4.52%. MS (FAB) *m*/*z* 268 $[PdL]^+$, no sign for dimer (**3d′**). IR: υ(C=N) 1585 cm^{-1}. υ(COO) 1555 cm^{-1}. υ(OH) 3118 cm^{-1}.

3.8. Preparation of [PdCl{C_6H_2-4,5-(OCH_3)$_2$-2-C(H)=$NCH_2CH_2OCH_3$-$_K$-C_1,N,O}] (**4e**)

To a suspension of $[Pd(OAc)_2]_3$ (200 mg, 0.89 mmol) in MeOH (35 ml), **1e** (199 g, 0.89 mmol) was added. The mixture was stirred at room temperature for 2 h, and then filtered over celite to remove (Pd^0). The resulting solution was rotary evaporated to dryness. The resulting solid was dissolved in a small amount of dichloromethane. Addition of hexane gave a green precipitate. The solid was filtered, washed with hexane and dried under vacuum. The green precipitate was washed through a short column of silica (CH_2Cl_2/acetone, 9:1), and the filtrate concentrated to small volume and treated with hexane to give more precipitate. The solid was washed with hexane giving **4e** which was pure by ^{1}H NMR spectrometry (0.2 g, 62%): Anal. Calc. for $C_{12}H_{16}O_3NClPd$: C, 39.58; H, 4.43; N, 3.85. Found: C, 39.48; H, 4.40; N, 3.92%. ^{1}H NMR: δ 2.04 (m, 2H, –CH_2–), 3.62 (t, 2H, *J* 5, NCH_2), 3.81 (s, 3H, OCH_3), 3.90 (t, 2H, *J* 5, CH_2O), 3.93 (s, 3H, OCH_3), 4.53 (br, 1H, OH), 6.76 (s, 1H, H^3), 7.18 (s, 1H, H^6), 7.72 (s, 1H, HC=N); ^{13}C NMR: δ 31.67 (–CH_2–), 56.31, 56.36 (2 × OMe + NCH_2), 61.93 (OCH_2), 110.31 (C^3), 117.26 (C^6), 137.05, 147.21 (2 × *C*-OMe), 146.62, 149.57 ($C^1 + C^2$), 172.75 (HC=N). MS (FAB) *m*/*z* 728 $[Pd_2L_2Cl_2]^+$, 693 $[Pd_2L_2Cl]^+$, 365 $[PdLCl]^+$. IR: υ(C=N) 1633 cm^{-1}.

3.9. Preparation of [PdCl{C_6H_4-2-C(H)=NCH_2CH_2-OMe-$_K$-C_1,N}(PPh_3)] (**5a**)

To a solution of **3a** (70 mg, 0.11 mmol) in CH_2Cl_2 (10 ml), PPh_3 (70 mg, 0.26 mmol) was added. This solution was stirred at room temperature for 5 h, after which time the ^{31}P NMR spectrum showed all the PPh_3 had reacted. The solvent was removed under reduced pressure affording **5a** as green crystals. (55 mg, 42%): Anal. Calc. For $C_{28}H_{27}ONClPdP$: C, 59.38; H, 4.81; N, 2.47. Found: C, 59.45; H, 4.72; N, 2.54%. ^{1}H NMR: δ 3.38 (s, 3H, OMe), 3.81 (m, 2H, CH_2O), 4.10 (m, 2H, NCH_2), 6.39 (t, 1H, *J* 6, H^6), 6.53 (dt, 1H, *J* 6.5, 1, H^5), 6.90 (dt, 1H, *J* 6.5, 1, H^4), 7.29 (dd, 1H, *J* 7.5, 1.5, H^3), 7.39 (m, 9H, (H_m, H_p) PPh_3), 7.75 (m, 6H, (H_o) PPh_3), 8.13 (d, 1H, J_{PH} 8, HC=N); ^{13}C NMR: δ 58.61 (CH_2), 59.05 (OMe), 71.35 (CH_2), 124.19, 129.98, 130.92, 138.36 (Ar–C^3, C^4, C^5, C^6), 128.25 (d, *J* 11.2, (C_m) PPh_3), 130.90 ((C_p) PPh_3), 131.70 ((C_i)PPh_3), 135.68 (d, *J* 11.5, (C_o) PPh_3), 148.48 (C^2), 158.31 (C^1), 177.25 (HC=N). ^{31}P–{^{1}H} NMR: 39.50. MS (FAB) *m*/*z* 530 $[M-Cl]^+$. IR: υ(C=N) 1626 cm^{-1}.

3.10. Preparation of [PdCl{C_6H_4-2-C(H)=NCH_2CH_2-CH_2OCH_3-$_K$-C_2,N}(PPh_3)] (**5b**)

To a solution of **3b** (70 mg, 0.11 mmol) in CH_2Cl_2 (10 ml), PPh_3 (58 mg, 0.22 mmol) was added. The solution was stirred at room temperature for 4 h, then the reaction was monitored by ^{31}P NMR and no free PPh_3 was observed. The solvent was removed under reduced pressure affording **5b** as a green solid (105 mg, 82%). The solid was recrystallised from dichloromethane/hexane. Anal. Calc. for $C_{29}H_{29}ONPClPd$: C, 60.01; H, 5.04; N, 2.41. Found: C, 59.92; H, 5.13; N, 2.34%. ^{1}H NMR: δ 2.17 (q, 2H, *J* 6.5, –CH_2–), 3.33 (s, 3H, OMe), 3.47 (t, 2H, *J* 6, CH_2O), 4.02 (m, 2H, NCH_2), 6.39 (t, 1H, *J* 6, H^6), 6.53 (dt, 1H, *J* 6.5, 1, H^5), 6.90 (dt, 1H, *J* 6.5, 1, H^4), 7.29 (dd, 1H, *J* 7.5, 1.5, H^3), 7.38 (m, 9H, (H_m, H_p) PPh_3), 7.73 (m, 6H, (H_o) PPh_3), 8.12 (d, 1H, J_{PH} 8, HC=N); ^{13}C NMR: δ 30.77 (–CH_2–), 56.40 (CH_2), 58.67 (OMe), 69.91 (CH_2), 124.19, 127.89, 129.88, 138.45 (Ar–C^3, C^4, C^5, C^6), 128.22 (d, *J* 11, (C_m) PPh_3), 130.89 ((C_p) PPh_3), 131.69 ((C_i) PPh_3), 135.65 (d, *J* 11.5, (C_o) PPh_3), 148.35 (C^2), 158.21 (C^1), 175.91 (HC=N); ^{31}P–{^{1}H} NMR: 42.49. MS (FAB) *m*/*z* 579 $[M]^+$, 544 $[M-Cl]^+$. IR: υ(C=N) 1626 cm^{-1}.

3.11. Preparation of [PdCl{C_6H_4-2-C(H)=NCH_2CH_2-OH-$_K$-C_1,N}(PPh_3)] (**5c**)

To a solution of **2c** (70 mg, 0.12 mmol) in CH_2Cl_2 (25 ml), PPh_3 (64 mg, 0.24 mmol) was added. The reaction

was stirred at room temperature for 4 h, the solvent was then removed under reduced pressure affording a white solid. The solid was dissolved in dichloromethane and treated with hexane giving **5c**. (69 mg, 52%). Anal. Calc. for $C_{27}H_{25}ONPClPd$: C, 58.71; H, 4.56; N, 2.54. Found: C, 58.56; H, 4.36; N, 2.37%. ^{1}H NMR: δ 2.59 (s, 1H, OH), 4.04 (s, 2H, CH_2O), 4.13 (s, 2H, NCH_2), 6.41 (t, 1H, *J* 6.5, H^6), 6.56 (t, 1H, *J* 7, H^5), 6.93 (t, 1H, *J* 7.5, H^4), 7.30 (d, 1H, *J* 7.5, H^3), 7.38 (m, 9H, (H_m, H_p) PPh_3), 7.75 (m, 6H, (H_o) PPh_3), 8.18 (d, 1H, J_{PH} 7.5, HC=N); ^{13}C NMR: δ 60.84 (CH_2), 62.63 (CH_2), 124.30, 130.15, 138.37 (Ar–C^3, C^4, C^5, C^6), 128.29 (d, *J* 11, (C_m) PPh_3), 130.92 ((C_p) PPh_3), 131.74 ((C_i) PPh_3), 135.55 (d, *J* 12, (C_o) PPh_3), 148.12 (C^2), 158.01 (C^1), 177.1 (HC=N); ^{31}P–{^{1}H} NMR: 41.14. MS (FAB) *m*/*z* 551 $[M]^+$, 516 $[M-Cl]^+$. IR: υ(C=N) 1624 cm^{-1}. υ(OH) 3430 cm^{-1}.

3.12. Preparation of [PdCl{C_6H_4-2-C(H)=NCH_2CH_2-CH_2OH-$_K$-C_1-N}(PPh_3)] (**5d**)

To a suspension of **4 d** (70 mg, 0.11 mmol) in CH_2Cl_2 (25 ml), PPh_3 (61 mg, 0.23 mmol) was added. The reaction was stirred at room temperature for 4 h, then the solvent removed under reduced pressure to dryness to give **5d** as a green precipitate. (0.105 g, 81%): Anal. Calc. for $C_{30}H_{31}ONPClPd$: C, 60.62; H, 5.26; N, 2.36. Found: C, 60.52; H, 4.99; N, 2.29%. ^{1}H NMR: δ 2.07 (q, 2H, *J* 6.5, –CH_2–), 2.97 (m, 1H, OH), 3.83 (m, 2H, CH_2O), 4.11 (m, 2H, NCH_2), 6.40 (m, 1H, H^6), 6.54 (dt, 1H, *J* 7, 1, H^5), 6.92 (dt, 1H, *J* 7, 1, H^4), 7.29 (dd, 1H, *J* 7.5, 1, H^3), 7.40 (m, 9H, (H_m, H_p) PPh_3), 7.73 (m, 6H, (H_o) PPh_3), 8.17 (d, 1H, J_{PH} 8, HC=N); ^{13}C NMR: δ 36.92 (–CH_2–), 55.57(CH_2), 60.05 (CH_2), 125.52, 129.79, 131.23, 139.53 (Ar–C^3, C^4, C^5, C^6), 129.45 (d, *J* 11, (C_m) PPh_3), 132.16 ((C_p) PPh_3), 132.59 ((C_i) PPh_3), 136.72 (d, *J* 12, (C_o) PPh_3), 149.41 (C^2), 158.85 (C^1), 177.74 (HC=N); ^{31}P–{^{1}H} NMR: 42.67. MS (FAB) *m*/*z* 530 $[M-Cl]^+$. IR: υ(C=N) 1614 cm^{-1}. υ(O–H) 3436 cm^{-1}.

3.13. Preparation of [PdCl{C_6H_2-4,5-(OCH_3)$_2$-2-C(H)=$NCH_2CH_2CH_2OH$-$_K$-C_1-N}(PPh_3)] (**5e**)

To a solution of **4e** (70 mg, 0.19 mmol) in CH_2Cl_2 (25 ml), PPh_3 (51 mg, 0.19 mmol) was added. The reaction was stirred at room temperature for 4 h, then the solvent removed under reduced pressure to dryness to give a green precipitate. The solid was washed with hexane. A small amount of the product was dissolved in dichloromethane and treated with hexane to give **5e** as a green crystals (91 mg, 76%): Anal. Calc. for $C_{30}H_{31}O_3NPClPd$: C, 57.52; H, 4.99; N, 2.24. Found: C, 57.61; H, 5.03; N, 2.29%. ^{1}H NMR: δ 2.05 (q, 2H, *J* 6.5, –CH_2–), 2.84 (s, 3H, OMe), 2.99 (br, 1H, OH), 3.77 (s, 3H, OMe), 3.81 (m, 2H, CH_2O), 4.04 (m, 2H, NCH_2), 5.95 (d, 1H, *J* 6, H^6), 6.86 (s, 1H, H^3), 7.40 (m, 9H, (H_m, H_p) PPh_3), 7.75 (m, 6-H, (H_o) PPh_3), 8.06 (d, 1H, J_{PH} 8, HC=N); ^{13}C NMR: δ 35.75 (–CH_2–), 53.75 (CH_2), 55.05, 55.81 (2× OCH_3), 58.71 (CH_2), 110.46 (C^3), 121.51 (d, *J* 11.5, C^6), 128.16 (d, *J* 11, (C_m) PPh_3), 130.93 ((C_p) PPh_3), 131.18 ((C_i) PPh^3), 135.37 (d, *J* 12, (C_o) PPh_3), 139.62, 145.58 (^{4}C,^{5}C), 148.81 (C^2), 151.08 (C^1), 175.45 (HC=N); ^{31}P–{^{1}H} NMR: 43.14. MS (FAB) *m*/*z* 627 $[M]^+$, 590 $[M-Cl]^+$. IR: υ(C=N) 1620 cm^{-1}. υ(O–H) 3436 cm^{-1}.

3.14. Preparation of [PdCl{C_6H_4-2-C(H)=NCH_2CH_2-OCH_3-$_K$-C_1,N}(py)] (**6a**)

To a solution of **3a** (70 mg, 0.11 mmol) in CH_2Cl_2 (10 ml), pyridine (18 mg, 0.22 mmol) was added. The reaction was stirred at room temperature overnight then evaporated to a small volume. Treatment with hexane gave **6a** as a green solid (62 mg, 71%). The product was recrystallised from dichloromethane/hexane to give green crystals which were suitable for X-ray diffraction. Anal. Calc. for $C_{15}H_{17}ON_2ClPd$: C, 47.02; H, 4.47; N, 7.31. Found: C, 46.97; H, 4.50; N, 7.31%. ^{1}H NMR: δ 3.38 (s, 3H, OMe), 3.87 (m, 2H, CH_2O), 3.89 (m, 2H, NCH_2), 6.16 (d, 1H, *J* 7.5, H^6), 6.93 (dt, 1H, *J* 7.5, 1.5, H^5), 7.05 (dt, 1H, *J* 7.5, 1.5, H^4), 7.29 (dd, 1H, *J* 7.5. 1, H^3), 7.44 (m, 2H, (H_m) py), 7.86 (m, 1H, (H_p) py), 7.91 (s, 1H, HC=N), 8.90 [d, 2H, *J* 5, (H_o) py]; ^{13}C NMR: δ 59.07 (OMe), 60.03 (CH_2), 70.76 (CH_2), 124.72, 127.68, 130.5, 138.23 (Ar–C^3, C^4, C^5, C^6), 125.65, 132.04, 153.36 [C_m, C_p, C_o (py)], 147.04 (C^2), 158.15 (C^1), 177.17 (HC=N). MS (FAB) *m*/*z* 382 $[M]^+$, 347 $[M-Cl]^+$, 268 $[M-pyCl]^+$. IR: υ(C=N) 1616 cm^{-1}.

3.15. Preparation of [PdCl{C_6H_4-2-C(H)=NCH_2CH_2-CH_2OMe-$_K$-C_1,N}(py)] (**6b**)

To a solution of **3b** (70 mg, 0.11 mmol) in CH_2Cl_2 (10 ml), pyridine (18 g, 0.22 mmol) was added. The reaction was stirred at room temperature for 5 h, and then evaporated to small volume. Treatment with hexane gave **6b** as a yellow solid. (75 mg, 86%): Anal. Calc. for $C_{16}H_{19}ON_2ClPd$: C, 48.38; H, 4.82; N, 7.05. Found: C, 48.45; H, 4.75; N, 7.11%. ^{1}H NMR: δ 2.24 (q, 2H, *J* 6.2 Hz, –CH_2–), 3.33 (s, 3H, OMe), 3.48 (t, 2H, *J* 5.7, CH_2O), 3.90 (t, 2H, *J* 6.7, NCH_2), 6.16 (d, 1H, *J* 7.3, H^6), 6.94 (dt, 1H, *J* 7.5, 1.5, H^5), 7.05 (dt, 1H, *J* 7.5, 1, H^4), 7.28 (m, 1H, H^3), 7.44 (m, 2H, H_m (py)), 7.86 (m, 1H, (H_p) py), 7.90 (s, 1H, HC=N), 8.89 (d, 2H, *J* 5, (H_o) py); ^{13}C NMR: δ 30.27 (–CH_2–), 57.39 (CH_2), 58.66 (OMe), 69.36 (CH_2), 124.75, 127.41, 130.47, 138.23 (Ar–C^3, C^4, C^5, C^6), 125.65, 132.10, 153.37 [C_m, C_p, C_o (py)], 146.92 (C^2), 158.11 (C^1), 176.05 (HC=N). MS (FAB) *m*/*z* 396 $[M]^+$, 361 $[M-Cl]^+$, 282 $[M-pyCl]^+$. IR: υ(C=N) 1614 cm^{-1}.

3.16. Preparation of [Pd(OTf){C_6H_4-2-C(H)=NCH_2-CH_2OMe-$_K$-C_1,N}(PPh_3)] (**9a**)

To a suspension of **5a** (120 mg, 0.21 mmol) in acetone (15 ml), AgOTf (55 mg, 0.21 mmol) was added. The

mixture was stirred under N_2 with exclusion of light for 2 h. This suspension was filtered through celite to remove AgCl. The resulting solution was evaporated to dryness affording an oil. Trituration with Et_2O gave **9a** as a brown solid. (121 mg, 82%): Anal. Calc. for $C_{29}H_{27}O_4NPSF_3Pd$: C, 51.22; H, 4.00; N, 2.06. Found: C, 52.06; H, 4.46; N, 1.99%. ^{1}H NMR: δ 3.34 (s, 3H, OMe), 3.78 (t, 2H, J 4.5, CH_2O), 4.02 (m, 2H, NCH_2), 6.35 (m, 1H, H^6), 6.56 (dt, 1H, J 7.5, 1, H^5), 6.96 (t, 1H, J 7.5, H^4), 7.30 (dd, 1H, J 7.5, 2, H^3), 7.47 (m, 9H, (H_m, H_p) PPh_3), 7.71 ([m, 6H, (H_o) PPh_3), 8.17 (d, 1H, J_{PH} 7.5, HC=N); ^{13}C NMR: δ 58.28 (NCH_2), 59.50 (OMe), 72.19 (OCH_2), 125.47, 129.51 (^{3}C, ^{5}C), 130.59 (d, J 5.5, C^3), 138.34 (d, J 12, C^6), 128.50 ((C_i) PPh_3), 129.08 (d, J 12, (H_m)PPh_3), 131.77 (d, J 2.5, (C_p)PPh_3), 135.27 (d, J 12, (C_o) PPh_3), 148.04 (C^2), 150.13 (C^1), 176.39 (HC=N); ^{31}P–{^{1}H} NMR: 39.94. MS (FAB) m/z 530 $[M-OTf]^+$. IR: υ(C=N) 1638 cm^{-1}.

3.17. Preparation of [Pd{C_6H_4-2-C(H)=NCH_2CH_2O-CH_3-$_K$-C_1,N,O}(PPh_3)](SbF_6) (7**a**, X = SbF_6)

To a suspension of **5a** (120 mg, 0.21 mmol) in dry CH_2Cl_2 (15 ml), $AgSbF_6$ (73 mg, 0.21 mmol) was added. The mixture was stirred under N_2 with exclusion of light for 2 h. and then filtered through celite to remove AgCl. The resulting solution was evaporated to dryness affording an oily product. Treatment with Et_2O gave **7a** (**X** = **SbF_6**) as a pale white solid. (151 mg, 91%): Anal. Calc. for $C_{28}H_{27}ONPSbF_6Pd$: C, 43.87; H, 3.55; N, 1.83. Found: C, 43.69; H, 3.39; N, 1.83%. ^{1}H NMR: δ 3.19 (s, 3H, OMe), 3.84 (m, 2H, CH_2O), 3.94 (m, 2H, NCH_2), 6.32 (dd, 1H, J 7.5, J_{PH} 4.5, H^6), 6.59 (dt, 1H, J 7.5, 1.5, H^5), 6.99 (t, 1H, J 7.5, H^4), 7.37 (dd, 1H, J 7.5, 1.5, H^3), 7.50 (m, 9H, (H_m, H_p) PPh_3), 7.70 (m, 6H, (H_o) PPh_3), 8.22 (d, 1H, J_{PH} 6.5, HC=N); ^{13}C NMR: δ 57.42 (NCH_2), 60.04 (OMe), 73.85 (OCH_2), 125.91, 130.16 (C^3, C^4, C^5), 138.34 (d, J 12, C^6), 128.18 ((C_i) PPh_3), 129.36 (d, J 12, (H_m)PPh_3), 132.18(d, J 2.5, (C_p) PPh_3), 135.10 (d, J 12, (C_o)PPh_3), 148.79 (C^2), 151.00 (C^1), 177.04 (HC=N); ^{31}P-{^{1}H} NMR: 39.94. MS (FAB) m/z 530 $[M-SbF_6]^+$. IR: υ(C=N) 1626 cm^{-1}.

3.18. Preparation of [Pd{C_6H_4-2-C(H)=$NCH_2CH_2CH_2O$-CH_3-$_K$-C_1,N,O}(PPh_3)](SbF_6) (7**b**, X = SbF_6)

To a suspension of **5b** (85 mg, 0.15 mmol) in acetone (15 ml), $AgSbF_6$ (51 mg, 0.15 mmol) was added. The suspension was stirred under N_2 with exclusion of light for 2 h then filtered through celite to remove AgCl. The filtrate was evaporated to dryness affording a brown oil. Treatment with Et_2O gave **7b** (**X** = **SbF_6**) as a pale white solid. (98 mg, 84%): Anal. Calc. for $C_{29}H_{29}ONPSbF_6Pd$: C, 44.62; H, 3.74; N, 1.79. Found: C, 44.55; H, 3.63; N, 1.84%.^{1}H NMR: δ 2.15 (q, 2H, J 5.5, –CH_2–), 2.95 (s, 3H, OMe), 3.62 (t, 2H, J 5.5, CH_2O), 3.92 (q, 2H, J 5, NCH_2), 6.29 (dd, 1H, J 7.5, 6, H^6), 6.58 (t, 1H, J 7.5, H^5), 7.01 (t, 1H, J 7.5, H^4), 7.37 (dd, 1H, J 7.5, 1.5, H^3), 7.55 (m, 9H, (H_m, H_p) PPh_3), 7.68 (m, 6H, (H_o) PPh_3), 8.23 (d, 1H, J_{PH} 8, HC=N); ^{13}C NMR: δ 28.36 (–CH_2–), 56.24 (CH_2), 62.43 (OMe), 73.71 (CH_2), 126.12, 130.07, 130.799 (C^3,C^4, C^5), 138.32 (d, J 10, C^6), 128.15 ((C_i) PPh_3), 129.43 (d, J 11, C_m, PPh_3), 132.28 (C_p (PPh_3)), 135.12 (d, J 13, C_o, PPh_3), 147.60 (C^2), 175.62 (HC=N); ^{31}P–{^{1}H} NMR: 39.85. MS (FAB) m/z 544 $[M-SbF_3]^+$. IR: υ(C=N) 1633 cm^{-1}.

3.19. Preparation of [Pd{C_6H_4-2-C(H)=$NCH_2CH_2CH_2$-OH-$_K$-C_1,N,O}(PPh_3)][OTf] (7**d**, X = OTf)

To a suspension of **5d** (35 mg, 0.062 mmol) in acetone (15 ml), AgOTf (16 mg, 0.062 mmol) was added. The mixture was stirred under N_2 with exclusion of light for 2 h. This suspension was filtered over celite to remove AgCl. The resulting solution was evaporated to dryness affording a oil product. Treatment with Et_2O gave **7d** (**X** = **OTf**) as a beige precipitate. (36 mg, 82%): Anal. Calc. for $C_{29}H_{27}O_4NPSF_3Pd$: C, 51.22; H, 4.00; N, 2.06. Found: C, 51.06; H, 3.96; N, 1.98%. ^{1}H NMR: δ 1.97 (q, 2H, J 5.5, –CH_2–), 3.69 (m, 2H, CH_2O), 3.80 (m, 2H, NCH_2), 5.72 (t, 1H, J 4.5, OH), 6.29 (dd, 1H, J 7.5, J_{PH} 5.5, H^6), 6.51 (dt, 1H, J 7.5, 1.5, H^5), 6.88 (dt, 1H, J 7.5, 1, H^4), 7.23 (dd, 1H, J 7.5, 1.5, H^3), 7.35 (m, 9H, (H_m, H_p) PPh_3), 7.60 (m, 6H, (H_o) PPh_3), 8.09 (d, 1H, J_{PH} 8, HC=N); ^{13}C NMR: δ 30.72 (–CH_2–), 56.30 (CH_2), 63.52 (CH_2), 125.39, 129.27 (^{4}C,^{5}C), 130.91 (d, J 5.5, C^3), 138.53 (d, J 11, C^6), 127.82 ((C_i) PPh_3), 128.90 (d, J 11, (C_m) PPh_3), 131.74 (d, J 2.5, (C_p) PPh_3), 135.35 (d, J 12, C_o) (PPh_3), 147.15 (C^2), 150.32 (C^1), 174.45 (HC=N); ^{31}P–{^{1}H} NMR: 39.81. MS (FAB) m/z 530 $[M-OTf]^+$. IR: υ(C=N) 1637 cm^{-1}.

3.20. Preparation of [Pd{C_6H_2-4,5-(OCH_3)$_2$-2-C(H)=$NCH_2CH_2CH_2OH$-$_K$-C_1,N,O} (PPh_3)][OTf] (7**e**, X = OTf)

To a suspension of **5e** (70 mg, 0.11 mmol) in acetone (15 ml), AgOTf (29 mg, 0.11 mmol) was added. The suspension was stirred under N_2 with exclusion of light for 2 h, and then filtered over celite to remove AgCl. The filtrate was evaporated to dryness giving an oil product. Treatment with Et_2O gave **7e** (**X** = **OTf**) as a beige solid. (72 mg, 83%): Anal. Calc. for $C_{31}H_{31}O_6NPSF_3Pd \cdot (0.5\ H_2O)$: C, 49.71; H, 4.31; N, 1.87. Found: C, 48.76; H, 3.88; N, 1.64%. ^{1}H NMR: δ 2.00 (m 2H, –CH_2–), 2.86 (s, 3H, OCH_3), 3.69 (m, 2H, CH_2O), 3.79 (s, 3H, OCH_3), 3.96 (m, 2H, NCH_2), 5.75 (br, 1H, OH), 5.86 (d, 1H, J 5.5, H^6), 6.91 (s, 1H, H^3), 7.49 (m, 9H, (H_m, H_p) PPh_3), 7.66 (m, 6H, (H_o) PPh_3), 8.07 (d, 1H, J_{PH} 8, HC=N); ^{13}C NMR: δ 30.83 (–CH_2–), 55.43, 56.15 (2 × OCH_3), 55.98 (CH_2), 63.68 (CH_2), 111.79 (C^3), 121.62 (d, J 12, C^6), 127.84 ((C_i) PPh_3), 128.51, 138.68 (C^4, C^5), 129.00 (d, J 11, C_m (PPh_3), 131.88 (d, (C_p) PPh_3), 135.35 (d, J 12.6, (C_o)PPh_3), 146.51 (C^1), 173.75 (HC=N); ^{31}P–{^{1}H}

Table 1
Crystallographic data for complexes **1e**, **2d′**, **3b**, **4d**, **5b**, **5e**, **6a**, **8a** (**S = NCMe**, **X = SbF_6**), **7b** (**X = SbF_6**) and **7e** (**X = OTf**)

	1e	**2d′**	**3b**	**4d**	**5b**	**5e**	**6a**	**8a (S=NCMe)**	**7b (X=SbF_6)**	**7e (X=OTf)**
Empirical formula	$C_{12}H_{17}NO_3$	$C_{49}H_{58}Cl_2N_4O_{12}Pd_4$	$C_{22}H_{28}Cl_2N_2O_2Pd_2$	$C_{10}H_{12}ClNOPd$	$C_{29}H_{29}ClNOPPd$	$C_{30}H_{31}ClNO_3PPd$	$C_{15}H_{17}ClN_2OPd$	$C_{30}H_{30}F_6N_2OPPdSb$	$C_{29}H_{29}F_6NOPPdSb$	$C_{62}H_{64}F_6N_2O_{13}P_2Pd_2S_2$
Formula weight	223.27	1391.49	636.16	304.06	580.35	626.38	383.16	807.68	780.65	1498.01
Temperature (K)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Orthorhombic	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$P2(1)/c$	$C2/c$	$C2/m$	$P2(1)/c$	$P\bar{1}$	$Pbca$	$P2(1)/c$	$P\bar{1}$	$P2(1)/n$	$P\bar{1}$
a (Å)	14.4521(19)	23.209(2)	13.9836(10)	8.903(3)	9.815(2)	12.6370(11)	8.8623(14)	8.446(2)	23.161(4)	11.9118(8)
b (Å)	8.9689(12)	10.0127(8)	6.8539(5)	14.411(5)	10.062(2)	17.3743(15)	33.874(5)	12.704(4)	11.1566(18)	15.2356(10)
c (Å)	9.4433(12)	23.4395(18)	13.5036(10)	7.949(3)	13.508(3)	24.840(2)	10.0552(16)	14.842(4)	23.447(4)	18.6514(12)
α (°)	90	90	90	90	108.157(3)	90	90.	79.513(5)	90.	96.2190(10)
β (°)	106.182(2)	105.753(2)	117.5830(10)	97.525(5)	92.487(4)	90	90.797(2)	84.809(5)	105.189(3)	104.4360(10)
γ (°)	90	90	90	90	96.512(3)	90	90.	83.799(4)	90.	106.3630(10)
U (Å^3)	1175.5(3)	5242.4(8)	1147.11(14)	1011.1(6)	1255.1(5)	5453.9(8)	3018.2(8)	1552.8(7)	5847.1(16)	3086.7(4)
Z	4	4	2	4	2	8	8	2	8	2
D_{calc} (Mg/m^3)	1.262	1.763	1.842	1.997	1.536	1.526	1.686	1.727	1.774	1.612
Absorption coefficient (mm^{-1})	0.090	1.516	1.822	2.062	0.932	0.870	1.403	1.563	1.656	0.786
F(000)	480	2776	632	600	592	2560	1536	796	3072	1524
Crystal size (mm)	0.29 × 0.21 × 0.14	0.26 × 0.13 × 0.03	0.31 × 0.14 × 0.06	0.19 × 0.14 × 0.05	0.43 × 0.23 × 0.21	0.29 × 0.15 × 0.07	0.25 × 0.22 × 0.07	0.24 × 0.15 × 0.13	0.40 × 0.07 × 0.02	0.34 × 0.21 × 0.15
θ Range (°)	1.47–25.00	1.81–26.00	1.70–26.00	2.31–26.00	1.59–25.00	1.64–26.00	1.20–26.00	1.40–26.00	1.10–26.00	1.15–26.00
Index ranges	$-17 \leqslant h \leqslant 17$, $-10 \leqslant k \leqslant 10$, $-11 \leqslant l \leqslant 11$	$-28 \leqslant h \leqslant 28$, $-11 \leqslant k \leqslant 12$, $-28 \leqslant l \leqslant 28$	$-17 \leqslant h \leqslant 17$, $-8 \leqslant k \leqslant 8$, $-16 \leqslant l \leqslant 16$	$-10 \leqslant h \leqslant 10$, $-17 \leqslant k \leqslant 17$, $-9 \leqslant l \leqslant 9$	$-11 \leqslant h \leqslant 11$, $-11 \leqslant k \leqslant 11$, $-16 \leqslant l \leqslant 15$	$-15 \leqslant h \leqslant 15$, $-21 \leqslant k \leqslant 21$, $-30 \leqslant l \leqslant 30$	$-10 \leqslant h \leqslant 10$, $-41 \leqslant k \leqslant 41$, $-12 \leqslant l \leqslant 12$	$-10 \leqslant h \leqslant 10$, $-15 \leqslant k \leqslant 15$, $-18 \leqslant l \leqslant 18$	$-28 \leqslant h \leqslant 28$, $-13 \leqslant k \leqslant 13$, $-28 \leqslant l \leqslant 28$	$-14 \leqslant h \leqslant 14$, $-18 \leqslant k \leqslant 18$, $-22 \leqslant l \leqslant 22$
Reflections collected	8226	19946	4524	7632	8241	40395	23412	12074	44768	24329
Independent reflections [R_{int}]	2071 [0.0233]	5154 [0.0591]	1241 [0.0253]	1985 [0.0495]	4313 [0.0152]	5369 [0.0838]	5924 [0.0247]	5977 [0.0545]	11486 [0.0916]	11968 [0.0336]
Data/restraints/parameters	2071/0/148	5154/0/321	1241/0/91	1985/0/127	4313/0/308	5369/0/347	5924/0/363	5977/0/381	11486/0/723	11968/0/806
Goodness-of-fit, F^2	1.103	0.924	1.087	1.018	1.049	1.136	1.047	0.995	0.873	0.986
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0356$, $wR_2 = 0.1044$	$R_1 = 0.0379$, $wR_2 = 0.0796$	$R_1 = 0.0223$, $wR_2 = 0.05903$	$R_1 = 0.0329$, $wR_2 = 0.0746$	$R_1 = 0.0219$, $wR_2 = 0.0561$	$R_1 = 0.0416$, $wR_2 = 0.0864$	$R_1 = 0.0225$, $wR_2 = 0.0538$	$R_1 = 0.0470$, $wR_2 = 0.1002$	$R_1 = 0.0432$, $wR_2 = 0.0740$	$R_1 = 0.0469$, $wR_2 = 0.0994$
R indices (all data)	$R_1 = 0.0390$, $wR_2 = 0.1060$	$R_1 = 0.0622$, $wR_2 = 0.0854$	$R_1 = 0.0232$, $wR_2 = 0.0594$	$R_1 = 0.0410$, $wR_2 = 0.0779$	$R_1 = 0.0228$, $wR_2 = 0.0566$	$R_1 = 0.0499$, $wR_2 = 0.0895$	$R_1 = 0.0274$, $wR_2 = 0.0553$	$R_1 = 0.0668$, $wR_2 = 0.1067$	$R_1 = 0.0754$, $wR_2 = 0.0807$	$R_1 = 0.0680$, $wR_2 = 0.1065$
Largest difference in peak and hole (e Å^{-3})	0.202 and −0.202	0.794 and −0.632	0.905 and −0.443	1.188 and −1.119	0.447 and −0.454	0.513 and −0.618	0.378 and −0.287	1.013 and −0.925	1.106 and −0.805	1.083 and −1.015

NMR: 39.86. MS (FAB) m/z 590 $[M-OTf]^+$. IR: υ(C=N) 1637 cm^{-1}.

3.21. X-ray crystal structure determinations

Details of the structure determinations of crystals of **1e**, **2d′**, **3b**, **4d**, **5b**, **5e**, **6a**, **8a** (**S** = **NCMe**, **X** = $\mathbf{SbF_6}$), **7b** (**X** = $\mathbf{SbF_6}$) and **7e** (**X** = **OTf**) are given in Table 1, those for **4e** and **7b** (**X** = **OTf**), **8b** (**S** = $\mathbf{OH_2}$, **X** = **OTf**), are in the Supplementary material. Data were collected on a Bruker Apex 2000 CCD diffractometer using graphite monochromated Mo Kα radiation, $\lambda = 0.7107$ Å at 150 K. The data were corrected for Lorentz and polarisation effects and empirical absorption corrections (SADABS), [29] were applied in all cases. The structures were solved by Patterson methods and refined by full-matrix least squares on F^2 using the program SHELXTL [30]. All hydrogen atoms bonded to carbon were included in calculated positions (C–H = 0.96 Å) using a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters without positional restraints. The figures were drawn using the program ORTEP [31].

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Appendix A. Supplementary material

CCDC 662102, 662103, 662104, 662105, 662106, 662107, 662108, 662109, 662110, 662111, 662112 and 662113 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.12.012.

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