Synthesis, structure and reactivity of Pd^{II} complexes with the terdentate imino alcohol ligand C_6H_3-3,4-$(OMe)_2$–C(H)=N-CH_2CH_2OH†

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The reaction of the imino alcohol C_6H_3-3,4-$(OMe)_2$-C(H)=NCH_2CH_2OH, **1**, with $Pd(OAc)_2$ yields the dinuclear orthometallated compound $[Pd(\mu\text{-}OAc)\{C_6H_2\text{-}4,5\text{-}(OMe)_2\text{-}2\text{-}C(H)=NCH_2CH_2OH\text{-}\kappa^2\text{-}C,N\}]_2$, **2**, which, by reaction with excess LiCl in MeOH, can be transformed into the halide-bridged complex $[Pd(\mu\text{-}Cl)\{C_6H_2\text{-}4,5\text{-}(OMe)_2\text{-}2\text{-}C(H)=NCH_2CH_2OH\text{-}\kappa^2\text{-}C,N\}]_2$, **3**. Complex **3** reacts with neutral monodentate ligands L that promote the cleavage of the halide bridging system to give the mononuclear $[Pd(Cl)\{C_6H_2\text{-}4,5\text{-}(OMe)_2\text{-}2\text{-}C(H)=NCH_2CH_2OH\text{-}\kappa^2\text{-}C,N\}(L)]$ (L = PPh_3 **4**; py **5**) complexes. The OH group does not interact with the Pd atom in complexes **2**–**5**. The reaction of **3** with $AgClO_4$ in NCMe gives the cationic monosolvate $[Pd\{C_6H_2\text{-}4,5\text{-}(OMe)_2\text{-}2\text{-}C(H)=NCH_2CH_2OH\text{-}\kappa^3\text{-}C,N,O\}(NCMe)](ClO_4)$, **6**, in which the orthometallated ligand is now C,N,O-terdentate through coordination of the OH group. The strength of the Pd–O(H) bond has been studied. Complex **6** reacts with an excess of a neutral monodentate ligand L to give $[Pd\{C_6H_2\text{-}4,5\text{-}(OMe)_2\text{-}2\text{-}C(H)=NCH_2CH_2OH\text{-}\kappa^3\text{-}C,N,O\}(L)](ClO_4)$ (L = PPh_3 **7**; py **8**), in which the incoming ligand L replaces the NCMe but does not cleave the Pd–O(H) bond. Alternatively, complexes **7** and **8** can be obtained by reaction of **3** with $AgClO_4$ and L. Complex **6** reacts with bidentate N-donor ligands, yielding $[Pd\{C_6H_2\text{-}4,5\text{-}(OMe)_2\text{-}2\text{-}C(H)=NCH_2CH_2OH\text{-}\kappa^3\text{-}C,N,O\}(L\text{–}L\text{-}\kappa^1\text{-}N)](ClO_4)$ (L–L = bipy **9**; *N*,*N*,*N*′,*N*′-tmeda **10**), in which the bipy or tmeda ligand is coordinated through only one N atom. The rupture of the Pd–O(H) bond can be accomplished by reacting **6** with diphosphine ligands, such as dppe, giving $[Pd\{C_6H_2\text{-}4,5\text{-}(OMe)_2\text{-}2\text{-}C(H)=NCH_2CH_2OH\text{-}\kappa^2\text{-}C,N\}(dppe\text{-}P,P)](ClO_4)$, **11**. Complexes **4** · $CHCl_3$ and **7** have been characterized by X-ray diffraction.

The synthesis of cyclometallated complexes has long been an active, expanding field of chemical research, and numerous reviews have recorded the ongoing developments in this area over the years.[1] The interest of chemists in this type of compound derives from their versatility as well as from their numerous applications. The recent literature includes contributions in which cyclometallated complexes are reported to serve as active catalysts,[2] to promote stoichiometric asymmetric transformations,[3] to be useful as analytical tools,[4] for the synthesis of heterocycles[5] and carbocycles,[6] to allow the resolution of racemic mixtures into their pure optically active components,[7] to promote unusual coordination environments,[8] and to give chiral metal complexes with the metal atom as a stereogenic center.[9]

Our interest in C,N-cyclometallated systems has been centred mainly on their use as ancillary ligands in the reactivity of Pd^{II} and Pt^{II} complexes towards α-stabilised phosphorus ylides[10] and towards α-amino acids.[4,11] We have now focussed our attention on C,N-cyclometallated systems with pendant auxiliary fragments, which could in principle act as terdentate ligands. Within this class of terdentate ligands, the [C,N,N] and [N,C,N] structural arrangements have been extensively studied by several groups.[1g,2g,3d,12] However, as far as we know, the synthesis and coordination properties of C,N,O-cyclometallated ligands have been much less studied,[13] in spite of the stability provided by the C,N-chelate and the hemilabile[14] behaviour of the oxygen fragment, which could confer upon it interesting catalytic properties. Moreover, very few Pd(II) complexes containing an alcoholic oxygen coordinated to the Pd(II) centre have been reported.[15]

In this context, we have explored the synthesis of Pd(II) complexes with the potentially terdentate Schiff base C_6H_3-3,4-$(OMe)_2$-C(H)=NCH_2CH_2OH, **1**, which combines three very different donor atoms—a "soft" orthometallatable C_{aryl} atom, an iminic nitrogen and a "hard" alcoholic oxygen. A related system derived from ferrocene, and its reactivity towards Pd^{II} and Pt^{II} complexes, has been reported very recently.[16] In this paper we report the synthesis of cyclometallated complexes of Pd(II) derived from **1**, in which this ligand acts as [C,N]-bidentate or [C,N,O]-terdentate. The Pd–O(H) bond in [C,N,O] complexes shows remarkable stability, the oxygen atom cannot be displaced from the coordination sphere of the Pd centre by addition of phosphines (PPh_3) or classical N-chelating ligands, such as tmeda (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) or bipy (2,2′-bipyridine).

Results and discussion

Synthesis of [C,N]-orthometallated derivatives (Scheme 1)

The imino alcohol C_6H_3-3,4-$(OMe)_2$-C(H)=NCH_2CH_2OH, **1**, is easily prepared by condensing 3,4-dimethoxybenzaldehyde

† Dedicated to Professor Rafael Usón on the occasion of his 75th birthday.

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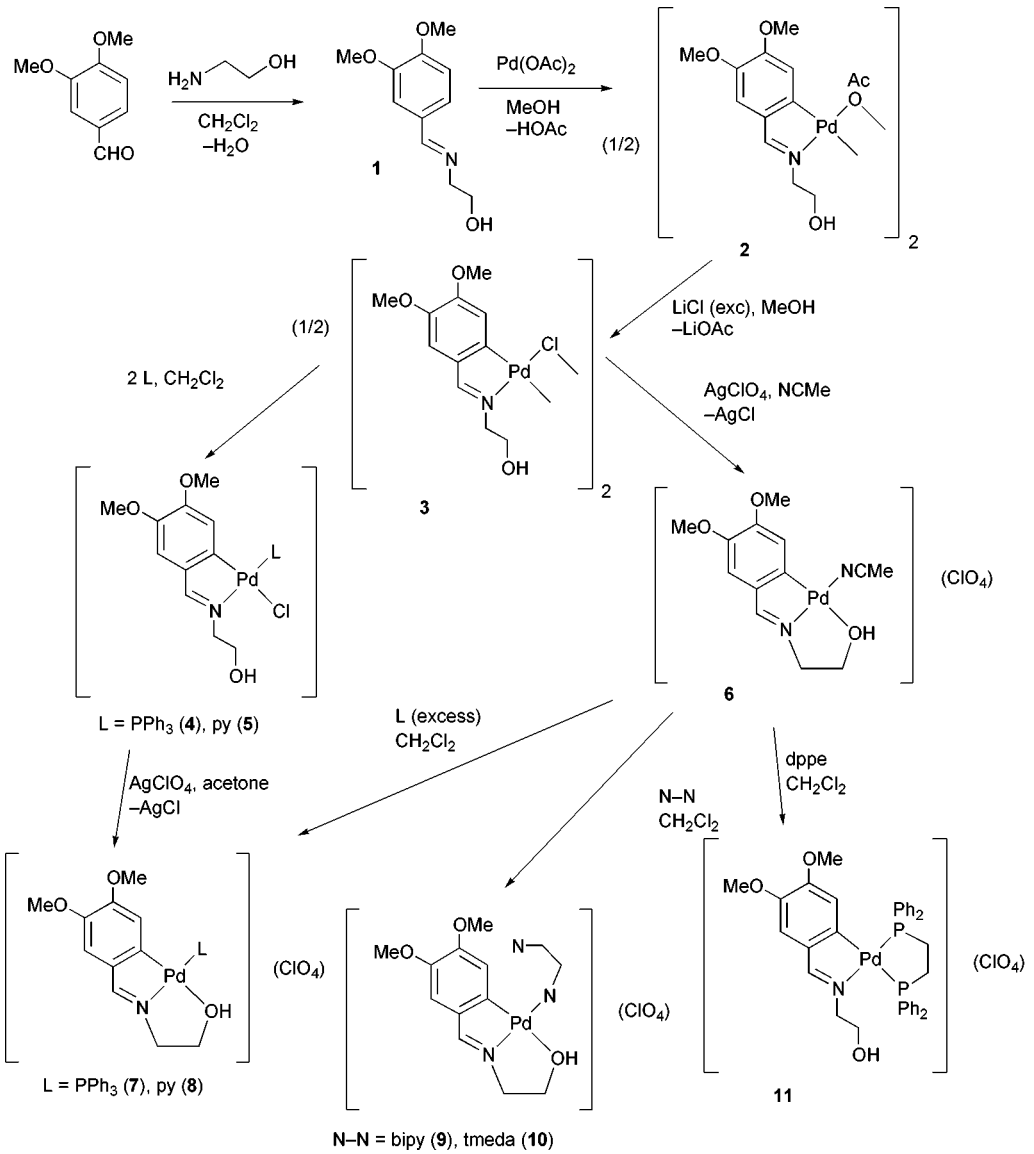

Scheme 1

with ethanolamine in the presence of $MgSO_4$. The characterization of **1** has been carried out using its analytical and spectroscopic data. The IR spectrum of solid **1** shows a strong absorption at 1645 cm^{-1}, indicating the presence of the iminic N=C bond, and another strong, broad, absorption at 3195 cm^{-1}, corresponding to the ν_{OH} stretch. This absorption appears at lower frequencies than those reported for "free" OH groups (range 3650–3590 cm^{-1})[17] and suggests in the solid state, the presence of some inter- or intramolecular H-bonds. The IR spectrum of **1** in solution ($CHCl_3$) shows two broad absorptions at 3610 and 3404 cm^{-1}, suggesting that these interactions disappear in solution at room temperature. The ^1H NMR spectrum of **1** shows only one set of signals, indicating that the imine is present in only one of the two possible geometric isomers (*Z* or *E*). This spectrum shows the expected aromatic and aliphatic resonances, in addition to a singlet at 8.14 ppm, attributed to the iminic proton C(H)=N, and a broad resonance at 2.82 ppm, attributed to the hydroxyl proton. The latter moves to 5.66 ppm on cooling (CD_2Cl_2, 218 K) but does not show fine structure. The $^{13}C\{^1H\}$ NMR spectrum of **1** shows the expected resonances for the proposed stoichiometry.

Ligand **1** reacts with $Pd(OAc)_2$ (OAc = acetate) in refluxing methanol to give an orange solid of stoichiometry $[Pd(OAc)\{C_6H_2\text{-}(OMe)_2\text{-}C(H)=NCH_2CH_2OH\}]$, **2**, according to its elemental analysis and mass spectrum. The presence of the acetate ligand can be inferred from the observation of a broad, strong absorption in the IR spectrum of **2** at 1607 cm^{-1}, which probably also contains the absorption corresponding to the imine group. The shift of the iminic stretch in **2** to lower energy, compared to **1**, suggests the N-coordination of the imine.[18] The IR spectrum of **2** also shows two sharp absorptions at 3515 and 3383 cm^{-1}, attributed to the OH stretch, which are shifted to higher energies as compared to **1** and thus suggest that the oxygen atom does not interact with the Pd atom. The ^1H NMR spectrum of **2** shows only one set of signals. In the aromatic region, three clear singlet resonances are seen, at 7.43 [C(*H*)=N], 6.64 and 6.34 (H_3 and H_6) ppm. The presence of only two singlet resonances for H_3 and H_6 suggest the orthometallation of the phenyl ring in the 6-position in **1**, and the upfield shift of the resonance ascribed to the iminic proton indicates that the imine is in the *E* form.[18] The ^1H NMR also shows signals attributed to the OMe, OCH_2CH_2N, and acetate groups, and a poorly resolved triplet resonance at 3.22 ppm ($^3J_{H-H} = 5$ Hz) assigned to the OH proton. In accord with the IR observations, the chemical shift of the OH group also suggests that there is no interaction between the Pd centre and the OH group. From all these data we propose for complex **2** the stereochemistry shown in Scheme 1—a dinuclear C,N-orthometallated complex with bridging acetate ligands $[Pd(\mu\text{-}OAc)\{C_6H_2\text{-}4,5\text{-}(OMe)_2\text{-}2\text{-}C(H)=NCH_2CH_2OH\}]_2$. The $^{13}C\{^1H\}$ NMR spectrum of **2** shows the expected signals for the proposed stoichiometry.

As expected, complex **2** reacts with an excess of LiCl in

MeOH, resulting in the replacement of the acetate bridging groups by chloride bridging ligands, giving the complex $[Pd(\mu\text{-}Cl)\{C_6H_2\text{-}4,5\text{-}(OMe)_2\text{-}2\text{-}C(H)=NCH_2CH_2OH\}]_2$, **3**, as an insoluble yellow solid. Complex **3** has the correct elemental analysis and mass spectrum. Its IR spectrum shows the disappearance of the acetate absorption and the appearance of a new absorption at 277 cm^{-1}, assigned to the Pd–Cl stretch, whose position confirms the presence of the chloride bridging system. The imine absorption appears as a sharp band at 1618 cm^{-1} and the OH stretch appears at 3529 cm^{-1}.

Complex **3** is insoluble in most of the usual organic solvents employed in NMR measurements, but it is sufficiently soluble in DMSO-d_6. The ^1H NMR spectrum shows, in the aromatic region, a pattern of resonances similar to that described for **2**, a broad singlet at 4.77 ppm attributed to the OH proton and a broad resonance (3.73–3.69 ppm) in which the methoxy and methylene protons coincide. More informative is the APT $^{13}C\{^1H\}$ NMR spectrum (APT = attached proton test), since it shows clear and separate resonances for all the expected carbon atoms in the molecule. The signal of the iminic carbon appears at 177.71 ppm, the orthometallated phenyl ring appears as six resonances (four with negative phase and two with positive phase) between 152 and 112 ppm; two negative peaks (around 60 ppm) and two positive peaks (around 55 ppm) account for the presence of the methylene and the methoxy groups, respectively.

Complex **3** reacts with monodentate ligands L to give the mononuclear derivatives $[PdCl\{C_6H_2\text{-}4,5\text{-}(OMe)_2\text{-}2\text{-}C(H)=N\text{-}CH_2CH_2OH\}L]$ (L = PPh_3 **4**; pyridine **5**) through cleavage of the halide bridging system. The elemental analyses and mass spectra of **4** and **5** are in good agreement with the proposed stoichiometry. The IR spectra of **4** and **5** show the expected absorptions corresponding to the presence of the PPh_3 and py ligands, and the iminic stretch appears at 1621 (**4**) and 1622 (**5**) cm^{-1}. The ν_{OH} absorption appears at 3459 (**4**) and 3394 (**5**) cm^{-1}, suggesting that the OH group does not interact with the Pd atom, while ν_{PdCl} appears at 293 (**4**) and 304 (**5**) cm^{-1}, shifted to higher energies with respect to **3**, in accord with the change from bridging to terminal chloride.

The ^1H NMR spectra of **4** and **5** show, at room temperature, resonances corresponding to all expected protons, except for the OH proton. At 218 K the latter resonance also appears, centered at 3.24 (**4**) and at 3.30 (**5**) ppm as triplets ($^3J_{H-H}$ = 5 Hz). The iminic proton appears in **4** as a doublet at 8.09 ppm ($^4J_{P-H}$ = 8.1 Hz), indicating the *trans* arrangement of the phosphine ligand and the iminic nitrogen (see Scheme 1). This stereochemistry is supported by the upfield shift of the resonance attributed to H_6 (5.83 ppm), due to the anisotropic shielding promoted by the phenyl rings of the PPh_3 ligand *cis* to the orthometallation position.[19] Moreover, the P-*trans*-to-N arrangement is the usual result of reactions between C,N-cyclometallated complexes and phosphine ligands,[19] due to the *transphobic* effect.[20] Similar conclusions can be derived from the analysis of the ^1H NMR spectrum of **5** (py-*trans*-to-N), since in this case the H_6 singlet signal appears at 5.50 ppm and the C(*H*)=N singlet resonance appears at around 7.90 ppm. The $^{31}P\{^1H\}$ NMR spectrum of **4** shows a single resonance at 43.42 ppm and the $^{13}C\{^1H\}$ NMR spectra of **4** and **5** show the expected resonances.

In complexes **2**–**5**, the OH group does not show any interaction with the Pd atom, as implied by the IR and NMR data, and as seen in the crystal structure of **4** (see below). The creation of coordination vacancies by halide abstraction has been a successful route to the O-coordination of the OH group.[15b]

Synthesis and reactivity of [C,N,O] complexes (Scheme 1)

Complex **3** reacts with $AgClO_4$ in a coordinating solvent (NCMe) to give the monosolvate $[Pd\{C_6H_2\text{-}4,5\text{-}(OMe)_2\text{-}2\text{-}C(H)=NCH_2CH_2OH\text{-}\kappa\text{-}C,N,O\}(NCMe)]ClO_4$, **6**, as a yellow solid. The elemental analysis of **6** clearly shows the presence of only one molecule of NCMe per cyclometallated unit, and the mass spectrum shows the correct isotopic pattern for the cation $[Pd\{C_6H_2(OMe)_2C(H)NCH_2CH_2OH\}(NCMe)]^+$ (m/z = 355 amu). The IR spectrum of **6** shows a broad absorption centered at 3251 cm^{-1}, assigned to the OH stretch, which has shifted to lower energies as compared to the corresponding values in **2**–**5**, suggesting the coordination of the alcoholic oxygen. In addition, the IR spectrum shows absorptions corresponding to the presence of the coordinated nitrile and the orthometallated imine. The ^1H NMR spectrum of **6** also provides valuable stereochemical information. The resonance attributed to the OH proton appears as a triplet at 5.01 ppm ($^3J_{H-H}$ = 5 Hz), clearly shifted downfield from the values found for the preceding complexes **2**–**5**, indicating the coordination of the oxygen atom. Similar downfield shifts have been reported in the literature[15b,21] and this shift, together with that observed for the ν_{OH} absorption in the IR spectrum, seems to be diagnostic for the coordination of the alcoholic oxygen. Moreover, only one resonance attributable to coordinated NCMe appears in the ^1H NMR spectrum (2.09 ppm) and in the $^{13}C\{^1H\}$ NMR spectrum (1.07 ppm). All of these data confirm the stereochemistry proposed for **6** in Scheme 1.

In light of the surprisingly easy coordination of the alcoholic oxygen in the presence of a solvent with good coordinating ability (acetonitrile)—a signal that the Pd–O(H) bond is relatively strong—we have examined the stability of the Pd–O(H) bond towards different ligands by reacting complex **6** with a variety of monodentate and bidentate ligands.

The reaction of complex **6** with an excess of monodentate ligands (L = PPh_3, pyridine) in CH_2Cl_2 at room temperature affords the corresponding cationic derivatives $[Pd\{C_6H_2\text{-}4,5\text{-}(OMe)_2\text{-}2\text{-}C(H)=NCH_2CH_2OH\text{-}\kappa\text{-}C,N,O\}(L)]ClO_4$ (L = PPh_3 **7**; py **8**), in accord with their elemental analyses. The mass spectra of **7** and **8** show the correct isotopic pattern for the cations $[Pd\{C_6H_2(OMe)_2C(H)NCH_2CH_2OH\}(PPh_3)]^+$ (m/z = 576 amu) and $[Pd\{C_6H_2(OMe)_2C(H)NCH_2CH_2OH\}(py)]^+$ (m/z = 393 amu). Thus, the reaction proceeds with simple substitution of the NCMe ligand in **6** by one incoming ligand L, without displacement of the alcoholic oxygen from the coordination sphere of the palladium centre, in spite of an excess of ligand L. This result can be rationalized, for complex **7**, taking into account that the "hard" oxygen atom is stabilized when *trans* to the "soft" orthometallated carbon atom,[10] as we have observed in the chemistry of α-keto-stabilized phosphorus ylides, and that the incorporation of a "soft" phosphine ligand *trans* to the carbon atom is an unfavourable process.[20] This explanation is not so straightforward in the case of complex **8**, since pyridine ligands can easily be accommodated *trans* to a carbon atom.[10] Complexes **7** and **8** can also be easily obtained by treatment of **4** and **5** with $AgClO_4$ in acetone. For complex **7** both methods gave good yields of analytically pure product, but in the case of complex **8**, this second route gave better results and, for this reason, this is the only method described (see Scheme 1 and Experimental).

The characterization of **7** and **8** as possessing [C,N,O]-coordinated ligands has been confirmed on the basis of their spectroscopic parameters. The IR spectra of **7** and **8** do not show the OH absorption, probably because this absorption is hidden in the polyethylene region (below 3100 cm^{-1}), which means that this absorption has been shifted to lower energies compared to complexes **4** and **5**. Moreover, the ^1H NMR spectrum of **7** in CD_2Cl_2 at room temperature shows the OH resonance at 5.50 ppm as a triplet; the position of this signal does not vary appreciably on cooling (218 K), suggesting a static structure on the NMR timescale. On the other hand, the ^1H NMR spectrum of **8** in acetone-d_6 at room temperature shows the OH resonance as a broad signal at 4.92 ppm. This shift to low-field, together with the aforementioned bands in the IR spectra of **7** and **8**, clearly signal the OH coordination

in these compounds. The $^{31}P\{^{1}H\}$ NMR spectrum of **7** shows a sharp singlet at 37.17 ppm and the $^{13}C\{^{1}H\}$ NMR spectra of **7** and **8** show the expected resonances for the proposed structures. Moreover, the O-coordination of the OH group in complex **7** has been unambiguously established by X-ray crystallographic methods (see below).

Similar results have been obtained in reactions between the solvate complex **6** and classical chelating N,N-bidentate ligands such as bipy (2,2′-bipyridyl) or tmeda (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine). The reaction of **6** with bipy or tmeda results in the precipitation of orange solids of stoichiometry $[Pd\{C_6H_2(OMe)_2C(H)NCH_2CH_2OH\}(L–L)](ClO_4)$ (L–L = bipy **9**; tmeda **10**), in accord with their elemental analyses and mass spectra. The IR spectra of **9** and **10** show a feature similar to that described for **7** and **8**—that is, the apparent disappearance of the OH band, probably obscured by the strong polyethylene absorption. The ^{1}H NMR spectrum of **9** is particularly informative. The resonance attributed to the OH proton appears as a poorly defined triplet at 5.06 ppm, in the same region as that observed for complexes **6**–**8**, suggesting the coordination of the OH group. The aromatic region (6.5–9 ppm) shows the presence of seven different resonances, with relative intensities 2 : 2 : 2 : 1 : 2 : 1 : 1. The three resonances with intensity 1 can be attributed to the iminic proton and to the aromatic protons H_3 and H_6 of the orthometallated group, by comparison of their chemical shifts with those seen for the preceding complexes. Thus, the four resonances with intensity 2 should be assigned to the aromatic protons of the bipy ligand, indicating that the two rings behave as equivalent on the NMR time scale. This fact strongly suggests that the bipy ligand is not coordinated through both nitrogen atoms, since in that case the OH group would no longer be bonded to the Pd atom (in spite of its chemical shift) and because the two halves of the bipy ligand would be inequivalent, giving eight different resonances. Moreover, the equivalence of the two halves of the bipy ligand also suggests that the molecular plane is a plane of symmetry on the NMR time scale, which can easily be rationalized through either a dissociative mechanism of the Pd–N bond or a fluxional process. The fluxional process could be "a single oscillatory motion of the potentially didentate ligand *via* a trigonal-bipyramidal transition state", which has been reported to account for the behaviour of $(NBu_4)[Pt(C_6F_5)_3(L–L)]$ (L–L = phen, bipy).[22] Unfortunately, complex **9** is only soluble in DMSO-d_6 (and then only slightly), precluding measurements at low temperature and also the measurement of the ^{13}C NMR spectrum.

We believe that all of these facts are in good agreement with the stereochemistry depicted in Scheme 1 for complex **9**, in which the OH fragment remains coordinated to the Pd atom and the bipy ligand acts as an N-monodentate ligand. The analysis of the ^{1}H NMR spectrum of **10** leads to similar conclusions.

The displacement of the OH group from the coordination sphere of the Pd atom can be accomplished easily by using strong phosphorus chelating ligands, such as dppe [bis(diphenylphosphino)ethane]. The reaction of **6** with dppe gives an orange solid identified as $[Pd\{C_6H_2$-4,5-$(OMe)_2$-2-$C(H)=NCH_2CH_2OH\}(dppe)](ClO_4)$, **11**, according to its elemental analysis. The IR spectrum of **11** now clearly shows the OH stretch at 3500 cm^{-1}, suggesting that the oxygen atom of the OH group is not bonded to the Pd atom, as described for **2**–**5**. Moreover, the $^{31}P\{^{1}H\}$ NMR spectrum of **11** shows the presence of two chemically inequivalent P atoms, strongly shifted downfield with respect to their position in the free phosphine, indicating that both P atoms are bonded to the Pd centre, as depicted in Scheme 1. The ^{1}H NMR spectrum of **11** gives additional proof of the proposed stereochemistry, with the resonances attributed to the iminic proton and to the H_3 and H_6 protons appearing as doublets or doublets of doublets by coupling with the ^{31}P nuclei. Also, the resonance assigned to the OH proton appears at 2.75 ppm, shifted to higher field compared to the starting compound **6**.

X-Ray crystal structures of complexes $4\cdot CHCl_3$ and 7

Crystals of complexes **4** and **7** of sufficient quality for X-ray measurements were grown by slow vapour condensation of Et_2O over a $CHCl_3$ (**4**) or CH_2Cl_2 (**7**) solution of the corresponding compound. The more relevant parameters concerning the data collection and refinement are presented in Table 1, and selected bond distances and angles are collected in Tables 2 ($4\cdot CHCl_3$) and 3 (**7**). Fig. 1 shows a drawing of complex **4** and Fig. 2 a drawing of the cationic organometallic fragment of complex **7**.

The palladium atom in **4** is located in a slightly distorted square-planar environment, surrounded by the C and N atoms of the orthometallated imine ligand, the P atom of the PPh_3 ligand and the Cl atom. The structural parameters (bond distances and angles) of the PPh_3 and the chlorine

Table 1 Crystal data and structure refinement for complexes $4\cdot CHCl_3$ and **7**

	$4\cdot CHCl_3$	**7**
Empirical formula	$C_{30}H_{30}Cl_4NO_3PPd$	$C_{29}H_{29}ClNO_7PPd$
Formula weight	731.78	676.35
T/K	296(2)	293(2)
λ/Å	0.710 73	0.710 73
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$Pna2_1$
a/Å	16.795(3)	23.732(2)
b/Å	12.090(3)	8.039(2)
c/Å	17.268(2)	14.922(2)
β/°	116.549(12)	
U/Å^3	3136.6(10)	2846.8(8)
Z	4	4
μ/mm^{-1}	1.015	0.850
Collected reflections	7456	2606
Unique reflections	7172	2600
R_{int}	0.0184	0.0436
R_1[a] $[I > 2\sigma(I)]$	0.0340	0.0506
wR_2[b] $[I > 2\sigma(I)]$	0.0826	0.1054

[a] $R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

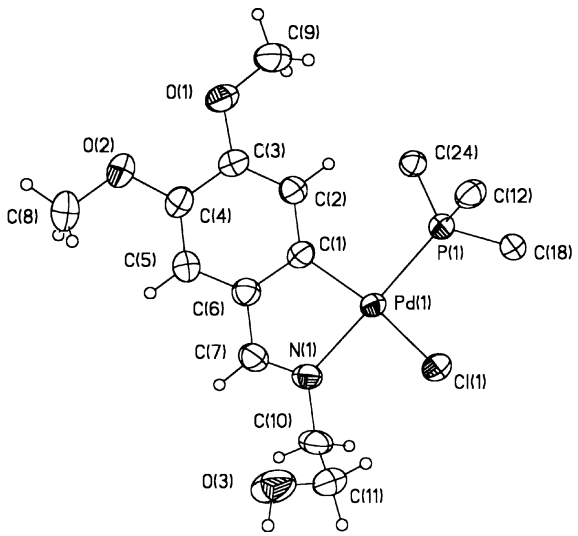

Fig. 1 Thermal ellipsoid plot of complex $[Pd(C_6H_2$-4,5-$(OMe)_2$-2-$C(H)=NCH_2CH_2OH)Cl(PPh_3)]$, **4**. Ph groups of the PPh_3 fragment (except C_{ipso}) are omitted for clarity. Atoms are drawn at 50% probability level.

Table 2 Selected bond lengths (Å) and angles (°) for **4** · $CHCl_3$

Pd(1)–C(1)	2.025(2)	Pd(1)–N(1)	2.103(2)
Pd(1)–P(1)	2.2625(8)	Pd(1)–Cl(1)	2.3892(8)
C(1)–C(2)	1.390(3)	C(1)–C(6)	1.406(4)
C(2)–C(3)	1.393(4)	C(3)–O(1)	1.367(3)
C(3)–C(4)	1.399(4)	O(1)–C(9)	1.416(4)
C(8)–O(2)	1.429(4)	C(4)–C(5)	1.371(4)
C(4)–O(2)	1.373(3)	C(5)–C(6)	1.394(4)
C(6)–C(7)	1.445(3)	C(7)–N(1)	1.275(3)
N(1)–C(10)	1.467(3)	C(10)–C(11)	1.496(4)
C(11)–O(3)	1.409(4)	P(1)–C(24)	1.822(3)
P(1)–C(18)	1.823(3)	P(1)–C(12)	1.825(3)
C(1)–Pd(1)–N(1)	81.53(9)	C(1)–Pd(1)–P(1)	95.01(7)
N(1)–Pd(1)–P(1)	174.34(6)	C(1)–Pd(1)–Cl(1)	166.81(7)
N(1)–Pd(1)–Cl(1)	91.27(6)	P(1)–Pd(1)–Cl(1)	92.98(3)
C(5)–C(6)–C(1)	122.0(2)	C(5)–C(6)–C(7)	121.2(2)
C(1)–C(6)–C(7)	116.8(2)	N(1)–C(7)–C(6)	118.8(2)
C(7)–N(1)–C(10)	119.3(2)	C(7)–N(1)–Pd(1)	112.02(17)
C(10)–N(1)–Pd(1)	128.69(18)	N(1)–C(10)–C(11)	111.5(2)
O(3)–C(11)–C(10)	110.2(3)	C(24)–P(1)–C(18)	103.81(12)
C(24)–P(1)–C(12)	107.04(12)	C(18)–P(1)–C(12)	103.45(12)
C(24)–P(1)–Pd(1)	113.21(9)	C(18)–P(1)–Pd(1)	113.39(9)
C(12)–P(1)–Pd(1)	114.88(10)		

ligands are similar to those found in other complexes containing these coordinated groups.[23] The Pd–C(1) [2.025(2) Å] and the Pd–N(1) [2.103(2) Å] bond distances, corresponding to the orthometallated imine, are slightly longer that those found in other metallated imines. For instance, the values reported in the related dinuclear complexes [Pd{3,4-$(OCH_2O)C_6H_2C(H)$=N(Cy)-*C2,N*}(μ-O_2CMe)]$_2$ and [Pd{3,4-$(OCH_2CH_2O)C_6H_2C(H)$=N(Cy)-*C6,N*}(μ-O_2CMe)]$_2$ for Pd–C are 1.974(2) and 1.949(6) Å, and for Pd–N 2.018(2) and 2.015(5) Å, respectively.[12c] On the other hand, there is no hydrogen bond between the OH group and the Cl ligand, in spite of their proximity. This type of intramolecular H-bonding is not uncommon and it has been reported in complexes such as [PdBr{$C_6H_4(CH_2CH_2OH)$-2}(tmeda)].[15b]

The palladium atom in complex **7** is also located in a slightly distorted square-planar environment, now surrounded by the C and N atoms of the orthometallated imine ligand, the P atom of the PPh_3 ligand and the oxygen atom of the alcoholic group, showing the terdentate [C,N,O]-coordination of the functionalised imine ligand. The vacant position generated in

Table 3 Selected bond lengths (Å) and angles (°) for **7**

Pd(1)–C(1)	2.002(12)	Pd(1)–N(1)	2.015(8)
Pd(1)–O(1)	2.216(8)	Pd(1)–P(1)	2.264(3)
C(1)–C(6)	1.339(16)	C(1)–C(2)	1.438(16)
C(2)–C(3)	1.418(18)	C(2)–C(9)	1.439(17)
C(3)–C(4)	1.391(19)	C(4)–O(2)	1.380(17)
C(4)–C(5)	1.39(2)	C(5)–O(3)	1.374(17)
C(5)–C(6)	1.397(18)	O(2)–C(7)	1.275(17)
O(3)–C(8)	1.370(16)	C(9)–N(1)	1.279(17)
N(1)–C(10)	1.480(19)	C(10)–C(11)	1.46(2)
C(11)–O(1)	1.445(15)	O(1)–H(1)	0.8200
C(1)–Pd(1)–N(1)	82.6(5)	C(1)–Pd(1)–O(1)	160.4(4)
N(1)–Pd(1)–O(1)	77.9(5)	C(1)–Pd(1)–P(1)	96.1(4)
N(1)–Pd(1)–P(1)	174.6(3)	O(1)–Pd(1)–P(1)	103.5(2)
C(6)–C(1)–C(2)	118.9(12)	C(6)–C(1)–Pd(1)	132.4(10)
C(2)–C(1)–Pd(1)	108.7(9)	C(3)–C(2)–C(1)	120.2(12)
C(3)–C(2)–C(9)	122.0(12)	C(1)–C(2)–C(9)	117.7(12)
C(4)–C(3)–C(2)	117.9(12)	O(2)–C(4)–C(3)	121.8(13)
O(2)–C(4)–C(5)	116.3(13)	C(3)–C(4)–C(5)	121.6(12)
O(3)–C(5)–C(4)	116.8(13)	O(3)–C(5)–C(6)	124.2(15)
C(4)–C(5)–C(6)	119.0(13)	C(1)–C(6)–C(5)	122.4(12)
C(7)–O(2)–C(4)	123.7(13)	C(8)–O(3)–C(5)	118.8(12)
N(1)–C(9)–C(2)	114.9(12)	C(9)–N(1)–C(10)	126.5(9)
C(9)–N(1)–Pd(1)	115.8(9)	C(10)–N(1)–Pd(1)	116.6(10)
C(11)–C(10)–N(1)	110.2(12)	O(1)–C(11)–C(10)	109.8(14)
C(11)–O(1)–Pd(1)	110.3(8)	C(11)–O(1)–H(1)	109.5
Pd(1)–O(1)–H(1)	126.9		

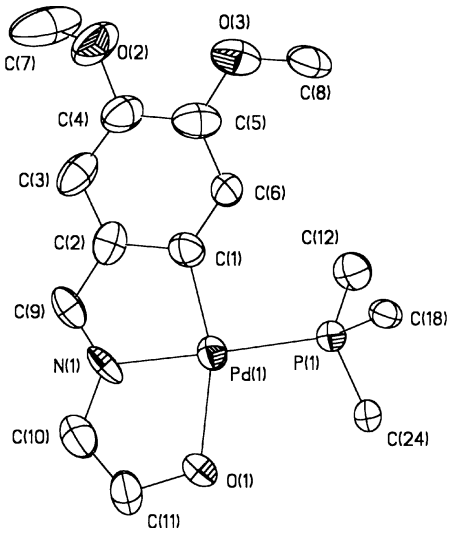

Fig. 2 Thermal ellipsoid plot of the [Pd(C_6H_2-4,5-$(OMe)_2$-2-C(H)=$NCH_2CH_2OH)(PPh_3)$]$^+$ cation of complex **7**. Ph groups of the PPh_3 fragment (except C_{ipso}) and H atoms are omitted for clarity. Atoms are drawn at 50% probability level.

4 by chloride abstraction is thus occupied by the oxygen atom. The bond distances Pd–C(1) [2.002(12) Å], Pd–N(1) [2.015(8) Å] and Pd–P(1) [2.264(3) Å] are similar to values found for related [C,N,O]-complexes.[13a] The Pd–O(1) bond distance is 2.216(8) Å, longer than those reported previously for similar structural situations. The Pd–O(H) bond distances found in related palladium complexes are: 2.076(4) Å in [Pd{$C_6H_4(CH_2CH_2OH)$-2}(tmeda)]NO_3,[15b] 2.045(6) Å in [PdClL]$_2$[Pd_2Cl_6] [where L = 1-(2-hydroxyethyl)-(2-aminoethyl-N^2)-5-methylisocytosine],[15d] 2.059(4) Å in {[$Me_2C(OH)$-$CH_2C(O)NMe_2$]PdCl(NO_2)}$_2$,[15a] and 2.148(2) Å in [$PdCl_2$-{$Ph_2PCH_2S(O)Me$}(MeOH)].[15c] This long Pd–O bond distance can be explained taking into account the O-coordination *trans* to the soft aryl carbon atom and the high *trans* influence of the latter. For example, the Pd–O bond distance reported for the aqua-complex [Pd(dmba){C(H)(PPh_3)C(O)NMe_2}(OH_2)]ClO_4, [2.200(5) Å],[24] (in which the OH_2 ligand is O-bonded *trans* to the orthometallated carbon atom) is similar to that found here. Finally, there is an intermolecular hydrogen bond between the hydroxyl group of the organometallic cation and one oxygen of the perchlorate anion [O(1)–H(1)–O(6), 2.90(2) Å, H(1)···O(6), 2.24 Å, O(1)–H(1)···O(6) 137.5°].

Conclusion

In conclusion, we have synthesized orthometallated complexes derived from the imino alcohol C_6H_3-3,4-$(OMe)_2$-C(H)=NCH_2CH_2OH **1**, in which this ligand acts as a C,N-chelating ligand (**2**–**5**, **11**) or as a C,N,O-terdentate ligand (**6**–**10**). The stability of the Pd–OH bond has been investigated and we have shown that this bond is remarkably stable towards neutral monodentate ligands L (PPh_3, py) and even towards classical neutral N,N-bidentate chelating ligands such as bipy or tmeda. The stability of the Pd–OH bond, together with the possibility of modifying the substituents on the orthometallated ring or of introducing chirality into the alcoholic fragment, suggests interesting possibilities for the utilisation of complexes of this type as versatile chiral catalysts. In fact, preliminary results of the catalytic activity of complexes **2**, **3**, **6** and **7** in the Heck reaction of methyl acrylate with iodobenzene, 4-bromobenzonitrile or 4-bromobenzaldehyde show that these complexes behave as good catalysts, giving yields of the corresponding olefin of about 80% with catalyst concentrations as low as 10^{-3} mol%. These results, together

with the synthesis of new chiral complexes based on chiral amino alcohols and their applications in asymmetric Heck-type reactions, will be reported in due course.

Experimental

Safety note: *Caution!* Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of these materials should be prepared and they should be handled with great caution. See ref. 25.

General procedures

Solvents were dried and distilled under nitrogen before use: diethyl ether and tetrahydrofuran over benzophenone ketyl, dichloromethane and chloroform over P_2O_5, acetonitrile over CaH_2, methanol over magnesium and *n*-hexane and toluene over sodium. Elemental analyses were carried out on a Perkin–Elmer 240-B microanalyser. Infrared spectra (4000–200 cm^{-1}) were recorded on a Perkin–Elmer 883 infrared spectrophotometer from nujol mulls between polyethylene sheets. ^1H (300.13 MHz), $^{13}C\{^1H\}$ (75.47 MHz) and $^{31}P\{^1H\}$ (121.49 MHz) NMR spectra were recorded in $CDCl_3$ or CD_2Cl_2 solutions at room temperature (unless otherwise stated) on a Bruker ARX-300 spectrometer; ^1H and $^{13}C\{^1H\}$ were referenced using the solvent signal as internal standard and $^{31}P\{^1H\}$ was externally referenced to H_3PO_4 (85%). Mass spectra (positive ion FAB) were recorded on a VG Autospec spectrometer from CH_2Cl_2 solutions.

Syntheses

C_6H_3-3,4-$(CH_3O)_2$-C(H)=NCH_2CH_2OH, 1. To a solution of 3,4-dimethoxybenzaldehyde (4.90 g, 29.5 mmol) in CH_2Cl_2 (20 mL), $H_2NCH_2CH_2OH$ (1.84 g, 29.51 mmol) and $MgSO_4$ were added. The resulting mixture was stirred at room temperature for 2 h, then filtered. The resulting solution was evaporated to dryness and the solid residue was treated with *n*-hexane, giving **1** as a white solid. This solid was filtered, washed with additional *n*-hexane (20 mL) and air dried. Obtained: 4.81 g (77% yield). Anal. calc. for $C_{11}H_{15}NO_3$: C, 63.14; H, 7.22; N, 6.69%. Found: C, 62.62; H, 7.74; N, 7.43%. IR (ν, cm^{-1}): 3195 (ν_{O-H}), 1645 ($\nu_{C=N}$), 1602, 1586, 1515 ($\nu_{C=C}$). ^1H NMR ($CDCl_3$, RT) δ: 8.14 (s, 1H, HC=N), 7.35 (d, 1H, H_2, $^4J_{H-H} = 1.2$), 7.06 (dd, 1H, H_6, $^3J_{H-H} = 8.4$, $^4J_{H-H} = 1.2$), 6.81 (d, 1H, H_5, $^3J_{H-H} = 8.4$ Hz), 3.86 (m, 8H, 2 CH_3O + CH_2), 3.67 (m, 2H, CH_2), 2.82 (br, 1H, OH). ^1H NMR (CD_2Cl_2, 218 K) δ: 7.80 (s, 1H, HC=N), 7.16 (s, 1H, H_2), 6.74, 6.72 (m, 2H, H_5, H_6), 5.66 (br, 1H, OH), 3.86 (m, 8H, 2 CH_3O + CH_2), 3.56 (m, 2H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, RT) δ: 162.76 (C=N), 151.39, 149.19, 128.94 (C_4, C_3, C_1), 123.29, 110.28, 109.65 (C_2, C_5, C_6), 63.22, 62.29 (CH_2), 55.88 (2 overlapped CH_3O).

[Pd(μ-OAc){C_6H_2-4,5-$(CH_3O)_2$- 2-C(H)=NCH_2CH_2OH-κ-C_1,*N*}]$_2$, 2. To a methanolic (20 mL) suspension of $Pd(OAc)_2$ (1.65 g, 7.35 mmol), the imine **1** was added (2.00 g, 9.57 mmol) and the resulting mixture was refluxed for 1.5 h. Some decomposition was evident and the hot solution was filtered over celite. After cooling, a yellow solid precipitated, which was collected, washed with MeOH (10 mL) and Et_2O (30 mL), air dried and identified as **2**. Obtained: 1.90 g (69.0% yield). Anal. calc. for $C_{26}H_{34}N_2O_{10}Pd_2$: C, 41.74; H, 4.58; N, 3.75%. Found: C, 41.11; H, 4.59; N, 3.01%. IR (ν cm^{-1}): 3515, 3383 (ν_{O-H}), 1607 ($\nu_{C=N} + \nu_{CO}$), 1577, 1552 ($\nu_{C=C}$). ^1H NMR (CD_2Cl_2, 218 K) δ: 7.43 (s, 1H, HC=N), 6.64, 6.34 (2s, 2H, H_3, H_6), 3.78 (s, 3H, CH_3O), 3.69 (s, 3H, CH_3O), 3.61 (br, 2H, CH_2), 3.22 (t, 1H, OH, $^3J_{H-H} = 5$), 3.08 (d, 1H, CH_2, $^2J_{H-H} = 12.6$), 2.82 (d, 1H, CH_2, $^2J_{H-H} = 12.6$ Hz), 2.08 (s, 3H, OAc). $^{13}C\{^1H\}$ NMR ($CDCl_3$, RT) δ: 181.67 (CO_2), 173.49 (C=N), 149.20, 148.57, 146.30, 136.73, 113.97, 109.77 (C_6H_2), 61.09, 60.82 (2 CH_2), 56.15, 55.85 (2 CH_3O), 24.39 (CH_3).

[Pd(μ-Cl){C_6H_2-4,5-$(CH_3O)_2$-2-C(H)=NCH_2CH_2OH-κ-C_1,*N*}]$_2$, 3. As described for **2**, a suspension of $Pd(OAc)_2$ (0.50 g, 2.2 mmol) in MeOH (20 mL) and the imine **1** (0.46 g, 2.2 mmol) were refluxed for 1.5 h. The hot solution was filtered in order to remove the Pd^0 formed. The resulting orange solution was treated with LiCl (0.19 g, 4.5 mmol), resulting in the precipitation of **3** as a yellow solid, which was filtered, washed with MeOH (20 mL) and air dried. Obtained: 0.640 g (81.6% yield). Anal. calc. for $C_{22}H_{28}Cl_2N_2O_6Pd_2$: C, 37.73; H, 4.03; N, 4.00%. Found: C, 37.89; H, 4.71; N, 4.05%. MS (FAB+) *m*/*z* (%): 665 (19) $[M - Cl]^+$. IR (ν cm^{-1}): 3529 (ν_{O-H}), 1618 ($\nu_{C=N}$), 1589, 1549 ($\nu_{C=C}$), 277 (ν_{Pd-Cl}). ^1H NMR (DMSO-d_6, RT) δ: 7.95 (s, 1H, HC=N), 7.67, 7.12 (2s, 2H, H_3, H_6), 4.77 (s, 1H, OH), 3.73–3.69 (m, 10H, 2 CH_3O + 2 CH_2). $^{13}C\{^1H\}$ NMR (DMSO-d_6, RT) δ: 177.71 (C=N), 151.68, 149.25, 146.25, 138.38, 115.27, 112.00 (C_6H_2), 60.65, 59.35 (2 CH_2), 55.59, 55.34 (2 CH_3O).

[PdCl{C_6H_2-4,5-$(CH_3O)_2$-2-C(H)=NCH_2CH_2OH-κ-C_1,*N*}(PPh_3)], 4. To a yellow suspension of complex **3** (0.502 g, 0.71 mmol) in 20 mL of CH_2Cl_2, PPh_3 (0.376 g, 1.43 mmol) was added, giving a yellow solution within a few seconds. This solution was stirred at room temperature for 1.5 h, then evaporated to dryness. The yellow residue was treated with Et_2O (25 mL), giving **4** as a yellow solid. This solid was filtered, washed with Et_2O (20 mL) and air dried. Obtained: 0.793 g (90.7% yield). Anal. calc. for $C_{29}H_{29}ClNO_3PPd$: C, 56.87; H, 4.77; N, 2.28%. Found: C, 56.71; H, 4.67; N, 2.15%. MS (FAB+) *m*/*z* (%): 576 (100) $[M - Cl]^+$. IR (ν cm^{-1}): 3459 (ν_{O-H}), 1621 ($\nu_{C=N}$), 1579, 1551 ($\nu_{C=C}$), 293 (ν_{Pd-Cl}). ^1H NMR (CD_2Cl_2, 218 K) δ: 8.09 (d, 1H, C(H)=N, $^4J_{P-H} = 8.1$), 7.70–7.64 (m, 6H, H_o, Ph), 7.5–7.45 (m, 3H, H_p, Ph), 7.40–7.36 (m, 6H, H_m, Ph), 6.85 (s, 1H, H_3), 5.83 (d, 1H, H_6, $^4J_{P-H} = 6$), 3.94, 3.90 (m, 4H, 2 CH_2), 3.65 (s, 3H, CH_3O), 3.24 (t, 1H, OH, $^3J_{H-H} = 5$ Hz), 2.73 (s, 3H, CH_3O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, RT) δ: 43.42. $^{13}C\{^1H\}$ NMR ($CDCl_3$, RT) δ: 176.08 (C=N), 151.43, 148.91, 145.57, 139.51, 110.78 (C_6H_2), 121.51 (d, C_6, $^3J_{C-P} = 14.5$), 135.38 (d, C_o, Ph, $^2J_{C-P} = 12.05$), 130.91 (d, C_p, Ph, $^4J_{C-P} = 1.5$), 130.87 (d, C_i, $^1J_{C-P} = 50.5$), 128.15 (d, C_m, $^3J_{C-P} = 11.3$ Hz), 62.5, 60.34 (2 CH_2), 55.82, 55.03 (2 CH_3O).

[PdCl{C_6H_2-4,5-$(CH_3O)_2$-2-C(H)=NCH_2CH_2OH-κ-C_1,*N*}(py)], 5. Complex **5** was obtained in a similar way as that described for **4**: complex **3** (0.30 g, 0.42 mmol) reacts with pyridine (0.066 g, 0.84 mmol) in CH_2Cl_2 (20 mL) to give **5** as a yellow solid. Obtained 0.327 g (90% yield). Anal. calc. for $C_{16}H_{19}ClN_2O_3Pd$: C, 44.77; H, 4.46; N, 6.53%. Found: C, 45.28; H, 4.53; N, 6.68%. MS (FAB+) *m*/*z* (%): 393 (20) $[M - Cl]^+$. IR (ν cm^{-1}): 3394 (ν_{O-H}), 1622 ($\nu_{C=N}$), 1604, 1591, 1548 ($\nu_{C=C}$), 304 (ν_{Pd-Cl}). ^1H NMR (CD_2Cl_2, 218 K) δ: 8.78 (d, 2H, H_o, py, $^3J_{H-H} = 5$), 7.90–7.85 (m, 2H, H_p (py) + HC=N), 7.43–7.38 (m, 2H, H_m, py), 6.90 (s, 1H, H_3), 5.50 (s, 1H, H_6), 3.96 (s, 2H, CH_2), 3.78–3.74 (m, 5H, NCH_2 + CH_3O), 3.42 (s, 3H, CH_3O), 3.30 (t, 1H, OH, $^3J_{H-H} = 5$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, RT) δ: 176.10 (C=N), 153.23, 151.75, 146.37, 138.17, 114.49, 110.57 (C_6H_2), 149.96, 138.00, 125.36 (py), 61.74, 61.56 (2 CH_2), 56.13, 55.48 (2 CH_3O).

[Pd{C_6H_2-4,5-$(CH_3O)_2$-2-C(H)=NCH_2CH_2OH-κ-C_1,*N*,*O*}(NCMe)](ClO_4), 6. To a solution of **3** (1.194 g, 1.70 mmol) in NCMe (50 mL), $AgClO_4$ (0.707 g, 3.40 mmol) was added. The resulting suspension was stirred at room temperature for 30 min with exclusion of light. The AgCl precipitated was removed by filtration and the resulting yellow solution was evaporated to dryness. The yellow residue was

treated with Et_2O (50 mL) giving **6** as a yellow solid, which was filtered, washed with additional Et_2O (30 mL) and air dried. Obtained: 1.215 g (78.2% yield). Anal. calc. for $C_{13}H_{17}ClN_2O_7Pd$: C, 34.30; H, 3.76; N, 6.15%. Found: C, 33.97; H, 4.11; N, 6.84%. MS (FAB+) *m/z* (%): 355 (11) $[M - ClO_4]^+$, 314 (100) $[M - ClO_4 - NCMe]^+$. IR (ν cm^{-1}): 3251 (ν_{O-H}), 2328, 2312, 2285 ($\nu_{C\equiv N}$), 1612 ($\nu_{C=N}$), 1590, 1553 ($\nu_{C=C}$). ^1H NMR (DMSO-d_6, RT) δ: 7.95 (s, 1H, HC=N), 7.10 (s, 1H, H_6), 6.86 (s, 1H, H_3), 5.01 (t, 1H, OH, $^3J_{H-H} = 5$ Hz), 3.78 (s, 3H, CH_3O), 3.70–3.65 (m, 5H, $CH_3O + CH_2$), 3.50 (m, 2H, CH_2), 2.09 (s, 3H, $NCCH_3$). $^{13}C\{^1H\}$ NMR (DMSO-d_6, RT) δ: 176.86 (C=N), 149.05, 146.62, 137.87, 114.58, 111.93 (C_6H_2), 60.07, 59.14 (2 CH_2), 55.60, 55.48 (2 CH_3O), 1.07 ($NCCH_3$). Two quaternary C atoms were not found, one in the C_6H_2 ring and the N≡C carbon.

[Pd{C_6H_2-4,5-$(CH_3O)_2$-2-C(H)=NCH_2CH_2OH-κ-C_1,*N*,*O*}(PPh$_3$)](ClO$_4$), 7. *Method a.* To a suspension of complex **4** (0.250 g, 0.408 mmol) in acetone (20 mL), $AgClO_4$ (0.085 g, 0.41 mmol) was added and the resulting suspension was stirred for 30 min at room temperature with exclusion of light. This suspension was filtered and the resulting solution was evaporated to dryness. By Et_2O addition (20 mL) and continuous stirring, complex **7** was obtained as a yellow solid, which was filtered and air dried. Obtained: 0.244 g (88.4% yield).

Method b. To a suspension of complex **6** (0.219 g, 0.481 mmol) in CH_2Cl_2 (20 mL), PPh_3 was added (0.288 g, 1.098 mmol). The initial suspension gradually dissolved and, after 15 min stirring at room temperature, a clear yellow solution was obtained. Removal of the solvent and treatment of the residue with Et_2O gave **7** as a yellow solid. Obtained: 0.265 g (81.5% yield). Anal. calc. for $C_{29}H_{29}ClNO_7PPd$: C, 51.49; H, 4.32; N, 2.07%. Found: C, 51.46; H, 4.23; N, 1.95%. MS (FAB+) *m/z* (%): 576 (100) $[M - ClO_4]^+$, 314 (19) $[M - ClO_4 - PPh_3]^+$. IR (ν cm^{-1}): 1632 ($\nu_{C=N}$), 1588, 1551 ($\nu_{C=C}$). ^1H NMR (CD_2Cl_2, 218 K) δ: 8.63 (d, 1H, HC=N, $^4J_{P-H} = 9$), 7.69–7.42 (m, 15H, Ph), 6.93 (s, 1H, H_3), 5.86 (d, 1H, H_6, $^4J_{P-H} = 5.1$), 5.50 (t, 1H, OH, $^3J_{H-H} = 5$ Hz), 4.13, 3.91, (m, 4H, 2 CH_2), 3.76, 2.90 (2s, 6H, 2 CH_3O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, RT) δ: 37.17. $^{13}C\{^1H\}$ NMR ($CDCl_3$, RT) δ: 173.03 (C=N), 150.10 (d, C_1, $^2J_{P-C} = 5.4$), 147.06, 142.07, 128.78, 112.85 (C_6H_2), 121.68 (d, C_6, $^3J_{C-P} = 10.9$), 135.14 (d, C_o, PPh_3, $^2J_{C-P} = 12.6$ Hz), 132.15 (d, C_p, PPh_3, $^4J_{C-P} = 1.9$), 129.50 (d, C_m, PPh_3, $^3J_{C-P} = 11.0$ Hz), 67.75, 57.07 (2 CH_2), 56.38, 55.55 (2 CH_3O). The C_i of the PPh_3 ligand was not found.

[Pd{C_6H_2-4,5-$(CH_3O)_2$-2-C(H)=NCH_2CH_2OH-κ-C_1,*N*,*O*}(py)](ClO$_4$), 8. Complex **8** was obtained following the same experimental method as that described for **7** in method a. Complex **5** (0.250 g, 0.582 mmol) reacted with $AgClO_4$ (0.121 g, 0.582 mmol) in acetone to give **8** as a yellow solid. Obtained: 0.132 g (45.81% yield). Anal. calc. for $C_{16}H_{19}ClN_2O_7Pd$: C, 38.96; H, 3.88; N, 5.68%. Found: C, 39.17; H, 3.91; N, 5.43%. MS (FAB+) *m/z* (%): 393 (100) $[M - ClO_4]^+$, 314 (65) $[M - ClO_4 - py]^+$. IR (ν cm^{-1}): 1607 ($\nu_{C=N}$), 1588, 1558 ($\nu_{C=C}$). ^1H NMR (acetone-d_6, RT) δ: 9.00 (d, 2H, H_o, py, $^3J_{H-H} = 5$), 8.20 (t, 1H, H_p, py, $^3J_{H-H} = 8$ Hz), 8.10 (s, 1H, HC=N), 7.77 (dd, 2H, H_m, py), 7.16 (s, 1H, H_3), 5.59 (s, 1H, H_6), 4.92 (br, s, 1H, OH), 3.92 (br, s, 2H, CH_2), 3.75 (s, 3H, OCH_3), 3.64 (m, 2H, CH_2), 3.49 (s, 3H, CH_3O). $^{13}C\{^1H\}$ NMR (acetone-d_6, RT) δ: 177.18 (C=N), 150.55, 147.57, 139.14, 115.70, 112.71 (C_6H_2), 153.43, 140.40, 127.02 (py), 61.46, 60.47 (2 CH_2), 55.91, 55.29 (2 CH_3O). One of the quaternary C atoms of the C_6H_2 group was not found.

[Pd{C_6H_2-4,5-$(CH_3O)_2$-2-C(H)=NCH_2CH_2OH-κ-C_1,*N*,*O*}(bipy)](ClO$_4$), 9. To a suspension of complex **6** (0.200 g, 0.439 mmol) in CH_2Cl_2, 2,2′-bipyridine (0.070 g, 0.44 mmol) was added. The initial yellow suspension gradually dissolved and its colour changed from yellow to orange. Stirring was continued at room temperature and, after the initial dissolution, an orange solid precipitated. This suspension was stirred for 4 h and the solid obtained, **9**, was filtered, washed with CH_2Cl_2 and air dried. Obtained: 0.225 g (85.8% yield). The product precipitated with 1.25 molecules of CH_2Cl_2, which could not be removed by recrystallization, nor by heating the product. The amount of the solvent of crystallization was determined by ^1H NMR integration of the corresponding resonance. Anal. calc. for $C_{21}H_{22}ClN_3O_7Pd \cdot 1.25CH_2Cl_2$: C, 39.51; H, 3.65; N, 6.21%. Found: C, 39.34; H, 3.58; N, 6.39%. MS (FAB+) *m/z* (%): 470 (37) $[M - ClO_4]^+$. IR (ν cm^{-1}): 1607 ($\nu_{C=N}$), 1588, 1549 ($\nu_{C=C}$). ^1H NMR (DMSO-d_6, RT) δ: 8.86 (d, 2H, H_α, bipy, $^3J_{H-H} = 5.5$), 8.58 (d, 2H, H_δ, bipy, $^3J_{H-H} = 7.5$ Hz), 8.36 (br, pseudo t, 2H, H_γ, bipy), 8.10 (s, 1H, HC=N), 7.86 (br, t, 2H, H_β, bipy), 7.15 (s, 1H, H_3), 6.50 (s, 1H, H_6), 5.06 (br, t, 1H, OH), 3.77 (br, 10H, 2 CH_3O + 2 CH_2). The product was too insoluble for ^{13}C NMR measurements.

[Pd{C_6H_2-4,5-$(CH_3O)_2$-2-C(H)=NCH_2CH_2OH-κ-C_1,*N*,*O*}(tmeda)](ClO$_4$), 10. Complex **10** was synthesized following the same procedure as for **9**. Complex **6** (0.200 g, 0.439 mmol) reacted with *N*,*N*,*N*′,*N*′-tmeda (0.056 g, 0.44 mmol) in CH_2Cl_2 (20 mL), giving **10** as an orange solid. Obtained: 0.203 g (87.0% yield). Anal. calc. for $C_{17}H_{30}ClN_3O_7Pd \cdot 0.5CH_2Cl_2$: C, 36.69; H, 5.45; N, 7.33%. Found: C, 36.42; H, 5.23; N, 7.34%. MS (FAB+) *m/z* (%): 430 (85) $[M - ClO_4]^+$, 316 (11) $[M - ClO_4 - tmeda]^+$. IR (ν cm^{-1}): 1608 ($\nu_{C=N}$), 1580, 1553 ($\nu_{C=C}$). ^1H NMR (DMSO-d_6, RT) δ: 8.01 (s, 1H, HC=N), 7.15 (s, 1H, H_3), 6.67 (s, 1H, H_6), 5.03 (t, 1H, OH, $^3J_{H-H} = 4.8$ Hz), 3.87 (s, 3H, CH_3O), 3.72 (s, 3H, CH_3O), 3.64 (m, 2H, CH_2), 3.53 (m, 2H, CH_2), 2.91 (br, 8H, 2 NMe_2 + CH_2, tmeda), 2.65 (br, 8H, 2 NMe_2 + CH_2, tmeda). The product was too insoluble for ^{13}C NMR measurements.

[Pd{C_6H_2-4,5-$(CH_3O)_2$-2-C(H)=NCH_2CH_2OH-κ-C_1,*N*}(dppe)](ClO$_4$), 11. To a suspension of complex **6** (0.200 g, 0.439 mmol) in CH_2Cl_2 (20 mL) was added dppe (0.175 g, 0.439 mmol). The initial yellow suspension gradually dissolved, giving an orange solution. This solution was stirred for 15 min at room temperature, then evaporated to dryness. By addition of Et_2O (25 mL) and continuous stirring, **11** was obtained as an orange solid, which was filtered and air dried. Obtained: 0.192 g (53% yield). Anal. calc. for $C_{37}H_{38}ClNO_7P_2Pd \cdot 0.75CH_2Cl_2$: C, 51.75; H, 4.54; N, 1.59%. Found: C, 51.79; H, 4.43; N, 1.85%. IR (ν cm^{-1}): 3500 (ν_{OH}), 1614 ($\nu_{C=N}$), 1584, 1548 ($\nu_{C=C}$). ^1H NMR ($CDCl_3$, RT) δ: 8.28 (d, 1H, HC=N, $^4J_{P-H} = 8.1$), 7.84–7.46 (m, 20H, Ph), 7.06 (d, 1H, H_3, $^5J_{P-H} = 3$), 6.10 (dd, 1H, H_6, $^4J_{P_{cis}-H} = 5.4$, $^4J_{P_{trans}-H} = 8.4$), 3.74 (s, 3H, OCH_3), 3.41 (m, 2H, CH_2), 2.93 (s, 3H, OCH_3), 2.87 (m, 2H, CH_2), 2.75 (t, 1H, OH, $^3J_{H-H} = 6$ Hz), 2.48–2.30 (m, 4H, CH_2-dppe). $^{31}P\{^1H\}$ NMR ($CDCl_3$, RT) δ: 61.24 (d, $^3J_{P-P} = 25.6$ Hz), 42.69 (d).

Crystal structure determination

Crystals of complexes **4** · $CHCl_3$ and **7** of sufficient quality for X-ray measurements were obtained by slow vapour condensation of Et_2O over a $CHCl_3$ (**4**) or CH_2Cl_2 (**7**) solution of the corresponding crude complex. Geometric and intensity data were measured using normal procedures on an automated Nonius CAD-4 four-circle diffractometer. After preliminary indexing and transformation of the cell to a conventional setting, axial photographs were taken of the *a*-, *b*- and *c*-axes to verify the Laue symmetry and cell dimensions. The scan parameters for intensity data collection were chosen on the basis of two-dimensional (ω–θ) plots of 25 reflections. Three monitor reflections were measured after every three hours of

beam time, and the orientation of the crystal was checked after every 400 intensity measurements. Absorption corrections[26] were based on azimuthal scans of 10 (**4**) or 12 (**7**) reflections that have Eulerian angle χ spread between 50 and $-40°$ when in their bisecting positions. Accurate unit cell dimensions were determined from 25 centered reflections in the 2θ range $27.2 \leqslant 2\theta \leqslant 31.9°$ (**4**) or $24.0 \leqslant 2\theta \leqslant 35.0°$ (**7**), each centered at four distinct goniometer positions. The structures were solved and developed by Patterson and Fourier methods.[27] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in idealized positions and treated as riding atoms, except for those of the methyl groups, which were first located in a local slant-Fourier calculation and then refined as riding atoms with the torsion angles about the O–C(methyl) bonds treated as variables. Each hydrogen atom was assigned an isotropic displacement parameter equal to 1.2 times the equivalent parameter of its parent atom. The interstitial chloroform in $\mathbf{4}\cdot CHCl_3$ was disordered and modelled as three equally populated congeners and their geometrical parameters restrained to be similar. The geometrical parameters of the perchlorate anion in **7** were also restrained to similarity. The structure was refined to F_o^2 and all reflections were used in the least-squares calculations.[28] Data reduction was done using the program XCAD4B.[29]

CCDC reference number 440/240. See http://www.rsc.org/suppdata/nj/b0/b006140i/ for crystallographic files in .cif format.

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