The First Crystal and Molecular Structure of a *syn*-Acetato-Bridged Dinuclear Cyclometallated Complex [Pd{2,3,4-$(MeO)_3C_6HC(H){=}NCH_2CH_2OH$}-($\mu$-OAc)]$_2$

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Treatment of the Schiff base ligands 2,3,4-$(MeO)_3C_6H_2C(H)$=NR (R = CH_2CH_2OH, **1**; R = Me, **17**; R = Et, **18**; R = Pr, **19**; R = *t*Bu, **20**) with palladium(II) acetate in toluene gave the dinuclear cyclometallated complexes [Pd{2,3,4-$(MeO)_3C_6HC(H)$=NR}(μ-O_2CMe)]$_2$ (R = CH_2CH_2OH, **2**; R = Me, **21**; R = Et, **22**; R = Pr, **23**; R = *t*Bu, **24**), with the ligand bonded to the palladium atom through the imine nitrogen and the C6 carbon atoms. The ^{1}H and ^{13}C{^{1}H} NMR spectra of the complexes showed the presence of the *anti* and *syn* isomers in solution. The *anti*/*syn* ratio varies with the solvent and the nature of the imine nitrogen substituent R. Complex **24** with the bulky *t*Bu group showed a 28:1 ratio in chloroform whilst the less bulky substituted complexes showed lower ratios. The X-ray crystal structure of the *syn* isomer of complex **2** is described. Reaction of the acetato-bridged complex **2** with PPh_3 gave the mononuclear complex **4**, in a bridge-splitting reaction. Reaction of **2** with the diphosphanes dppm, dppp and dppb in a 1:1 molar ratio gave the dinuclear cyclometallated complexes **5**, **6** and **7**, respectively. Treatment of **2** with an aqueous solution of sodium chloride gave the chloro-bridged complex **3**. Treatment of the cyclometallated chloro-bridged complex **3** with PPh_3 in acetone yielded the mononuclear complex **8**, and reaction of **3** with silver triflate gave the cyclometallated complex **9**, with the palladium atom bonded to four different atoms C, N, O and P. Treatment of **3** with the tertiary diphosphanes dppp, dppb and dppf, in a 1:1 molar ratio gave the dinuclear complexes **10**, **11** and **12**, respectively, with terminal chloride ligands. However, reaction of **3** with the small "bite" diphosphane dppm gave **13**, with a bridging chloride ligand. Reaction of **11** with silver triflate in acetone gave the new dinuclear complex **14**, with the Schiff base ligand as [C,N,O] terdentate. Reaction of **3** with the diphosphane dppe in a 1:2 molar ratio, and silver perchlorate, gave the mononuclear complex **15**. Treatment of **3** with the triphosphane bis(2-diphenylphosphanylethyl)phenylphosphane in a 1:2 molar ratio, followed by treatment with sodium perchlorate, gave **16**, in which the palladium atom was bonded to the triphosphane through the three phosphorus atoms. The X-ray crystal structures of complexes **8**, **9**, **15** and **16** are also reported.

Introduction

Cyclometallated compounds have attracted much attention in recent years and abundant reports concerning them have appeared.[1−7] They are important not only because they show numerous applications in organic and organometallic synthesis[8] and in biologically active compounds,[9,10] among others, but also due to the new structural features they promote.[11,12] Lately, we have been interested in the study of Schiff base cyclometallated complexes prepared by direct reaction of the ligand with palladium(II) acetate, which gives dimeric acetato-bridged complexes with the characteristic open-book geometry;[13,14] these species are good starting materials for a great number of cyclometallated derivatives. Two different dispositions are possible for such compounds: the *syn* isomer with overall C_s symmetry, and the *anti* isomer with overall C_2 symmetry. The latter is by far the most common, and the known crystal structures of dinuclear acetato-bridged complexes correspond to the *anti* isomer.[10,15−27] We therefore sought to isolate and characterise the *syn* isomer in a pure form by modifying the steric requirements of the substituent at the imine nitrogen atom, i.e., substituents with small or negligible steric hindrance, which should allow the nitrogen atoms to lie above each other in the *syn* form without repulsions arising from the N-R groups, and in the present paper we report the crystal and molecular structure of a dinuclear acetato-bridged cyclometallated complex **2**, which, to the best of our knowledge, is the first example of a *syn* isomer. Compound **2** was obtained as an equilibrium mixture of the *anti* and *syn* isomers, and the features involved in the

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equilibrium are also described. As we have observed before in related compounds with terdentate [C, N, X] (X = N, O, S] ligands,[28–31] the reactivity of the acetate dimeric compounds, and of their chloro-bridged derivatives, is fairly extensive, especially when they react with mono-, di- and triphosphanes, and herein we also report this chemistry, as well as the synthesis of [C, N, O] derivatives with Pd−O bond formation via halide abstraction by a silver(I) salt. The crystal structures of the cyclometallated compounds **8**, **9**, **15** and **16** are also given.

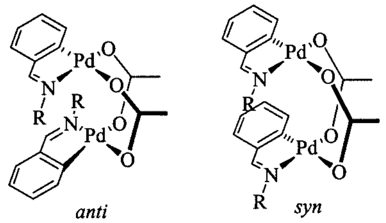


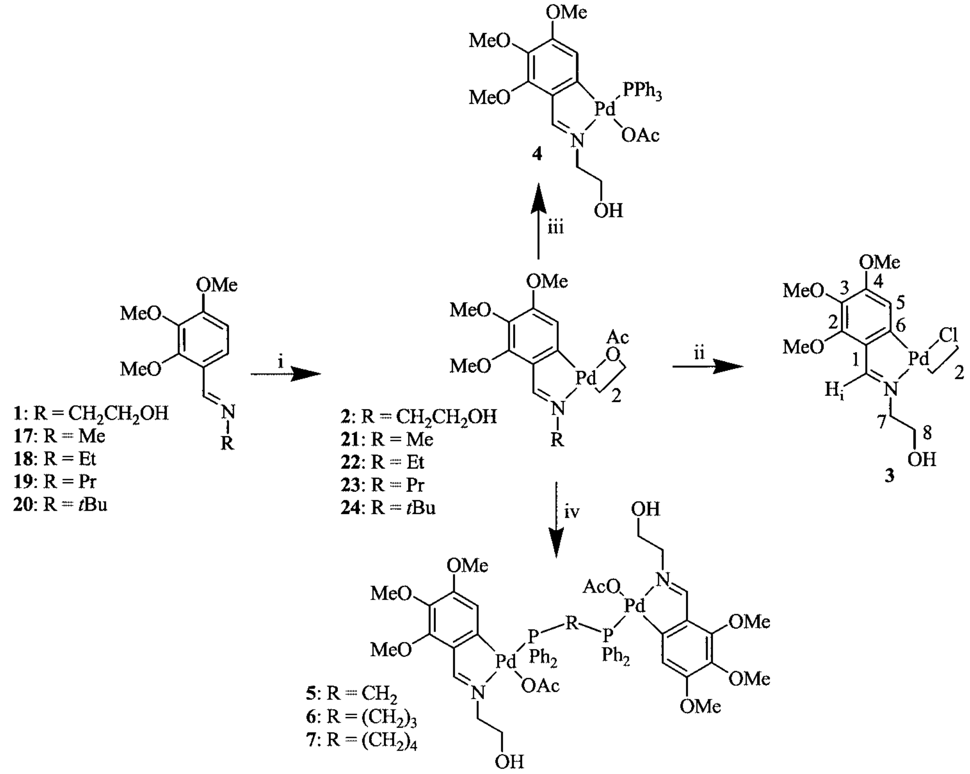
Figure 1. Isomers of compound **2**

Results and Discussion

For the convenience of the reader the compounds and reactions are shown in Schemes 1, 2 and 3. The compounds described in this paper were characterised by elemental analysis (C, H, N), IR spectroscopy and by ^{1}H, $^{31}P\{^{1}H\}$ and, in part, $^{13}C\{^{1}H\}$ NMR spectroscopy and FAB mass spectrometry (data in the Exp. Sect.).

Reaction of the Schiff base ligand 2,3,4-$(MeO)_3$-$C_6H_2C(H){=}NCH_2CH_2OH$ (**1**) with palladium(II) acetate (Scheme 1) gave the dinuclear acetato-bridged complex $[Pd\{2,3,4\text{-}(MeO)_3C_6HC(H){=}NCH_2CH_2OH\}(\mu\text{-}O_2CMe)]_2$ (**2**) as an orange air-stable solid which was fully characterised. *Syn* and *anti* isomers are possible for the folded arrangement of the acetato-bridged dimers: the *anti* isomer with C_2 symmetry and the *syn* isomer with C_s symmetry (see Figure 1), with the *anti* disposition being by far the most frequent.[14]

If both isomers are present in the final product two resonances would be expected for the *H*C=N and aromatic protons and three for the *Me*COO protons in the ^{1}H NMR spectrum: one for the *anti* isomer and two for the *syn* isomer. Thus, the ^{1}H NMR spectrum of **2** shows two sets of signals, one for each isomer. The resonance corresponding to the HC=N proton appears as a singlet (δ = 7.57 and 7.81 ppm, for the *anti* and *syn* isomers, respectively) shifted to lower frequency due to the coordination of the imine group to the palladium atom through the lone pair of the nitrogen atom.[32] The H^5 resonance also appears as a singlet, confirming metallation of the C6 carbon. The ^{1}H NMR spectrum shows the signal of the *Me*COO protons as a singlet at δ = 2.07 ppm, for the *anti* isomer, and as two singlets at δ = 2.25 and 2.02 ppm for the *syn* isomer. The IR spectrum of **2** shows the $\nu(C{=}N)$ stretch at 1604 cm^{-1}, shifted



Scheme 1. (i) $Pd(ACO)_2$, (toluene), (ii) NaCl (acetone/water), (iii) PPh_3 (acetone), (iv) dppm, dppp or dppb (acetone, 1:1 molar ratio)

to lower wavenumbers (relative to the free ligand) due to N-coordination of the imine.[33,34] The IR spectrum also shows strong bands assigned to the symmetric and asymmetric ν(COO) vibrations, in agreement with bridging acetate ligands[35] (see Exp. Sect.). The ν(O−H) stretch appears at 3384 cm^{-1}, close to its position in the spectrum of the free ligand, in agreement with a noncoordinated hydroxyl group. From the integration of the peaks corresponding to both isomers in the ^{1}H NMR spectrum we concluded that the *anti*/*syn* ratio is ca. 5:1

The ^{13}C{^{1}H} NMR spectrum showed the presence of signals corresponding to both isomers, with the C=N, C6 and C1 resonances shifted toward higher frequency, thus confirming that metallation had occurred.[28] The mass FAB spectrum of **2** shows a cluster of peaks, centred at 808 amu, which correspond to [M]$^+$. The isotopic pattern is in good agreement with the expected dinuclear structure.

The synthesis of complex **2** was performed under different reaction conditions: toluene at 60 °C, chloroform at room temperature and boiling methanol. Irrespective of the method used the *anti*/*syn* ratio is ca. 5:1 in all cases, which seems to be the equilibrium ratio. Although we cannot ascertain completely that the solid state of **2** contains only crystals of the *syn* form, the ^{1}H NMR spectrum of the solid, freshly dissolved in CDCl$_3$, also shows the presence of both isomers in the resulting solution in a 5:1 ratio, and the relative amount of isomers does not vary perceptively with temperature: heating a chloroform solution does not change the ^{1}H NMR spectrum of **2**, nor its concentration. However, the solvent in which the spectra were recorded does have a noticeable effect on the isomer ratio. Thus, the ^{1}H NMR spectrum in [D$_3$]acetonitrile shows an *anti*/*syn* ratio of 3:1 and a solution in [D$_6$]acetone a ratio of ca. 4:1, whereas dissolution in [D$_6$]DMSO causes partial decomposition of the compound. Nevertheless, the ^{1}H NMR spectrum recorded after removal of [D$_6$]acetone from the NMR tube and dissolution of the product in CDCl$_3$, again shows the initial 5:1 ratio. Therefore, it seems that solubility factors could account for such an equilibrium. Furthermore, we also considered that steric factors should be regarded, i.e., the bulkiness of the -N−R group could also influence the *anti*/*syn* ratio. It is known that most of the acetato-bridged dimer complexes for which the existence of *syn* and *anti* isomers has been reported are phenylimidazole derivatives. The imidazole ligand, after [C,N] coordination to the palladium atom, adopts a *quasi* planar disposition,[36−39] and we therefore suppose that the small steric repulsion between the imidazole rings in the *syn* disposition should favour this geometry. However, Schiff base ligands with more or less bulky substituents at the imine nitrogen should favour a *trans* disposition in order to avoid the steric hindrance. In complex **2**, the CH$_2$CH$_2$OH moiety allows a *cis* disposition of the ligands. To confirm this we prepared analogues to **1**, ligands **17−20**, which, upon reaction with palladium(II) acetate in toluene (Scheme 1), gave the acetato-bridged complexes [Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=NR}(μ-O$_2$CMe)]$_2$, (**21**, R = Me; **22**, R = Et; **23**, R = Pr; **24**, R = *t*Bu). The resonances for the *anti* and *syn* isomers were ascribed accordingly (see Exp. Sect.).

The integration of the signals corresponding to both isomers showed that the *anti*/*syn* ratio is ca. 7.5:1 for complexes **21**, **22** and **23** in CDCl$_3$, whereas in [D$_6$]acetone a 5:1 ratio is observed (cf. compound **2**), and for complex **24**, with the bulky *t*Bu moiety bonded to the imine nitrogen a value of 28:1 is found.

Molecular Structure of [Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=NCH$_2$CH$_2$OH}(μ-OAc)]$_2$ (2)

Suitable crystals were grown by slowly evaporating a chloroform/*n*-hexane solution of the complex. The molecular structure is illustrated in Figure 2. Crystal data are given in Table 1 and selected bond lengths and angles with estimated standard deviations are shown in Table 2.

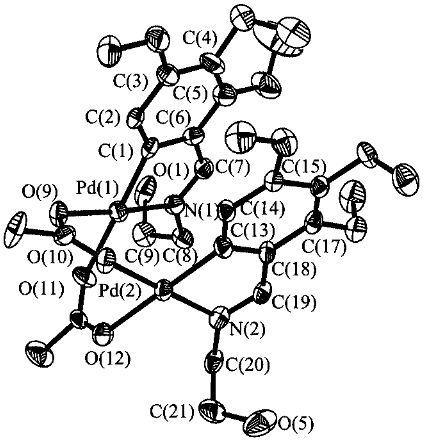


Figure 2. Molecular structure of [Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=NCH$_2$CH$_2$OH)}(μ-OAc)]$_2$ (**2**), with labelling scheme; hydrogen atoms have been omitted for clarity

The structure consists of dimeric molecules at van der Waals distances. The molecular structure corresponds to the *syn* isomer, with the cyclometallated moieties in an open-book disposition and two acetate ligands bridging the palladium atoms. Although a large number of crystal structures of dinuclear acetato-bridged cyclometallated complexes have been reported, to the best of our knowledge this is the first example of a *syn* disposition of the metallated ligands.

The Pd(1)−Pd(2) bond length of 2.8514(13) Å is similar to values reported for related complexes [13] and can be regarded as nonbonding. Each palladium atom is bonded in a slightly distorted square-planar geometry to four atoms: a carbon atom of the phenyl ring and the imine nitrogen atom of the Schiff base ligand, and two oxygen atoms of the bridging acetate ligands.

The sum of the angles around the palladium atoms is approximately 360°. The angles between adjacent atoms in the coordination sphere are close to the expected value of 90°, with the most noticeable distortions corresponding to the C(1)−Pd(1)−N(1) and C(13)−Pd(2)−N(2) angles [81.9(4) and 82.1(4)°, respectively] due to chelation. The

Table 1. Crystallographic Data for complexes **2**, **8**, **9** and **16**

	2	**8**	**9**	**15**	**16**
Empirical formula	$C_{28}H_{42}N_2O_{14}Pd_2$	$C_{30}H_{31}NO_4ClPPd$	$C_{31}H_{31}NO_7F_3ClPPdS$	$C_{38}H_{40}NO_8ClP_2Pd$	$C_{46}H_{49}NO_8ClP_3Pd$
Formula mass	843.44	642.38	756.00	842.50	978.62
T [K]	293(2)	293(2)	293(2)	293(2)	293(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Triclinic	Orthorhombic	Monoclinic
Space group	$P2_1/a$	$P\bar{1}$	$P\bar{1}$	Pbca	$P2_1/n$
a [Å]	10.552(1)	9.631(1)	9.280(1)	17.267(2)	11.397(2)
b [Å]	28.406(2)	10.174(1)	10.860(1)	18.250(2)	21.492(4)
c [Å]	12.173(1)	15.029(1)	17.512(1)	24.162(3)	19.189(4)
α [°]		96.623(1)	99.472(1)		
β [°]	109.814(2)	107.717(1)	104.640(1)		106.739(4)
γ [°]		95.514(1)	106.296(1)		
V [Å^3]	3432.7(5)	1386.9(1)	1585.4(1)	7614.0(1)	4501.0(1)
Z	4	2	2	8	4
μ [mm^{-1}]	1.114	0.860	0.767	0.693	0.632
Max., min. transmissions	0.81, 0.73	0.88, 0.75	0.70, 0.70	0.95, 0.75	0.96, 0.83
$\rho_{calc.}$ [gcm^{-3}]	1.632	1.538	1.584	1.470	1.444
θ range [°]	1.43 to 25.00	1.43 to 29.10	2.02 to 28.32	1.69 to 28.32	1.46 to 26.45
Reflections collected	18957	10056	11258	45948	9253
Independent reflections	6053 (R_{int} = 0.020)	6786 (R_{int} = 0.037)	7716 (R_{int} = 0.017)	9254 (R_{int} = 0.072)	9253 (R_{int} = 0.028)
R_1[a]	0.0776	0.0460	0.0294	0.0412	0.0466
wR_2[b]	0.1690	0.1992	0.0776	0.1137	0.0829

[a] $R_1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$, $[F > 4\sigma(F)]$. [b] $wR_2 = \Sigma[w(F_0{}^2 - F_c{}^2)^2/\Sigma w(F_0{}^2)^2]^{1/2}$, all data.

Table 2. Selected bond lengths (Å) and angles (°) for complex **2**

Pd(1)−Pd(2)	2.8514(13)		
Pd(1)−C(1)	1.973(11)	Pd(2)−C(13)	1.963(10)
Pd(1)−N(1)	2.018(9)	Pd(2)−N(2)	2.012(9)
Pd(1)−O(9)	2.084(7)	Pd(2)−O(10)	2.064(8)
Pd(1)−O(11)	2.131(7)	Pd(2)−O(12)	2.130(8)
C(1)−C(6)	1.396(15)	C(13)−C(18)	1.384(15)
C(6)−C(7)	1.434(15)	C(18)−C(19)	1.424(14)
N(1)−C(7)	1.276(13)	N(2)−C(19)	1.298(13)
C(1)−Pd(1)−N(1)	81.9(4)	C(13)−Pd(2)−N(2)	82.1(4)
C(1)−Pd(1)−O(9)	93.3(4)	C(13)−Pd(2)−O(10)	95.0(4)
N(1)−Pd(1)−O(9)	175.1(4)	N(2)−Pd(2)−O(10)	175.8(3)
C(1)−Pd(1)−O(11)	178.6(4)	C(13)−Pd(2)−O(12)	176.0(4)
N(1)−Pd(1)−O(11)	97.7(4)	N(2)−Pd(2)−O(12)	94.8(4)
O(9)−Pd(1)−O(11)	87.2(3)	O(10)−Pd(2)−O(12)	88.2(3)

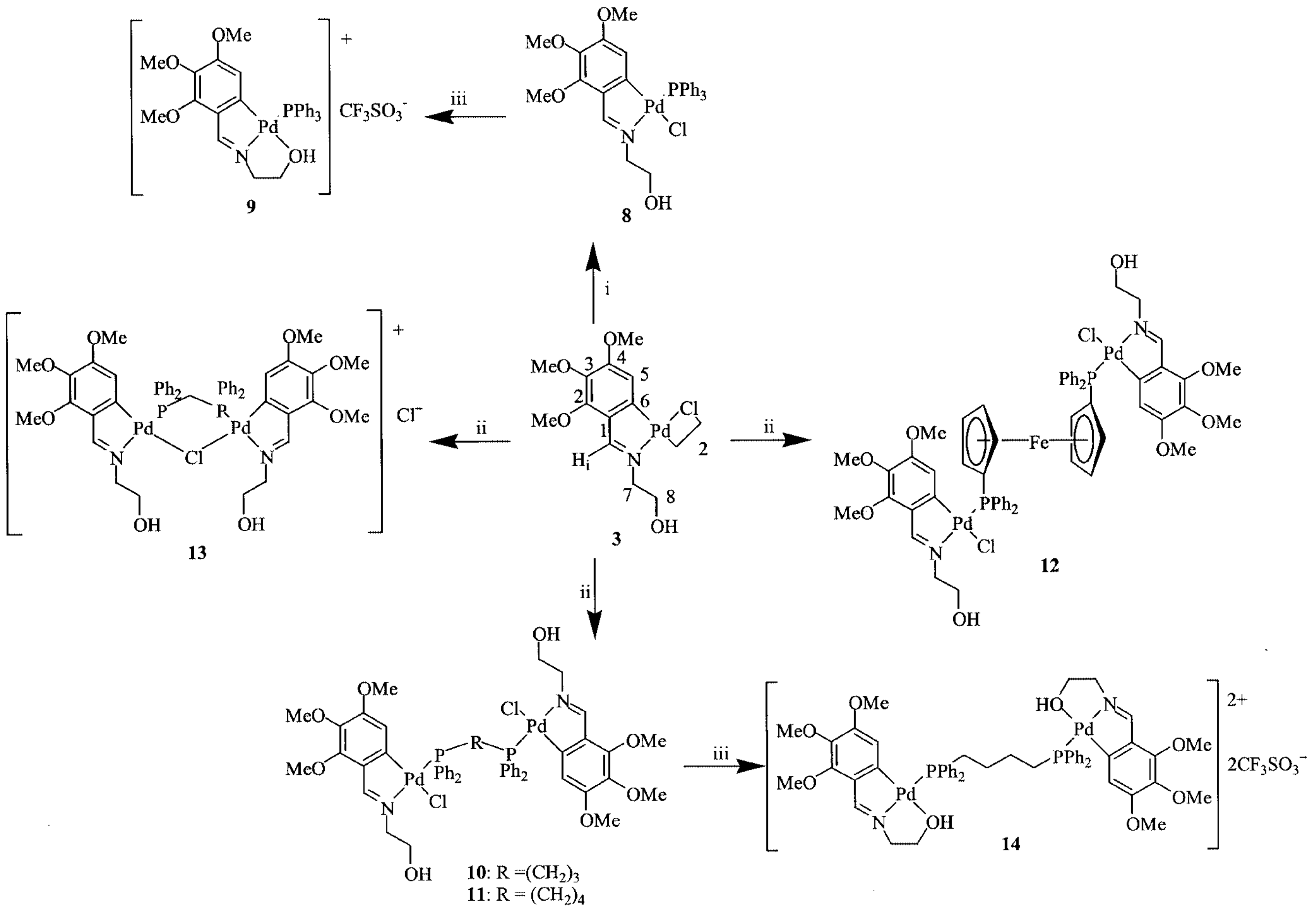
Pd(1)−C(1) and Pd(2)−C(13) bond lengths of 1.973(11) and 1.963(10) Å, respectively, are somewhat shorter than the values predicted from their covalent radii[40] but similar to values found earlier.[13,14] However, the Pd(1)−N(1) and Pd(2)−N(2) bond lengths of 2.018(9) and 2.012(9) Å, respectively, are in agreement with the value based on the sum of the covalent radii for nitrogen and palladium,[40] and are similar to values reported previously.[13,14] The differing Pd(1)−O(9) and Pd(1)−O(11) [2.084(7) and 2.131(7) Å, respectively] and Pd(2)−O(10) and Pd(2)−O(11) [2.064(8) and 2.130(8) Å, respectively] bond lengths reflect the higher *trans* influence of the aryl carbon as compared to the imine nitrogen atom.

As a result of the palladium atoms being bridged by two mutually *cis* μ-acetate ligands the metallated Schiff bases are forced to lie above one another in the dimeric molecules. This leads to inter-ligand repulsions and results in the coordination planes of the palladium atoms (planes 1 and 2) being tilted at an angle of 25.0°. The disposition of the chelating C,N ligands is not completely eclipsed, probably as a consequence of these repulsions. This is shown by the dihedral angles C(1)−Pd(1)−Pd(2)−C(13), N(1)−Pd(1)−Pd(2)−N(2), O(9)−Pd(1)−Pd(2)−O(10) and O(11)−Pd(1)−Pd(2)-0(12) of 17.3(5), 17.6(4), 15.3(3) and 14.0(3)°, respectively. No intra- or intermolecular O−H···O−H bonding is observed.

Reactivity of the Acetato-Bridged Complex 2

The reaction of **2** with aqueous sodium chloride gave the chloro-bridged complex [Pd{2,3,4-$(MeO)_3C_6HC(H)=NCH_2CH_2OH$}(μ-Cl)]$_2$ (**3**; Scheme 2), which was fully characterised (see Exp. Sect.). The IR spectrum of this complex shows the absence of the ν(COO) bands. The ^{1}H NMR spectra of **3** shows the HC=N and H^5 resonances at δ = 8.08 and 7.51 ppm, respectively.

Reaction of **2** with PPh_3 gave the complex [Pd{2,3,4-$(MeO)_3C_6HC(H)=NCH_2CH_2OH$}($O_2CMe$)($PPh_3$)] (**4**) as an air-stable solid which was fully characterised (see Exp. Sect.). The IR spectrum of **4** shows strong bands at 1290 and 1570 cm^{-1} assigned to the symmetric and asymmetric ν(COO) vibrations, respectively, in agreement with those expected for monocoordinate acetate ligands.[35] The IR spectrum also shows the νC=N stretch at 1613 cm^{-1}. This absorption is shifted to lower wavenumbers relative to the free ligand due to N-coordination of the imine;[32] the ν(O−H) band at 3400 cm^{-1} (3402 cm^{-1} in the free ligand) is as ex-



Scheme 2. (i) PPh_3 (acetone), (ii) dppm, dppp, dppb or dppf (acetone, 1:1 molar ratio), (iii) $AgCF_3SO_3$ (acetone)

pected for a noncoordinated OH group. The ^1H NMR spectrum shows the $HC{=}N$ and H^5 resonances coupled to the phosphorus nucleus [$\delta = 8.31$ ($J_{P,H} = 7.8$) and $\delta = 5.70$ ($J_{P,H} = 5.8$ Hz), respectively], and the $C(4){-}OCH_3$ resonance shifted towards lower frequency by ca. 0.8 ppm, relative to complex **2**, due to the shielding effects of the phosphane phenyl ring;[41] in the $^{31}P\{^1H\}$ spectrum the resonance of the coordinated phosphane appears as a singlet at $\delta = 40.8$ ppm. These findings are in agreement with a phosphorus *trans* to nitrogen arrangement, as we and others have observed earlier, which seems to be the more common arrangement for the entering phosphane.[41−46] The novel term *transphobia* has been introduced by J. Vicente et al. to describe the restricted coordination of mutually *trans* phosphanes and phenyl carbon atoms.[44,45]

The FAB-mass spectrum shows peaks centred at 666 and 608 amu assigned to the $[MH]^+$ and $[M - OAc]^+$ fragments, respectively.

Reaction of complex **2** with $Ph_2PCH_2PPh_2$ (dppm), $Ph_2P(CH_2)_3PPh_2$ (dppp) or $Ph_2P(CH_2)_4PPh_2$ (dppb), in a 1:1 complex-to-phosphane molar ratio gave the dinuclear cyclometallated complexes $[\{Pd[2,3,4\text{-}(MeO)_3C_6HC(H){=}NCH_2CH_2OH](O_2CMe)\}_2(\mu\text{-}Ph_2P(CH_2)_nPPh_2)]$ (**5**, $n = 1$; **6**, $n = 3$; **7**, $n = 4$). The IR spectra of these complexes are in agreement with monocoordinate acetate ligands and with noncoordinated hydroxyl groups (vide supra). The ^1H NMR spectra show the coupling of the $HC{=}N$ and the H^5 resonances to the phosphorus nucleus, and in the $^{31}P\{^1H\}$ NMR spectra the resonance of the phosphorus nuclei appears as a singlet at ca. $\delta = 31$ ppm in accordance with the centrosymmetric nature of the complexes. We tentatively propose this structure in accordance with the conductivity data for **5**, **6** and **7**, which show them to be nonelectrolytes.

Reaction of the cyclometallated chloro-bridged complex **3** with PPh_3 in acetone yielded the mononuclear complex $[Pd\{2,3,4\text{-}(MeO)_3C_6HC(H){=}NCH_2CH_2OH\}(Cl)(PPh_3)]$ (**8**) which was fully characterised (see Exp. Sect.). The IR and NMR spectra of **8** are similar to those for complex **4**; the most noticeable difference in the IR spectra is the absence of the ν(COO) bands.

The ^1H NMR spectrum shows doublets assigned to the $HC{=}N$ and H^5 protons coupled to the ^{31}P nucleus [$\delta = 8.38$ ppm ($J_{P,H} = 8.3$) and $\delta = 5.74$ ppm ($J_{P,H} = 6.3$ Hz), respectively], and the $^{31}P\{^1H\}$ NMR spectrum shows a singlet resonance at $\delta = 40.3$ ppm. The mass FAB spectrum shows peaks centred at 606 amu corresponding to the $[M - Cl]^+$ fragment.

Treatment of **3** with the tertiary diphosphanes $Ph_2P(CH_2)_3PPh_2$ (dppp), $Ph_2P(CH_2)_4PPh_2$ (dppb) and $Ph_2PC_5H_4FeC_5H_4PPh_2$ (dppf) in a 1:1 molar ratio gave the dinuclear complexes $[\{Pd[2,3,4\text{-}(MeO)_3C_6HC(H){=}NCH_2CH_2OH](Cl)\}_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}]$, (**10**, $n = 3$; **11**,

n = 4), and the trinuclear compound [{Pd[2,3,4-(MeO)$_3$-C$_6$HC(H)=NCH$_2$CH$_2$OH](Cl)}$_2${μ-Ph$_2$PC$_5$H$_4$FeC$_5$H$_4$-PPh$_2$}] (**12**), respectively. The IR and NMR spectra of these complexes show similar features to those described for the spectra of compound **8** suggesting a similar disposition around the palladium atoms. The ^{31}P{^{1}H} NMR spectrum shows a singlet resonance for the phosphorus nuclei indicating the symmetric nature of the complexes. Conductivity measurements in dry acetonitrile showed the complexes to be molecular nonelectrolytes.

However, when complex **3** was reacted with Ph$_2$PCH$_2$PPh$_2$ (dppm) the dinuclear complex [{Pd[2,3,4-(MeO)$_3$C$_6$HC(H)=NCH$_2$CH$_2$OH]}$_2$(μ-Cl)(μ-Ph$_2$PCH$_2$-PPh$_2$)][Cl] (**13**) was obtained (see Exp. Sect.). The ^{1}H NMR spectrum also shows coupling of the *H*C=N and H^5 protons to the phosphorus nucleus and the ^{31}P{^{1}H} NMR spectra shows a singlet resonance. The specific molar conductivity in dry acetonitrile (175.1 ohm^{-1} cm^2 mol^{-1}) is in agreement with the value expected for a 1:1 electrolyte.[47] This behaviour is in contrast to that observed for compound **5**, where a 1:1 electrolyte formulation with both palladium atoms bridged by the diphosphane and by one acetate ligand would be possible. However, the low conductivity values preclude this formulation for **5**.

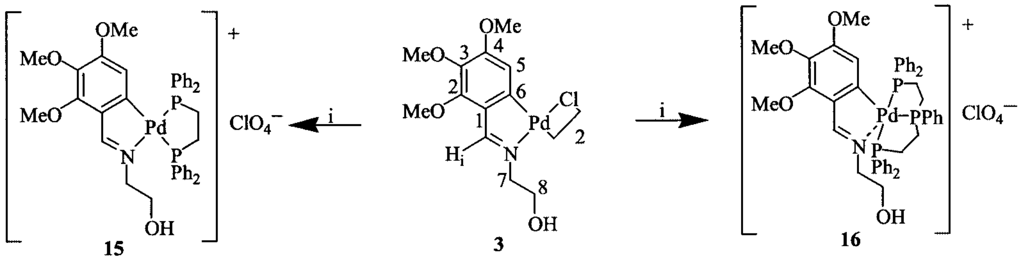
In order to promote coordination of the hydroxyl oxygen, thus giving a coordinated [C,N,O] ligand, we treated the cyclometallated complexes **8** and **11** with silver triflate to remove the chloride moiety. Thus, treatment of **8** with silver triflate gave the complex [Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=NCH$_2$CH$_2$OH}(PPh$_3$)][CF$_3$SO$_3$] (**9**) and an AgCl precipitate. The IR spectrum shows a band assigned to the ν(O−H) vibration at 3245 cm^{-1} shifted to lower wavenumber (3402 and 3365 cm^{-1} in the spectra of the free ligand and compound **8**, respectively) due to Pd−O bond formation.[48] The most noteworthy differences in the ^{1}H NMR spectrum of **9** from that of **8** are in the lowfield shift of the -O*H* hydroxyl proton resonance which appears as a triplet at δ = 7.02 ppm ($J_{H,H}$ = 5.6 Hz), (for complex **8** a broad resonance at ca. δ = 3.2 ppm was assigned to O*H*) and the resolution of the C*H*$_2$C*H*$_2$OH signals, which appear as a multiplet in the spectrum of **8** at δ = 4.03 ppm and as two broad resonances at δ = 4.13 and 3.89 ppm for **9**.

In the ^{13}C{^{1}H} NMR spectrum the resonances assigned to the *C*H$_2$*C*H$_2$OH carbon atoms appear at δ = 67.7 and 56.8 ppm shifted to high and low frequency, respectively, relative to compound **8** (δ = 62.9 and 61.8 ppm in the spectrum of **8**). We have observed a similar behaviour in the ^{13}C{^{1}H} NMR spectra of cyclometallated complexes derived from the Schiff base ligand 2-ClC$_6$H$_4$C(H)=NCH$_2$CH$_2$NMe$_2$ with formation of a new Pd−NMe$_2$ bond after treatment with a silver(I) salt.[29] Conductivity measurements carried out in dry acetonitrile gave a value for the molar conductivity of 116.2 ohm^{-1} cm^2 mol^{-1}, characteristic of 1:1 electrolytes.[47]

Similarly, when compound **11** was treated with silver triflate in acetone the new dinuclear complex [{Pd[2,3,4-(MeO)$_3$C$_6$HC(H)=NCH$_2$CH$_2$OH]}$_2${μ-Ph$_2$P(CH$_2$)$_4$PPh$_2$}]-[CF$_3$SO$_3$]$_2$ (**14**) was obtained with the Schiff base ligand as [C,N,O] terdentate. The IR spectrum of this complex shows a broad band due to the ν(O−H) stretch centred at ca. 3250 cm^{-1}. The ^{1}H NMR spectrum shows similar features to those observed for the spectrum of **9**. Similarly, the ^{13}C{^{1}H} NMR spectrum shows the signals assigned to the methylene carbon atoms at δ = 66.3 and 57.5 ppm. Conductivity measurements carried out in dry acetonitrile showed the complex to be a 1:2 electrolyte.

Reaction of complex **3** with the diphosphane Ph$_2$P(CH$_2$)$_2$PPh$_2$ (dppe) in a 1:2 molar ratio, followed by treatment with sodium perchlorate, gave the mononuclear complex [Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=NCH$_2$CH$_2$OH}-{PPh$_2$(CH$_2$)$_2$PPh$_2$-*P,P*}][ClO$_4$] (**15**; Scheme 3) as an air-stable solid which was fully characterised (see Exp. Sect.). The ^{1}H NMR spectrum shows the signal corresponding to H^5 at δ = 5.93 ppm, coupled to both phosphorus atoms ($J_{H,P}$ = 8.8, 5.8 Hz). However, the *H*C=N resonance only shows coupling to the ^{31}P nucleus *trans* to nitrogen (δ = 8.50 ppm; $J_{H,P}$ = 8.3 Hz). The ^{31}P{^{1}H} NMR spectrum shows two doublets for the two nonequivalent phosphorus nuclei (δ = 61.0, 43.0 ppm; $J_{P,P}$ = 25.4 Hz). The resonance at lower frequency was assigned to the phosphorus nucleus *trans* to the phenyl carbon atom in accordance with the higher *trans* influence of the latter with respect to the C=N nitrogen atom.[49] The ^{13}C{^{1}H} spectrum shows coupling of the C6 resonance to the two phosphorus nuclei (δ = 156.0 ppm; $J_{P,C}$ = 12.0, 5.6 Hz). Conductivity measurements were in accordance with a 1:1 electrolyte formulation.

Treatment of **3** with the triphosphane bis(2-diphenylphosphanylethyl)phenylphosphane in a 1:2 molar ratio, followed by treatment with sodium perchlorate, gave [Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=NCH$_2$CH$_2$OH}{(PPh$_2$CH$_2$-CH$_2$)$_2$PPh-*P,P,P*}][ClO$_4$] (**16**; Scheme 3). The phosphorus resonances in the ^{31}P{^{1}H} NMR spectrum of **16** are shifted downfield from their values in the free phosphane sug-



Scheme 3. (i) 1: dppe or triphos (acetone, 1:2 molar ratio), 2: NaClO$_4$

gesting coordination of the three phosphorus atoms to the metal centre. A triplet resonance at δ = 86.0 ppm was assigned to the central ^{31}P nucleus *trans* to the phenyl carbon atom, and a doublet at δ = 44.5 was assigned to the two equivalent mutually *trans* phosphorus nuclei. This latter signal appears at lower frequency due to the higher *trans* influence of the phosphane ligand.[49] The resonance of the proton in the *ortho* position to the metallated carbon atom appears as a doublet of triplets showing coupling to the central ^{31}P atom ($J_{P,H}$ = 8.8 Hz) and to the terminal phosphorus atoms ($J_{P,H}$ = 2.4 Hz). The shift of the ν(C=N) stretching vibration to lower wavenumber in the IR spectrum and the upfield shift of the HC=N proton resonance in the ^{1}H NMR spectra indicate the existence of a palladium-nitrogen interaction in solution. These results strongly agree with those previously obtained by us in related pentacoordinate palladium(II) species,[12] and although the proposed structure in Scheme 3 seems slightly different from the solid state structure (Figure 6), we suggest the former as the probable solution disposition; for a thorough discussion regarding this issue see ref.[12] The C=N signal in the ^{13}C{^{1}H} NMR spectrum at δ = 167.3 ppm coupled to the central phosphorus ($J_{P,C}$ = 5.7 Hz) is also indicative of a Pd-N interaction. Molar conductivity measurements showed that complex **16** is a 1:1 electrolyte. The FAB-mass spectrum shows a set of peaks centred at 979 and 877 amu assigned to the [M]$^{+}$ and the [M − ClO$_4$]$^{+}$ fragments, respectively.

Molecular Structure of Complexes 8, 9, 15 and 16

Suitable crystals were grown by slowly evaporating chloroform solutions of the complexes. Crystal data are given in Table 1 and selected bond lengths and angles with estimated standard deviations are shown in Table 3.

[Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=NCH$_2$CH$_2$OH}(Cl)-(PPh$_3$)] (8)

The crystal structure of this complex (Figure 3) consists of discrete molecules separated by van der Waals distances. The palladium atom is bonded in a slightly distorted square-planar geometry to the C(1) carbon atom of the phenyl ring, to the imine N(1) atom of the Schiff base ligand, to the Cl(1) atom and to the P(1) phosphorus atom of the triphenylphosphane ligand. The angles between adjacent atoms in the coordination sphere of palladium are close to the expected value of 90° with the most noticeable distortions corresponding to the bite angle C(1)−Pd(1)−N(1) of 82.8(2)°. The sum of the angles about palladium is approximately 360°.

The geometry around palladium is planar [mean deviation from the least-square plane Pd(1), C(1), N(1), P(1), Cl(1), (plane 1), of 0.960 Å] and approximately co-planar with the metallated ring [Pd(1), C(1), C(6), C(7), N(1), mean deviation 0.0166 Å (plane 2)] and with the phenyl ring [plane 3, mean deviation of 0.0031 Å] (angles between planes are: plane 1:2, 6.0°; plane 1:3, 10.1°; 2:3, 5.0°). All bond lengths and angles are normal. The OH group, hydrogen H(1) and the Cl(1) atom are bonded by intramolecular H-bonding [O(1)−H(1)···Cl(1): 3.079(6) Å, 173.8°].

Table 3. Selected bond lengths (Å) and angles (°) for complexes **8**, **9**, **15** and **16**

	8	**9**	**15**	**16**
Pd(1)−C(1)	2.061(5)	1.997(2)	2.052(4)	2.064(4)
Pd(1)−P(1)	2.2443(13)	2.2751(5)	2.2557(10)	2.2893(12)
Pd(1)−N(1)	2.093(4)	2.028(2)	2.108(3)	2.480(3)
Pd(1)−Cl(1)	2.4263(15)			
Pd(1)−O(1)		2.208(1)		
Pd(1)−P(2)			2.33347(10)	2.2773(11)
Pd(1)−P(3)				2.3243(12)
C(1)−C(6)	1.407(7)	1.411(3)	1.409(5)	1.387(5)
C(6)−C(7)	1.482(8)	1.448(3)	1.447(5)	1.456(5)
N(1)−C(7)	1.285(7)	1.271(3)	1.279(5)	1.274(4)
C(1)−Pd(1)−N(1)	82.80(19)	82.31(7)	80.6(1)	76.0(1)
N(1)−Pd(1)−P(1)	171.37(12)	177.29(5)	175.22(9)	113.81(9)
C(1)−Pd(1)−P(1)	92.60(15)	99.85(5)	95.9(1)	95.9(1)
C(1)−Pd(1)−Cl(1)	171.38(14)			
P(1)−Pd(1)−Cl(1)	94.48(5)			
N(1)−Pd(1)−Cl(1)	90.78(13)			
N(1)−Pd(1)−O(1)		77.46(6)		
C(1)−Pd(1)−O(1)		159.33(7)		
P(1)−Pd(1)−O(1)		100.19(4)		
P(2)−Pd(1)−P(1)			84.52(4)	84.24(4)
P(2)−Pd(1)−N(1)			98.79(9)	109.69(9)
C(1)−Pd(1)−P(2)			176.8(1)	173.7(1)
N(1)−Pd(1)−P(3)				90.61(9)
P(1)−Pd(1)−P(3)				155.43(4)
P(2)−Pd(1)−P(3)				85.01(4)
C(1)−Pd(1)−P(3)				92.4(1)

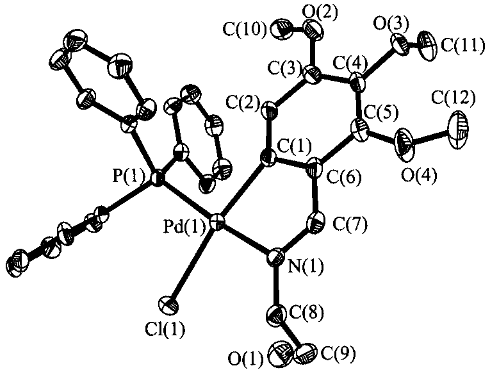


Figure 3. Molecular structure of complex [Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=NCH$_2$CH$_2$OH}(Cl)(PPh$_3$)] (**8**), with labelling scheme; hydrogen atoms have been omitted for clarity

[Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=NCH$_2$CH$_2$OH}(PPh$_3$)]-[CF$_3$SO$_3$] (9)

The crystal structure of this complex (Figure 4) contains one [Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=NCH$_2$CH$_2$OH)}(PPh$_3$)]$^{+}$ cation and one CF$_3$SO$_3$$^{-}$ anion per asymmetric unit.

The palladium atom is bonded in a slightly distorted square-planar geometry to the C(1) carbon atom of the phenyl ring, the imine N(1) nitrogen atom, the O(1) oxygen atom and to the phosphorus atom of the triphenylphos-

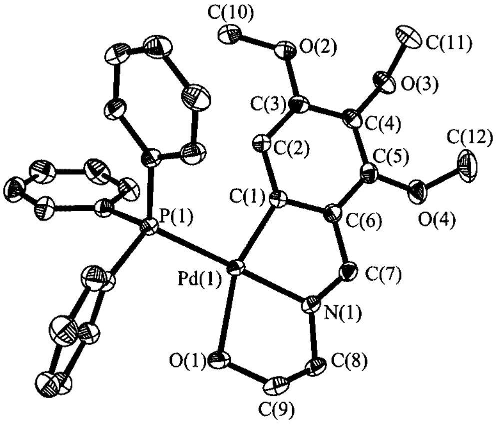


Figure 4. Perspective view of the cation of complex [Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=NCH$_2$CH$_2$OH}(PPh$_3$)][CF$_3$SO$_3$] (**9**), with labelling scheme; hydrogen atoms have been omitted for clarity

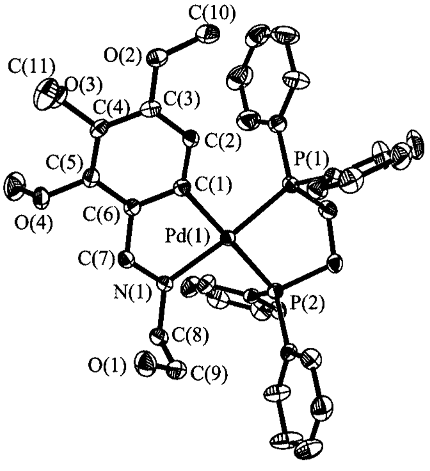


Figure 5. Perspective view of the cation of complex [Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=NCH$_2$CH$_2$OH}{PPh$_2$(CH$_2$)$_2$PPh$_2$-*P,P*}][ClO$_4$] (**15**), with labelling scheme; hydrogen atoms have been omitted for clarity

phane ligand P(1). The angles between adjacent atoms in the coordination sphere of palladium are close to the expected value of 90°, with the most noticeable distortions corresponding to the C(1)−Pd(1)−N(1) and N(1)−Pd(1)−O(1) angles of 81.31(7)° and 78.46(6)°, respectively. The sum of the angles about palladium is approximately 360°.

The cation of **9** forms hydrogen bonds with the CF$_3$SO$_3$ anion [O(1)−H(1)···O(2s): 3.783(3) Å, 165(4)°].

The most noticeable differences between the structures of complexes **8** and **9** correspond to a shortening of the Pd−C and Pd−N bond lengths [2.061(5) and 2.093(4) Å, respectively, for complex **8** vs. 1.997(2) and 2.028(2) Å, also respectively, for complex **9**] and the greater C(1)−Pd(1)−P(1) angle [92.60(15)° for complex **8**; 99.85(5)° for complex **9**]. The latter is probably due to the steric repulsion between the large chlorine Cl(1) atom in complex **8**, as opposed to the smaller O(1) oxygen atom in complex **9**, and the bulky PPh$_3$ ligand. In complex **9**, the small "bite" of the NCH$_2$CH$_2$OH chelate [shown by the N(1)−Pd(1)−O(1) bond angle of 77.46(6)°], which forces the O(1) hydroxyl oxygen and the phosphorus P(1) atoms apart, also reduces repulsion.

[Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=NCH$_2$CH$_2$OH}{PPh$_2$-(CH$_2$)$_2$PPh$_2$-P,P}][ClO$_4$] (15)

The crystal structure of this complex (Figure 5) contains one [Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=NCH$_2$CH$_2$OH}{PPh$_2$-(CH$_2$)$_2$PPh$_2$-*P,P*}]$^+$ cation and one ClO$_4$$^-$ anion per asymmetric unit. The palladium atom is bonded to four atoms: the adjacent C(1) carbon atom and the N(1) nitrogen of the Schiff base ligand **1**, and the phosphorus atoms P(1) and P(2) of the dppe ligand. The different *trans* influences of the C(1) carbon atom and the N(1) nitrogen atom are reflected in the somewhat enlarged Pd(1)−P(2) bond length of 2.3335(1) Å [Pd(1)−P(1): 2.256(1) Å]. These distances are in agreement with values previously reported.[28,48,50] Hydrogen bonding between the O−H(1) hydroxyl hydrogen and O(3s) oxygen atom of the perchlorate anion was found [O(1)−H(1)···O(3s): 3.021(6) Å, 156(11)°].

Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=NCH$_2$CH$_2$OH}{(PPh$_2$-CH$_2$CH$_2$)$_2$PPh-P,P,P}][ClO$_4$] (16)

The crystal structure of this complex (Figure 6) contains one [Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=NCH$_2$CH$_2$OH}{(PPh$_2$-CH$_2$CH$_2$)$_2$PPh-*P,P,P*}]$^+$ cation and one ClO$_4$$^-$ anion per asymmetric unit. The palladium atom is bonded to the C(1) carbon atom of the metallated ring and to the three phosphorus atoms P(1), P(2) and P(3), of the triphos ligand. A fifth interaction with the imine nitrogen completes the coordination sphere about the palladium atom.

The Pd(1)−N(1) distance of 2.480(3) Å is somewhat longer than the values of 2.338(3) Å, reported recently by us in a similar complex with a triphos ligand[51] and 2.23(2)

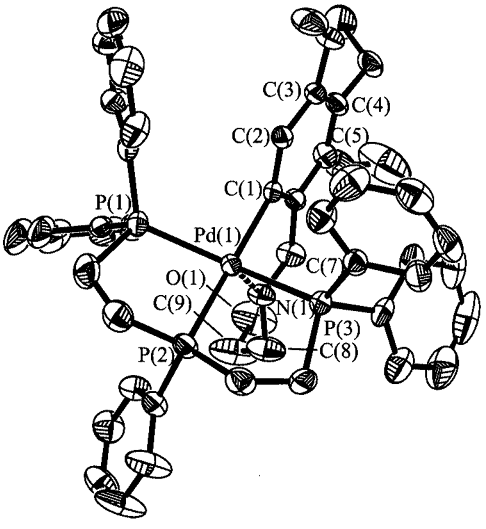


Figure 6. Perspective view of the cation of complex [Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=NCH$_2$CH$_2$OH}{(PPh$_2$CH$_2$CH$_2$)$_2$PPh-*P,P,P*}]-[ClO$_4$] (**16**), with labelling scheme; hydrogen atoms have been omitted for clarity

Å found in an authentic pentacoordinate palladium(II) complex.[52] However, the Pd−N bond length is shorter than the weak interactions in the range 2.576(4)−2.805(5) found in other five-coordinate complexes of palladium.[44,53−58] The coordination around the palladium atom may be viewed as a trigonal bipyramid, with the Pd(1), N(1), P(1) and P(3) atoms in the equatorial plane (r.m.s. for the mean plane; 0.0158 Å); the metallated carbon atom and the central phosphorus atom are at the apical positions. However, the trigonal bipyramidal geometry is severely distorted as shown by the N(1)−Pd(1)−P(1) and N(1)−Pd(1)−P(3) bond angles of 113.81(9) and 91.61(9)°, respectively, which differ considerably from the ideal value of 120°. Nevertheless, the bond angle values at palladium preclude the geometry from being considered as square pyramidal.

The Pd(1)−C(1) bond length of 2.064(4) Å is similar to values reported for related five-coordinate complexes.[12,51] The Pd(1)−P(1), Pd(1)−P(2) and Pd(1)−P(3) bond lengths of 2.2893(12), 2.2773(11) and 2.3243(12) Å, respectively, are also similar to those found in related Pd^{II} complexes.[12,51]

Hydrogen bonding between the O−H(4) hydroxyl hydrogen and the O(7) oxygen atom of the disordered perchlorate anion was found [O(1)−H(4)···O(7a): 2.692(3) Å, 167.3(4)°; O(1)−H(4)···O(7b): 2.990(3) Å, 140.7(4)°].

Experimental Section

General Remarks: Solvents were purified by standard methods.[59] Chemicals were reagent grade. The phosphanes PPh_3, $Ph_2PCH_2PPh_2$ (dppm), $Ph_2P(CH_2)_2PPh_2$ (dppe), $Ph_2P(CH_2)_3PPh_2$ (dppp), $Ph_2P(CH_2)_4PPh_2$ (dppb), $Ph_2PC_5H_4FeC_5H_4PPh_2$ (dppf) and $(Ph_2PCH_2CH_2)_2PPh$ (triphos), were purchased from Aldrich. Microanalyses were carried out using a Carlo Erba Elemental Analyser, Model 1108. IR spectra were recorded as Nujol mulls or polythene discs on a Perkin−Elmer 1330 or on a Mattson spectrophotometer. NMR spectra were obtained as $CDCl_3$ solutions. They are referenced to $SiMe_4$ (^1H, $^{13}C\{^1H\}$) or 85% H_3PO_4 ($^{31}P\{^1H\}$) and were recorded on a Bruker AC-200F spectrometer. All chemical shifts are reported downfield from these standards. The FAB mass spectra were recorded using a VG Quatro mass spectrometer with a Cs ion gun; 3-nitrobenzyl alcohol was used as the matrix.

CAUTION: Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of these materials should be prepared and handled with great caution.

Preparation of 2,3,4-$(MeO)_3C_6H_2C(H){=}NCH_2CH_2OH$ (1): 2,3,4-$(MeO)_3C_6H_2COH$ (3.21 g, 16.38 mmol) and $NH_2CH_2CH_2OH$ (1.01 g, 16.45 mmol) were added to 50 cm^3 of dry chloroform. The mixture was heated under reflux in a Dean−Stark apparatus for 4 h. After cooling to room temperature, the solvent was evaporated to give a yellow oil. Yield: 3.52 g (90%). IR (nujol mull): ν(O−H) = 3402m; ν(C=N) = 1642s cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 3.71, 3.68, 3.67 (s, 9 H, OMe), 3.54 (br. s, 2 H, $-CH_2$), 4.01 (br. s, 2 H, $-CH_2$), 6.50 (d, $J_{H5,H6}$ = 8.8 Hz,1 H, H^5), 7.47 (d, 1 H, H^6), 8.36 (s, 1 H, H_i) ppm. $^{13}C\{^1H\}$ NMR (50.28 MHz, $CDCl_3$): δ = 61.8, 60.8, 55.9 (OCH_3), 63.5, 62.3 (C8, C9), 107.7 (C5), 122.1 (C6), 122.4 (C1), 141.7 (C3), 155.9, 153.8 (C2, C4), 158.6 (C=N) ppm. FAB-MS: *m/z* = 240 $[MH]^+$.

The Schiff base ligands **19** and **20** were prepared similarly.

2,3,4-$(MeO)_3C_6H_2C(H){=}NCH_2CH_2CH_3$ (19): Yield: 3.50 g (90%). IR (nujol mull): ν(C=N) = 1638s cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 0.90 (t, $J_{H,H}$ = 7.3 Hz, 3 H, $NCH_2CH_2CH_3$), 1.67 (m, 2 H, $NCH_2CH_2CH_3$), 3.51 (t, $J_{H,H}$ = 7.3 Hz, 2 H, NCH_2CH_2), 3.83, 3.88 (s, 9 H, OMe), 6.67 (d, $J_{H5,H6}$ = 8.8 Hz,1 H, H^5), 7.64 (d, 1 H, H^6), 8.47 (s, 1 H, H_i) ppm.

2,3,4-$(MeO)_3C_6H_2C(H){=}NC(CH_3)_3$ (20): Yield: 3.91 g (95%). IR (nujol mull): ν(C=N) = 1636s cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.15 [s, 9 H, $NC(CH_3)_3$], 3.73, 3.79 (s, 9 H, OMe), 6.56 (d, $J_{H5,H6}$ = 8.8 Hz, 1 H, H^5), 7.56 (d, 1 H, H^6), 8.42 (s, 1 H, H_i) ppm.

Preparation of 2,3,4-$(MeO)_3C_6H_2C(H){=}NCH_3$ (17): A pressure tube containing 2,3,4-$(MeO)_3C_6H_2COH$ (3.21 g, 16.38 mmol) and 40 cm^3 of dry chloroform was cooled to −20 °C and an excess of NH_2Me (1.53 g, 49.14 mmol; 200% excess), also cooled to −20 °C, was added. The tube was sealed and heated to 80 °C for 24 h. After cooling to room temperature, the solvent and the unreacted NH_2Me were removed under vacuum to give a yellow oil. Yield: 3.26 g (95%). IR (nujol mull): ν(C=N) = 1644s cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 3.50 (s, 3 H, $N-CH_3$), 3.87, 3.88, 3.92 (s, 9 H, OMe), 6.71 (d, $J_{H5,H6}$ = 8.8 Hz, 1 H, H^5), 7.63 (d, 1 H, H^6), 8.52 (s, 1 H, H_i) ppm.

Ligand **18** was prepared similarly.

2,3,4-$(MeO)_3C_6H_2C(H){=}NCH_2CH_3$ (18): Yield: 3.51 g (96%). IR (nujol mull): ν(C=N) = 1638s cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.04 (t, 3 H, NCH_2CH_3), 3.37 (q, $J_{H,H}$ = 7.3 Hz, 2 H, NCH_2CH_3), 3.59, 3.60, 3.66 (s, 9 H, OMe), 6.44 (d, $J_{H5,H6}$ = 8.8 Hz, 1 H, H^5), 7.43 (d, 1 H, H^6), 8.29 (s, 1 H, H_i) ppm.

Preparation of $[Pd\{2,3,4\text{-}(MeO)_3C_6HC(H){=}NCH_2CH_2OH\}(\mu\text{-}O_2CMe)]_2$ (2): A pressure tube was charged with 2,3,4-$(MeO)_3C_6H_2C(H){=}NCH_2CH_2OH$ (**1**) (0.219 g, 0.92 mmol), palladium(II) acetate (0.206 g, 0.92 mmol) and 20 cm^3 of dry toluene was then sealed under argon. The mixture was heated for 24 h at 60 °C. After cooling to room temp. the solution was filtered through celite to remove the black palladium formed. The solvent was then removed under vacuum to give a brown oil, which was chromatographed on a column packed with silica gel. Elution with dichloromethane/ethanol (92:8) afforded the final product as a yellow oil after solvent removal. Yield: 0.30 g (40%). M.p. 111.3 °C. $C_{28}H_{38}N_2O_{12}Pd_2$ (807.4): calcd. C 41.6, H 4.7, N 3.5; found C 40.9, H 4.8, N 3.6. IR (polythene disc): ν(O−H) = 3384m cm^{-1}; ν(C=N) = 1604sh, m cm^{-1}; ν_{as}(COO) = 1563s cm^{-1}; ν_s(COO) = 1421s cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$), *anti* isomer: δ = 2.07 (s, 3 H, OAc), 3.73, 3.80, 3.84 (s, 9 H, OMe), 2.23 (br. s, 2 H, $-CH_2$), 6.22 (s, 1 H, H^5), 7.57 (s, 1 H, H_i); *syn* isomer: δ = 2.25, 2.02 (s, 3 H, OAc), 3.20 (br. s, 1 H, OH), 3.68, 3.71, 3.82 (s, 9 H, OMe), 6.00 (s, 1 H, H^5), 7.81 (s, 1 H, H_i) ppm. $^{13}C\{^1H\}$ NMR (50.28 MHz, $CDCl_3$), *anti* isomer: δ = 24.4 (CH_3COO), 61.7, 61.3, 55.9 (OCH_3), 61.6 (C8, C9), 110.2 (C5), 130.7 (C1), 137.9 (C6), 154.4, 151.3, 151.0 (C2, C3, C4), 170.6 (C=N), 181.5 (CH_3COO) ppm; *syn* isomer: δ = 24.4, 24.1 (CH_3COO), 61.6, 60.6, 55.5 (OCH_3), 110.6 (C5), 130.3 (C1), 137.3 (C6), 154.1, 151.3, 150.9 (C2, C3, C4), 171.2 (C=N), 182.2, 180.9 (CH_3COO) ppm. FAB-MS: *m/z* = 808 $[M]^+$, 659 $[M - OAc - CH_2CH_2OH]^+$, 404 $[M - OAc - L - Pd]^+$, 344 $[M - 2OAc - L - Pd]^+$.

Compounds **21**, **22**, **23** and **24** were prepared similarly and isolated as yellow solids.

$[Pd\{2,3,4\text{-}(MeO)_3C_6HC(H){=}NCH_3\}(\mu\text{-}O_2CMe)]_2$ (21): Yield: 0.39 g (50%). M.p. 120.3 °C. $C_{26}H_{34}N_2O_{10}Pd_2$ (747.4): calcd. C

41.8, H 4.6, N 3.7; found C 41.6, H 4.8, N 3.9. IR (polythene disc): ν(C=N) = 1610sh, m cm^{-1}; ν$_{as}$(COO) = 1572s cm^{-1}; ν$_s$(COO) = 1413s cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$), *anti* isomer: δ = 2.13 (s, 3 H, OAc), 2.88 (s, 3 H, NCH$_3$), 3.73, 3.83, 3.86 (s, 9 H, OMe), 6.34 (s, 1 H, H^5), 7.27 (s, 1 H, H$_i$); *syn* isomer: δ = 2.05, 2.23 (s, 3 H, OAc), 3.28 (s, 3 H, NCH$_3$), 3.69, 3.69, 3.78 (s, 9 H, OMe), 5.99 (s, 1 H, H^5), 7.73 (s, 1 H, H$_i$) ppm.

[Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=NCH$_2$CH$_3$}(μ-O$_2$CMe)]$_2$ (22): Yield: 0.38 g (50%). M.p. 125.7 °C (dec.). $C_{28}H_{38}N_2O_{10}Pd_2$ (775.4): calcd. C 43.4, H 4.9, N 3.6; found C 42.8, H 4.8, N 3.5. IR (polythene disc): ν(C=N) = 1604sh, m cm^{-1}; ν$_{as}$(COO) = 1566s cm^{-1}; ν$_s$(COO) = 1413s cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$), *anti* isomer: δ = 1.10 (t, $J_{H,H}$ = 7.3 Hz, 3 H, NCH$_2$C*H*$_3$), 2.01 (s, 3 H, OAc), 2.77 (m, 1 H, NC*H*$_2$CH$_3$), 3.19 (m, 1 H, NC*H*$_2$CH$_3$), 3.74, 3.81, 3.84 (s, 9 H, OMe), 6.32 (s, 1 H, H^5), 7.44 (s, 1 H, H$_i$); *syn* isomer: δ = isomer: 0.85 (t, $J_{H,H}$ = 7.3 Hz, 3 H, NCH$_2$C*H*$_3$), 1.99, 2.21 (s, 3 H, OAc), 3.65, 3.68, 3.77 (s, 9 H, OMe), 5.99 (s, 1 H, H^5), 7.74 (s, 1 H, H$_i$) ppm.

[Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=NCH$_2$CH$_2$CH$_3$}(μ-O$_2$CMe)]$_2$ (23): Yield: 0.37 g (50%). M.p. 141.3 °C. $C_{30}H_{42}N_2O_{10}Pd_2$: calcd. C 44.9, H 5.3, N 3.5; found C 45.4, H 4.9, N 3.7. IR (polythene disc): ν(C=N) = 1606sh, m cm^{-1}; ν$_{as}$(COO) = 1558s cm^{-1}; ν$_s$(COO) = 1415s cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$), *anti* isomer: δ = 0.76 (t, $J_{H,H}$ = 7.3 Hz, 3 H, NCH$_2$CH$_2$C*H*$_3$), 1.60 (m, 2 H, NCH$_2$C*H*$_2$), 2.01 (s, 3 H, OAc), 2.55 (m, 1 H, NC*H*$_2$CH$_2$), 3.13 (m, 1 H, NC*H*$_2$CH$_2$), 3.75, 3.81, 3.84 (s, 9 H, OMe), 6.32 (s, 1 H, H^5), 7.41 (s, 1 H, H$_i$); *syn* isomer: δ = 0.90 (t, $J_{H,H}$ = 7.3 Hz, 3 H, NCH$_2$CH$_2$C*H*$_3$), 1.98, 2.20 (s, 3 H, OAc), 3.65, 3.67, 3.77 (s, 9 H, OMe), 5.98 (s, 1 H, H^5), 7.69 (s, 1 H, H$_i$) ppm.

[Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=NC(CH$_3$)$_3$}(μ-O$_2$CMe)]$_2$ (24): Yield: 0.37 g (50%). M.p. 121.7 °C. $C_{32}H_{46}N_2O_{10}Pd_2$ (831.5): calcd. C 46.2, H 5.6, N 3.4; found C 46.6, H 5.3, N 3.5. IR (polythene disc): ν(C=N) = 1601sh, m cm^{-1}; ν$_{as}$(COO) = 1570s cm^{-1}; ν$_s$(COO) = 1413s cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$), *anti* isomer: δ = 1.10 [s, 9 H, NC(CH$_3$)$_3$], 2.04 (s, 3 H, OAc), 3.66, 3.72, 3.86 (s, 9 H, OMe), 6.13 (s, 1 H, H^5), 7.79 (s, 1 H, H$_i$),; *syn* isomer: δ = 1.18 [s, 9 H, NC(CH$_3$)$_3$], 1.94, 1.98 (s, 3 H, OAc), 3.95, 3.67, 3.77 (s, 9 H, OMe), 6.02 (s, 1 H, H^5), 8.00 (s, 1 H, H$_i$) ppm.

Preparation of [Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=NCH$_2$CH$_2$OH}(μ-Cl)]$_2$ (3): A solution of **2** (0.310 g, 0.384 mmol) in 15 cm^3 of acetone was treated with a saturated solution of NaCl in ca. 20 cm^3 of water. The yellow precipitate formed was filtered off, washed with water and dried under vacuum. Yield 0.24 g (84%). M.p. 215.1 °C (dec.). $C_{24}H_{32}Cl_2N_2O_8Pd_2$ (760.2): calcd. C 37.9, H 4.2, N 3.7; found C 37.7, H 4.8, N 3.6. IR (nujol mull): ν(O−H) = 3487m cm^{-1}; ν(C=N) = 1605s cm^{-1}. ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 3.31, 3.62 (br. s, 4 H, -CH$_2$), 3.67, 3.76, 3.84 (s, 9 H, OMe), 4.71 (br. s, 1 H, OH), 7.51 (s, 1 H, H^5), 8.08 (s, 1 H, H$_i$). FAB-MS: *m*/*z* = 785 [M + Na]$^+$.

Preparation of [Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=NCH$_2$CH$_2$OH}(O$_2$CMe)(PPh$_3$)] (4): PPh$_3$ (0.014 g, 0.05 mmol) was added to a suspension of **2** (0.023 g, 0.03 mmol) in acetone (15 cm^3). The mixture was stirred for 12 h and the solvent was then removed to give a white solid which was recrystallised from dichloromethane/hexane. Yield: 0.029 g (83%). M.p. 182.5 °C. $C_{32}H_{34}NO_6PPd$ (666.0): calcd. C 57.7, H 5.1, N 2.1; found C 57.6, H 4.8, N 2.3. IR (polythene disc): ν(O−H) = 3400m cm^{-1}; ν(C=N) = 1613s cm^{-1}; ν$_{as}$(COO) = 1570s cm^{-1}; ν$_s$(COO) = 1290s cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ = 1.31 (s, 3 H, OAc), 2.88 [s, 3 H, C(4)−OMe], 3.92, 3.70 (s, 6 H, OMe), 3.74, 3.89 (br. s, 4 H, -CH$_2$), 5.70 (d, $J_{P,H}$ = 5.8 Hz, 1 H, H^5), 8.31 (d, $J_{P,H}$ = 7.8 Hz, 1 H, H$_i$) ppm. ^{31}P{^{1}H} NMR (80.9 MHz, CDCl$_3$): δ = 40.8 (s) ppm. FAB-MS: *m*/*z* = 666 [MH]$^+$, 608 [M − OAc]$^+$.

Compounds **5**, **6** and **7** were obtained following a similar procedure, using a cyclometallated complex/diphosphane molar ratio of 1:1, as yellow (**5 and 6**) or white (**7**) air stable solids.

[{Pd[2,3,4-(MeO)$_3$C$_6$HC(H)=NCH$_2$CH$_2$OH](O$_2$CMe)}$_2$(μ-Ph$_2$PCH$_2$PPh$_2$)] (5): Yield: 0.027 g (48%). M.p. 166.7 °C (dec.). $C_{53}H_{60}N_2O_{12}P_2Pd_2$ (1191.8): calcd. C 53.4, H 5.1, N 2.3; found C 54.0, H 4.9, N 2.4. IR (polythene disc): ν(O−H) = 3307m cm^{-1}; ν(C=N) = 1614m, sh cm^{-1}; ν$_{as}$(COO) = 1573s cm^{-1}; ν$_s$(COO) = 1286s cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ = 1.65 (s, 3 H, OAc), 2.91 [s, 3 H, C(4)−OMe], 3.10 (br. s, 1 H, OH), 3.63, 4.01 (s, 6 H, OMe), 3.75, 4.03 (br. s, 4 H, -CH$_2$), 5.45 (d, $J_{P,H}$ = 5.4 Hz, 1 H, H^5), 8.36 (d $J_{P,H}$ = 8.2 Hz, 1 H, H$_{i,}$) ppm. ^{31}P{^{1}H} NMR (80.9 MHz, CDCl$_3$): δ = 32.0 (s) ppm. FAB-MS: *m*/*z* = 1073 [M − 2OAc]$^+$; 728 [MH − 2OAc − L − Pd]$^+$.

[{Pd[2,3,4-(MeO)$_3$C$_6$HC(H)=NCH$_2$CH$_2$OH](O$_2$CMe)}$_2${μ-Ph$_2$P(CH$_2$)$_3$PPh$_2$}] (6): Yield: 0.032 g (49%). M.p. 217.3 °C (dec.). $C_{55}H_{64}N_2O_{12}P_2Pd_2$ (1219.9): calcd. C 54.1, H 5.3, N 2.3; found C 54.3, H 5.1, N 2.4. IR (polythene disc): ν(O−H) = 3345m cm^{-1}; ν(C=N) = 1612m, sh cm^{-1}; ν$_{as}$(COO) = 1573s cm^{-1}; ν$_s$(COO) = 1284s cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): 1.54 (s, 3 H, OAc), 2.99 [s, 3 H, C(4)−OMe], 3.69, 3.93 (s, 6 H, OMe), 3.66, 3.88 (br. s, 4 H, -CH$_2$), 5.73 (d, $J_{P,H}$ = 5.3 Hz, 1 H, H^5], 8.28 (d, $J_{P,H}$ = 7.3 Hz, 1 H, H$_i$) ppm. ^{31}P{^{1}H} NMR (80.9 MHz, CDCl$_3$) 32.3 (s) ppm. FAB-MS: *m*/*z* = 756 [M − 2OAc − L − Pd]$^+$.

[{Pd[2,3,4-(MeO)$_3$C$_6$HC(H)=NCH$_2$CH$_2$OH](O$_2$CMe)}$_2${μ-Ph$_2$P(CH$_2$)$_4$PPh$_2$}] (7): Yield: 0.030 g (76%). M.p. 187.6 °C (dec.). $C_{56}H_{66}N_2O_{12}P_2Pd_2$: calcd. C 54.5, H 5.4, N 2.3; found C 54.2, H 5.0, N 2.7. IR (polythene disc): ν(O−H) = 3399m cm^{-1}; ν(C=N) = 1614m, sh cm^{-1}; ν$_{as}$(COO) = 1573s cm^{-1}; ν$_s$(COO) = 1286s cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ = 1.61 (s, 3 H, OAc), 2.97 [s, 3 H, C(4)−OMe], 3.68, 3.88 (s, 6 H, OMe), 3.71, 3.92 (br. s, 4 H, -CH$_2$), 5.73 (d, $J_{P,H}$ = 5.8 Hz, 1 H, H^5), 8.25 (d, $J_{P,H}$ = 7.3 Hz, 1 H, H$_i$) ppm. ^{31}P{^{1}H} NMR (80.9 MHz, CDCl$_3$): δ = 32.8 (s) ppm. FAB-MS: *m*/*z* = 769 [M − 2OAc − L − Pd]$^+$.

Preparation of [Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=NCH$_2$CH$_2$OH}(Cl)(PPh$_3$)] (8): PPh$_3$ (0.074 g, 0.28 mmol) was added to a suspension of **3** (0.108 g, 0.14 mmol) in acetone (15 cm^3). The mixture was stirred for 12 h and the solvent was then removed to give a white solid which was recrystallised from dichloromethane/hexane. Yield: 0.12 g (66%). M.p. 199.8 °C (dec.). $C_{30}H_{31}ClNO_4PPd$ (642.4): calcd. C 56.1, H 4.9, N 2.2; found C 56.6, H 4.5, N 2.1. IR (nujol mull): ν(O−H) = 3365m cm^{-1}; ν(C=N) = 1619s cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ = 2.82 [s, 3 H, C(4)−OMe], 3.2 (br. s, 1 H, OH), 3.70, 3.95 (s, 6 H, OMe), 4.03 (m, 4 H, CH$_2$), 5.74 (d, $J_{P,H}$ = 6.3 Hz, 1 H, H^5), 8.38 (d, $J_{P,H}$ = 8.3 Hz, 1 H, H$_i$) ppm. ^{13}C{^{1}H} NMR: (50.28 MHz, CDCl$_3$): δ = 62.9, 61.8 (C8, C9), 61.8, 60.7, 55.2 (O*C*H$_3$), 118.0 (d, $J_{P,C}$ = 12.1 Hz, C5), 133.3 (C1), 154.4 (d, $J_{P,C}$ = 5.4 Hz, C6), 154.0, 152.0, 137.5 (C2, C3, C4), 173.1 (d, $J_{P,C}$ = 2.8 Hz, C=N). P-phenyl: δ = 128.1 (d, $J_{P,C}$ = 11.3 Hz, C$_m$), 130.1 (d, $J_{P,C}$ = 50.4 Hz, C$_i$), 135.4 (d, $J_{P,C}$ = 12.1 Hz, C$_o$), 130.8 (d, $J_{P,C}$ = 2.1 Hz, C$_p$) ppm. ^{31}P{^{1}H} NMR (80.9 MHz, CDCl$_3$): δ = 43.0 (s) ppm. FAB-MS: *m*/*z* = 606 [M − Cl]$^+$.

Compounds **10**, **11**, **12** and **13** were synthesised similarly, using a cyclometallated complex/diphosphane molar ratio of 1:1, as yellow solids.

[{Pd[2,3,4-(MeO)$_3$C$_6$HC(H)=NCH$_2$CH$_2$OH](Cl)}$_2${μ-Ph$_2$P-(CH$_2$)$_3$PPh$_2$}] (10): Yield: 2.7 mg (76%). M.p. 182.6 °C (dec.).

$C_{51}H_{58}Cl_2N_2O_8P_2Pd_2$ (1172.7): calcd. C 52.2, H 5.0, N 2.4; found C 52.4, H 4.9, N 2.5. IR (nujol mull): ν(O−H) = 3420m cm^{-1}; ν(C=N) = 1613s cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.88 [s, 3 H, C(4)−OMe], 3.67, 3.92 (s, 6 H, OMe), 3.96 (br. s, 4 H, -CH_2), 5.74 (d, $J_{P,H}$ = 6.3 Hz, 1 H, H^5), 8.26 (d, $J_{P,H}$ = 8.3 Hz, 1 H, H_i) ppm. $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$): δ = 33.4 (s) ppm. FAB-MS: *m*/*z* = 1136 [MH − Cl]$^+$, 1103 [MH − 2Cl]$^+$, 756 [MH − 2Cl − L − Pd]$^+$.

[{Pd[2,3,4-$(MeO)_3C_6HC(H)=NCH_2CH_2OH$](Cl)}$_2${μ-$Ph_2P(CH_2)_4PPh_2$}] (11): Yield: 41 mg (79%). M.p. 148.9 °C (dec.). $C_{52}H_{60}Cl_2N_2O_8P_2Pd_2$ (1186.7): calcd. C 52.6, H 5.1, N 2.4; found C 52.7, H 5.3, N 2.1. IR (nujol mull): ν(O−H) = 3426m cm^{-1}; ν(C=N) = 1614s cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.88 [s, 3 H, C(4)−OMe], 3.70, 3.92 (s, 6 H, OMe), 4.01 (br. s, 4 H, -CH_2), 5.79 (d, $J_{P,H}$ = 5.8 Hz, 1 H, H^5), 8.32 (d, $J_{P,H}$ = 7.8 Hz, 1 H, H_i) ppm. $^{13}C\{^1H\}$ NMR (50.28 MHz, $CDCl_3$): δ = 62.6, 60.4 (C8, C9), 61.8, 60.7, 55.1 (O*C*H_3), 117.4 (d, $J_{P,C}$ = 12.1 Hz, C5), 133.2 (d, $J_{P,C}$ = 1.4 Hz, C1), 154.5 (d, $J_{P,C}$ = 6.5 Hz, C6), 153.7, 152.1, 137.5 (C2, C3, C4), 172.6 (d, $J_{P,C}$ = 4.2 Hz, C=N); P-phenyl: δ = 128.6 (d, $J_{P,C}$ = 10.1 Hz, C_m), 130.8 (C_p), 130.0 (d, $J_{P,C}$ = 46.8 Hz, C_i), 133.9 (d, $J_{P,C}$ = 12.1 Hz, C_o); P(CH_2)$_4$P: δ = 29.3 (d, $J_{P,C}$ = 33.3 Hz, P*C*H_2CH_2), 26.1 (d, $J_{P,C}$ = 16.3 Hz, PCH_2*C*H_2) ppm. $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$): δ = 33.9 (s) ppm. FAB-MS: *m*/*z* = 770 [MH − 2Cl − L − Pd]$^+$.

[{Pd[2,3,4-$(MeO)_3C_6HC(H)=NCH_2CH_2OH$](Cl)}$_2${μ-$Ph_2PC_5H_4FeC_5H_4PPh_2$}] (12): Yield: 74 mg (71%). M.p. 168.4 °C (dec.). $C_{58}H_{60}Cl_2FeN_2O_8P_2Pd_2$ (1314.6): calcd. C 53.0, H 4.6, N 2.1; found C 52.7, H 5.0, N 2.3. IR (nujol mull): ν(O−H) = 3399m cm^{-1}; ν(C=N) = 1614s cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.85 [s, 3 H, C(4)−OMe], 3.74, 3.96 (s, 6 H, OMe), 4.03 (br. s, 4 H, -CH_2), 5.22, 4.53 (br. s, 4 H, $H^{ferr.}$), 5.76 (d, $J_{P,H}$ = 6.3 Hz, 1 H, H^5), 8.36 (d, $J_{P,H}$ = 8.3 Hz, 1 H, H_i) ppm. $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$): δ = 31.7 (s) ppm. FAB-MS: *m*/*z* = 898 [M − 2Cl − L − Pd]$^+$.

[{Pd[2,3,4-$(MeO)_3C_6HC(H)=NCH_2CH_2OH$]}$_2$(μ-Cl)(μ-$Ph_2PCH_2PPh_2$)][Cl] (13): Yield: 7.9 mg (65%). M.p. 145.6 °C (dec.). $C_{49}H_{54}Cl_2N_2O_8P_2Pd_2$ (1144.6): calcd. C 51.4, H 4.8, N 2.4; found C 51.0, H 5.1, N 2.7. IR (nujol mull): ν(O−H) = 3514, 3441m cm^{-1}; ν(C=N) = 1613s cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.88 [s, 3 H, C(4)−OMe], 3.67, 3.91 (s, 6 H, OMe), 3.99 (br. s, 4 H, -CH_2), 4.70 (m, 2 H, PCH_2P), 5.50 (d, $J_{P,H}$ = 6.3 Hz, 1 H, H^5), 8.24 (d, $J_{P,H}$ = 8.3 Hz, 1 H, H_i) ppm. $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$): δ = 30.2 (s) ppm. FAB-MS: *m*/*z* = 1109 [M − Cl]$^+$, 728 [M − 2Cl − L − Pd]$^+$. Specific molar conductivity: Λ_m = 175.1 ohm^{-1}·cm^2·mol^{-1} (in acetonitrile).

Preparation of [Pd{2,3,4-$(MeO)_3C_6HC(H)=NCH_2CH_2OH$}($PPh_3$)][$F_3CSO_3$] (9): A suspension of **4** (0.093 g, 0.14 mmol) in acetone (15 cm^3) was treated with silver triflate (0.037 g, 0.14 mmol) and stirred for 2 h. The solution was filtered through Celite to eliminate the AgCl precipitate and then the solvent was removed to give a yellow solid which was recrystallised from dichloromethane/hexane. Yield: 0.095 g (44%). M.p. 223.7 °C (dec.). $C_{31}H_{31}F_3NO_7PPdS$ (756.0): calcd. C 49.2, H 4.1, N 1.8; found C 49.6, H 4.0, N 1.9. IR (nujol mull): ν(O−H) = 3245m cm^{-1}; ν(C=N) = 1625s cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.91 [s, 3 H, C(4)−OMe], 3.73, 3.97 (s, 6 H, OMe), 3.89, 4.13 (br. s, 4 H, -CH_2), 5.62 (d, $J_{P,H}$ = 4.9 Hz, 1 H, H^5), 7.02 (t, J_{HO,CH_2} = 5.6 Hz, 1 H, OH,], 8.27 (d, $J_{P,H}$ = 9.8 Hz, 1 H, H_i) ppm. $^{13}C\{^1H\}$ NMR (50.28 MHz, $CDCl_3$): δ = 67.7, 56.8 (C8, C9), 61.9, 60.8, 55.5 (O*C*H_3), 117.6 (d, $J_{P,C}$ = 10.6 Hz, C5), 135.9 (C1), 144.4 (d, $J_{P,C}$ = 5.7 Hz, C6), 155.0, 155.1, 152.8 (C2, C3, C4), 169.3 (d, $J_{P,C}$ = 4.2 Hz, C=N); P-phenyl: δ = 129.1 (d, $J_{P,C}$ = 10.6 Hz, C_m), 131.8 (d, $J_{P,C}$ = 2.9 Hz, C_p), 134.5 (d, $J_{P,C}$ = 12.1 Hz, C_o) ppm. $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$): δ = 36.1 (s) ppm. FAB-MS: *m*/*z* = 606 [M − CF_3SO_3]$^+$. Specific molar conductivity: Λ_m = 116.2 ohm^{-1}·cm^2·mol^{-1} (in acetonitrile).

Compound **14** was obtained following a similar procedure using complex **11** as starting material.

[{Pd[2,3,4-$(MeO)_3C_6HC(H)=NCH_2CH_2OH$]}$_2${μ-$Ph_2P(CH_2)_4PPh_2$}][$CF_3SO_3$]$_2$ (14): Yield 0.024 g (63%). M.p. 173.5 °C (dec.). $C_{54}H_{60}F_6N_2O_{14}P_2Pd_2S_2$ (1413.9): calcd. C 45.9, H 4.3, N 2.0; found C 45.7, H 4.3, N 2.0. IR (nujol mull): ν(O−H) = 3250m cm^{-1}; ν(C=N) = 1619s cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.99 [s, 3 H, C(4)−OMe], 3.70, 3.94 (s, 6 H, OMe), 3.87, 4.19 (br. s, 4 H, -CH_2), 5.63 (d, $J_{P,H}$ = 5.4 Hz, 1 H, H^5), 6.89 (br. s, 1 H, OH), 8.24 (d, $J_{P,H}$ = 9.3 Hz, 1 H, H_i) ppm. $^{13}C\{^1H\}$ NMR (50.28 MHz, $CDCl_3$): δ = 66.3, 57.5 (C8, C9), 61.9, 60.7, 55.4 (O*C*H_3), 117.1 (d, $J_{P,C}$ = 11.3 Hz, C5), 138.2 (C1), 146.7 (d, $J_{P,C}$ = 2.8 Hz, C6), 155.1, 154.9, 156.6 (C2, C3, C4), 170.2 (d, $J_{P,C}$ = 2.8 Hz, C=N); P-phenyl: δ = 129.1 (d, $J_{P,C}$ = 10.6 Hz, C_m), 131.6 (d, $J_{P,C}$ = 2.1 Hz, C_p), 133.8 (d, $J_{P,C}$ = 12.1 Hz, C_o);. P(CH_2)$_4$P: δ = 27.4 (d, $J_{P,C}$ = 29.1 Hz, P*C*H_2CH_2), 26.2 (d, $J_{P,C}$ = 17.1 Hz, PCH_2*C*H_2) ppm. $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$): δ = 30.2 (s) ppm. FAB-MS: *m*/*z* = 1265 [M − CF_3SO_3]$^+$, 770 [MH − L − Pd − 2CF_3SO_3]$^+$. Specific molar conductivity: Λ_m = 237.1 ohm^{-1}·cm^2·mol^{-1} (in acetonitrile).

Preparation of [Pd{2,3,4-$(MeO)_3C_6HC(H)=NCH_2CH_2OH$}{$PPh_2(CH_2)_2PPh_2$-*P*,*P*}][$ClO_4$] (15): $PPh_2(CH_2)_2PPh_2$ (0.067 g, 0.17 mmol) was added to a suspension of **3** (0.064 g, 0.08 mmol) in acetone (20 cm^3). The mixture was stirred for 1 h, after which an excess of sodium perchlorate was added. The mixture was stirred for a further 4 h, and then the complex was precipitated out by addition of water, filtered off and dried in vacuo. Recrystallization from dichloromethane/hexane gave the final compound as a yellow solid. Yield: 0.11 g (80%). $C_{38}H_{40}ClNO_8P_2Pd$ (842.5): calcd. C 54.2, H 4.8, N 1.7; found C 53.9, H 4.6, N 1.7. IR (nujol mull): ν(O−H) = 3555, 3488m cm^{-1}; ν(C=N) = 1606s cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.97 [s, 3 H, C(4)−OMe], 3.73, 3.96 (s, 6 H, OMe), 2.91, 3.42 (br. s, 4 H, -CH_2), 5.93 (dd, $J_{P,H}$ = 8.8, 5.8 Hz, 1 H, H^5), 8.50 (d, $J_{P,H}$ = 8.3 Hz, 1 H, H_i) ppm. $^{13}C\{^1H\}$ NMR (50.28 MHz, $CDCl_3$): δ = 63.6, 59.3 (C8, C9), 62.1, 60.8, 55.5 (O*C*H_3), 117.5 (dd, $J_{P,C}$ = 12.1, 3.5 Hz, C5), 138.0 (d, $J_{P,C}$ = 1.4 Hz, C1), 156.0 (dd, $J_{P,C}$ = 12.0, 5.6 Hz, C6), 164.0, 164.6, 153.6 (C2, C3, C4), 179.4 (d, $J_{P,C}$ = 4.5 Hz, C=N); P-phenyl: δ = 127.3, 126.2 (d, $J_{P,C}$ = 36.9, 50.4 Hz, C_i), 129.9, 129.8 (d, $J_{P,C}$ = 10.6, 11.3 Hz, C_m), 132.5, 132.7 (d, $J_{P,C}$ = 2.8 Hz, C_p), 134.1, 133.4 (d, $J_{P,C}$ = 12.1, 12.7 Hz, C_o); P(CH_2)$_2$P: δ = 30.5 (dd, $J_{P,C}$ = 35.1, 18.0 Hz, P*C*H_2CH_2P), 26.1 (dd, $J_{P,C}$ = 29.8, 9.2 Hz, PCH_2*C*H_2P) ppm. $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$): δ = 43.0 (d, $J_{P,P}$ = 25.4 Hz), 61.0 (d) ppm. FAB-MS: *m*/*z* = 742 [M − ClO_4]$^+$. Specific molar conductivity: Λ_m = 142.8 ohm^{-1}·cm^2·mol^{-1} (in acetonitrile).

Compound **16** was obtained following a similar procedure as a yellow, air stable, solid.

[Pd{2,3,4-$(MeO)_3C_6HC(H)=NCH_2CH_2OH$}{$(PPh_2CH_2CH_2)_2PPh$-*P*,*P*,*P*}][$ClO_4$] (16): Yield: 7.8 mg (59%). $C_{46}H_{49}ClNO_8P_3Pd$ (978.7): calcd. C 56.4, H 5.0, N 1.4; found C 56.9, H 4.6, N 1.5. IR (nujol mull): ν(O−H) = 3501m cm^{-1}; ν(C=N) = 1614s cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.80 [s, 3 H, C(4)−OMe], 3.71, 3.88 (s, 6 H, OMe), 2.82, 3.36 (br. s, 4 H, -CH_2), 5.25 (dd, $J_{P,H}$ = 8.8, 2.4 Hz, 1 H, H^5), 8.40 (s, 1 H, H_i) ppm. $^{13}C\{^1H\}$ NMR (50.28 MHz, $CDCl_3$): δ = 167.3 (d, $J_{P,C}$ = 5.7 Hz, C=N), 163.3, 161.1, 154.1 (C2, C3, C4), 154.0 (m, C6), 116.3 (m, C5), 62.8, 61.6

(C8, C9), 62.1, 60.9, 54.8 (OCH_3); P$(CH_2)_2$P: δ = 32.3, 25.9 (m) ppm. $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$): δ = 44.5 (d, $J_{P,P}$ = 26.3), 86.0 (t) ppm. FAB-MS: m/z = 979 $[M]^+$, 877 $[M - ClO_4]^+$. Specific molar conductivity,: Λ_m = 125.9 ohm^{-1} cm^2 mol^{-1} (in acetonitrile).

X-ray Crystallographic Study: Three-dimensional, room temperature X-ray data were collected on a Siemens Smart CCD diffractometer by the ω scan method using graphite-monochromated Mo-K_α radiation. All the measured reflections were corrected for Lorentz and polarisation effects and for absorption by semi-empirical methods based on symmetry equivalent and repeated reflections. The structures were solved by direct methods and refined by full-matrix least-squares on F^2. Hydrogen atoms were included in calculated positions (except the -OH hydrogens which were located in a difference Fourier map) and refined in a riding mode. The O(6), O(7) and O(8) oxygen atoms of the perchlorate counterion in complex **16** were found to be disordered over two positions (with occupancies of approximately 50%). The refinement was carried out taking into account both components. Refinement converged at a final R = 0.0776, 0.0460, 0.0294, 0.0412 and 0.0466 (for complexes **2**, **8**, **9**, **15** and **16**, respectively, observed data, F) and wR_2 = 0.1690, 0.1992, 0.0776, 0.1137 and 0.0829 (for complexes **2**, **8**, **9**, **15** and **16**, respectively, unique data, F^2), with allowance for the thermal anisotropy of all non-hydrogen atoms. The structure solution and refinement were carried out using the program package SHELX-97.[60]

CCDC-178027 (**2**), -178028 (**8**), -178029 (**9**), -178030 (**15**) and -178031 (**16**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

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