Activation of C–H and C–Br bonds in cyclopalladation reactions of Schiff base ligands: Influence of the benzylidene ring substituents

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Abstract

Reaction of $Pd(AcO)_2$ with the Schiff base ligands 2-Br-4,5-$(OCH_2O)C_6H_2C(H)=N(Cy)$ (**a**) and 4,5-$(OCH_2CH_2)C_6H_3C(H)=N(Cy)$ (**b**) leads to the cyclometallated compounds $[Pd\{2\text{-Br-}4,5\text{-}(OCH_2O)C_6HC(H)=N(Cy)\text{-}C6,N\}(\mu\text{-}O_2CMe)]_2$ (**1a**) and $[Pd\{4,5\text{-}(OCH_2CH_2)C_6H_2C(H)=N(Cy)\text{-}C6,N\}(\mu\text{-}O_2CMe)]_2$ (**1b**), respectively, via C–H activation. Treatment of **a** with $Pd_2(dba)_3$ gave $[Pd\{4,5\text{-}(OCH_2O)C_6H_2C(H)=N(Cy)\text{-}C2,N\}(\mu\text{-Br})]_2$ (**6a**), via C–Br activation. The metathesis reaction of **1a** and **1b** with aqueous sodium chloride gave the corresponding cyclopalladated dimers with bridging chloride ligands, **2a** and **2b**, respectively. Treatment of the halogen-bridged compounds with tertiary tri- and diphosphines in the appropriate molar ratio gave the mono and dinuclear compounds **3a**–**5a**, **7a**–**9a** and **3b**–**5b**. The structure of compounds **3a**, **4a**, **5a**, **8a**, **2b**, **3b** and **5b** has been determined by X-ray diffraction analysis.
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Keywords: Palladium; Schiff base; C–H activation; C–Br activation; Triphosphine; Diphosphine

1. Introduction

The synthesis of cyclometallated compounds is known to be a very useful route to the formation of transition metal complexes bearing carbon–metal bonds and has become a well researched field since its beginning in the early 1960s [1], and one of the best developed areas of organometallic chemistry [2]. Moreover, as these compounds are generally rather stable, they are relatively easy to characterize. The most popular way to achieve the synthesis of cyclometalated complexes has been through C–H activation, and therefore this reaction was, and still is, considered as an important model for C–H activation of hydrocarbons by transitions metals.

The numerous applications of cyclometalated compounds as chiral auxiliaries [3], as building blocks for molecular architectures of higher complexity [4] or as compounds with interesting mesogenic [5] and luminescent and electronic properties [6], as well as their potential use in medicine and biology [7] and in catalytic and synthetic processes [8] has contributed significantly to the popularity of these species. The most widely used transition metal is without any doubt palladium, and thus cyclopalladated compounds, *i.e.*, the palladacycles, are known for many types of ligands.

Regioselectivity in cyclopalladation reactions has been observed for a number of substrates; the factors that govern metallation appear to depend on many parameters, including hybridization of the palladated carbon atom, the type and structural characteristics of the ligand, and the palladium source, which ultimately determines kinetic and thermodynamic preferences for palladation. In the present paper, we report the reactions of $Pd(AcO)_2$ or $[Pd_2(dba)_3]$ with Schiff base ligands, where metallation *via* C–H or C–Br activation may proceed at either of the two

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ortho positions of the phenyl ring, and the reactivity of the resulting compounds with *P*-donor ligands.

## 2. Results and discussion

2.1. Cyclopalladated dimer complexes

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

The Schiff base ligands **a** and **b** were prepared by reaction of cyclohexylamine with 2-bromopiperonal or 3,4-

dihydrobenzofuran-5-carboxaldehyde, respectively, as air-stable solids, which were fully characterized (see Section 3).

Reaction of ligand **a** with palladium(II) acetate in toluene at 60 °C for 24 h gave a yellow solid identified as [Pd{2-Br-4,5-(OCH_2O)C_6HC(H)=N(Cy)-*C6,N*}(μ-O_2CMe)]_2 (**1a**), after C–H activation at the six-position (*ortho* to the OCH_2O group). The ^1H NMR spectrum for **1a** showed a singlet assigned to the H3 proton, and absence of the H6 signal upon metallation at C6. On the other hand, treatment of ligand **b** with palladium(II) acetate under similar reaction conditions afforded compound [Pd{4,5-(OCH_2CH_2)C_6H_2C(H)=N(Cy)-*C6,N*}(μ-O_2CMe)]_2 **1b** after C–H activation at the six-position exclusively. Two doublets assigned to the H2 and H3 protons were observed in the ^1H NMR spectrum, with the resonance for the H6
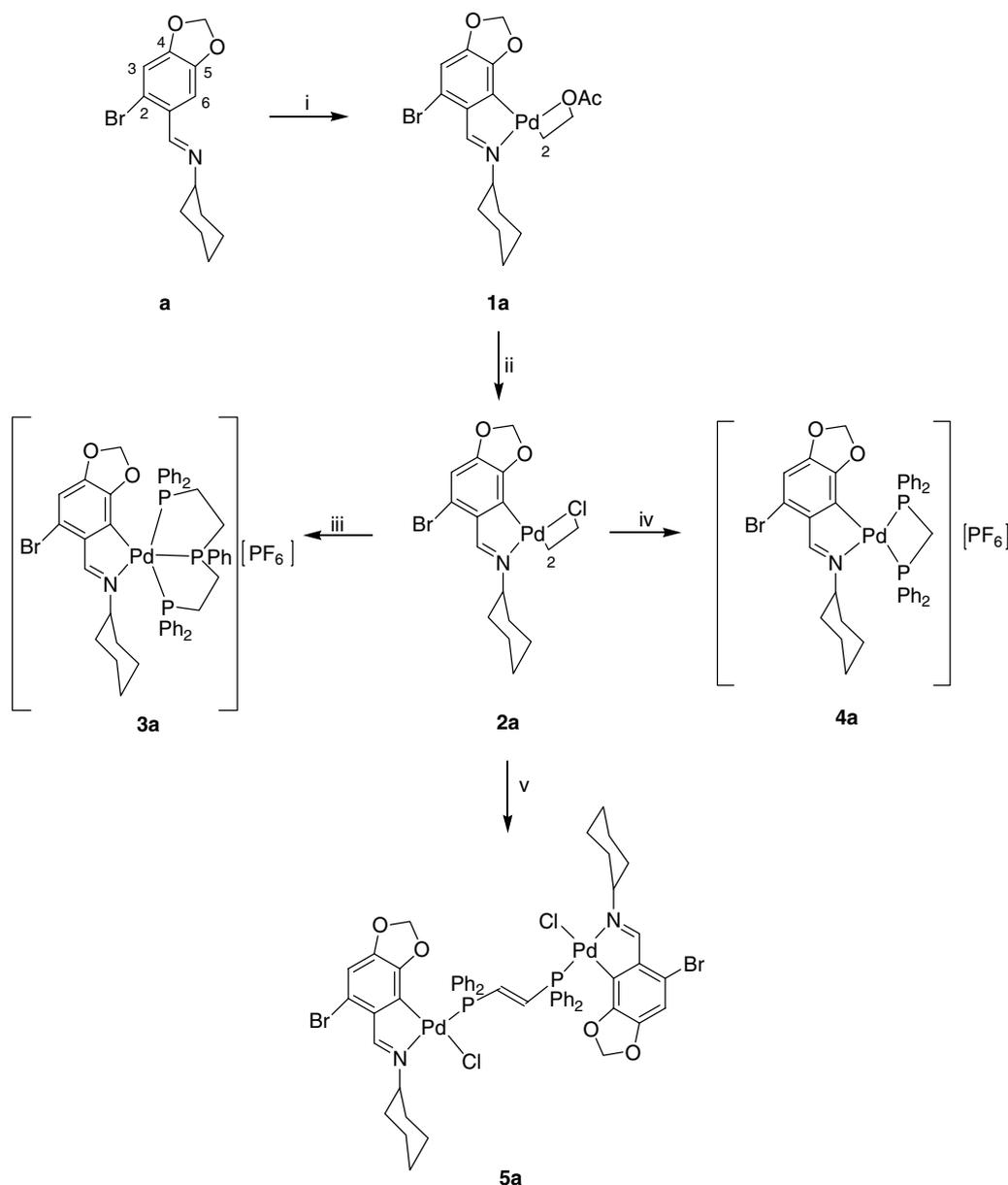
Scheme 1. (i) Pd(AcO)_2, toluene; (ii) NaCl, acetone/water; (iii) triphos (1:2), NH_4PF_6, acetone–water; (iv) dppm (1:2), NH_4PF_6, acetone/water; (v) *t*-dppe (1:1), acetone/water.
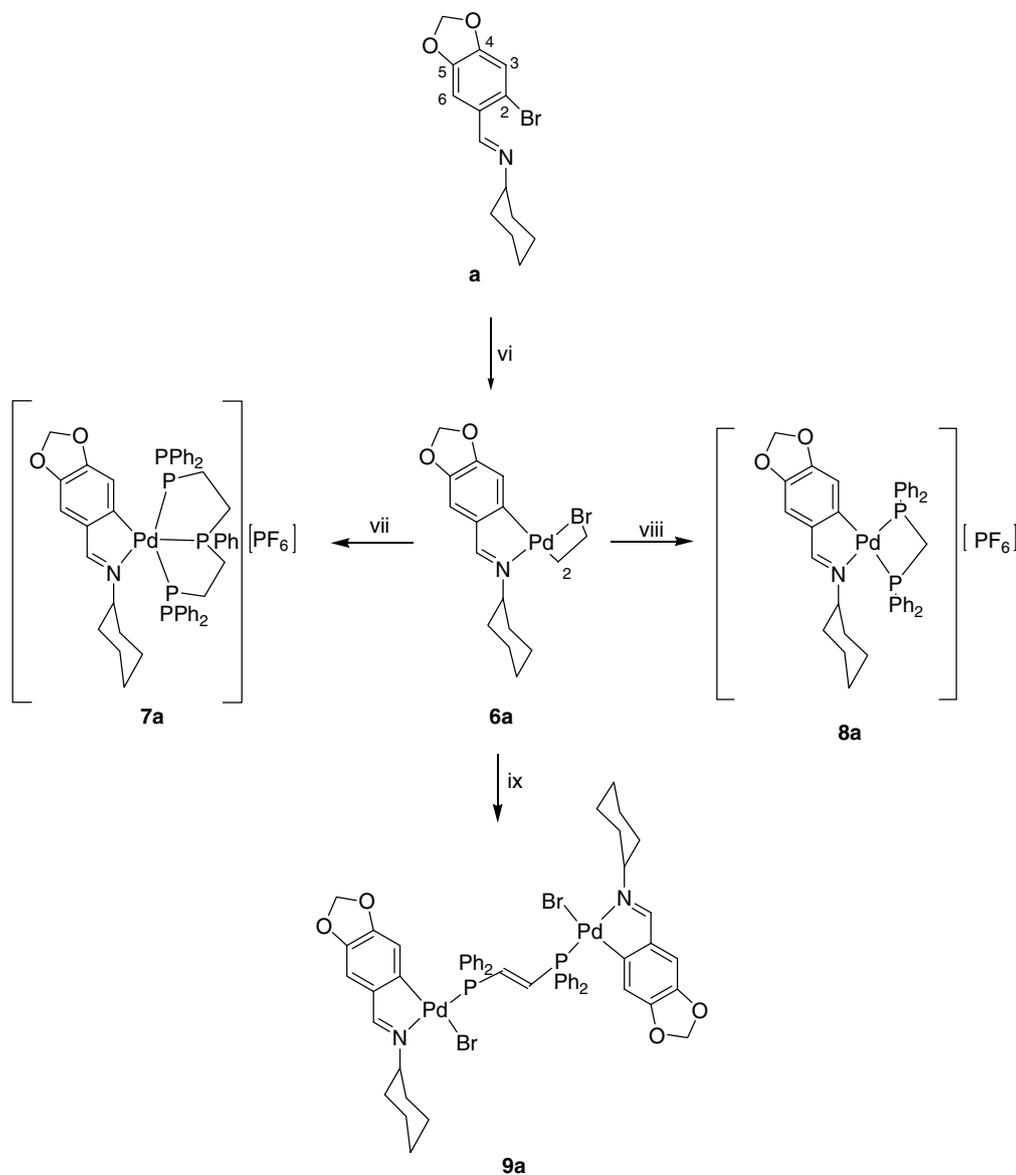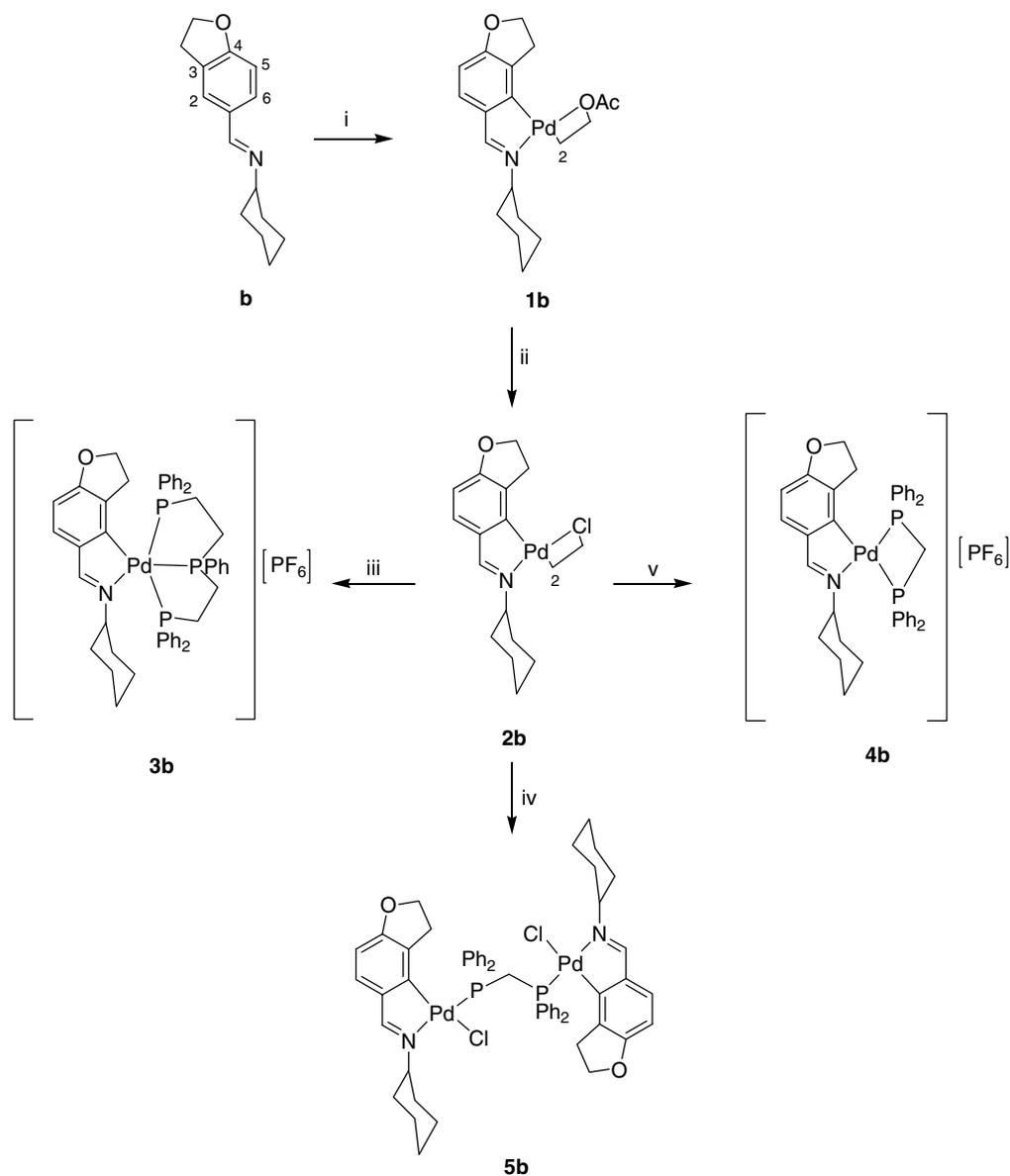
Scheme 2. (i) Pd(dba)$_2$, toluene; (ii) triphos (1:2), NH$_4$PF$_6$, acetone/water; (iii) dppm (1:2), NH$_4$PF$_6$, acetone/water; (iv) *t*-dppe (1:1), acetone/water.

proton being absent. The ^{13}C–{^{1}H} NMR spectra were in accordance with the proposed structures, showing a strong downfield shift of the HC=N and C6 carbon resonances *ca.* 10 and *ca.* 20 ppm, respectively, from those for the free Schiff bases consequent upon cyclometallation (see Section 3) [9].

In the IR spectra of complexes **1a** and **1b** the v(C=N) stretch appeared at lower frequency, *ca.* 20 cm^{-1}, than in the free imine spectra, in accordance with nitrogen coordination to metal center [10]. This was supported by the upfield shift of the HC=N resonance in the ^{1}H NMR spectra, *ca.* 1.0 ppm [11]. The v_{as}(COO) and v_s(COO) values were consistent with bridging acetato groups [12]; a singlet resonance *ca.* 2.0 ppm in the ^{1}H NMR spectra, as well as two singlets at *ca.* 130 and 23 ppm in the ^{13}C–{^{1}H} NMR were assigned to the equivalent methyl acetate groups (C*H*$_3$COO, CH$_3$*C*OO and *C*H$_3$COO resonances,

respectively), consistent with an *anti* geometry of the cyclometallated moieties in an ''open book'' arrangement linked by two acetate-bridging ligands between the palladium atoms, as has been observed in the related dimmer compounds [13].

We have reported the influence of phenyl ring substituents in the cyclometallation of related ligands as depicted in Fig. 1. The methoxy group at the C3 carbon atom hinders direct metallation by palladium(II) at the C2 carbon atom and the C6 carbon is selectively metallated, whereas the less sterically demanding methyl group allows attack at the C2 atom [14]. In the case of cyclic substituents, the metallated carbon atom depends on their ring size: the presence of a OCH$_2$CH$_2$O group impedes approach of the metal the aromatic C2–H bond and only allows attack at the C6 atom; in contrast, the presence of the smaller OCH$_2$O group allows the isolation of a mixture of two products, derived

Scheme 3. (i) Pd(AcO)$_2$, toluene; (ii) NaCl, acetone/water; (iii) triphos (1:2), NH$_4$PF$_6$, acetone/water; (iv) dppm (1:2), NH$_4$PF$_6$, acetone/water; (v) dppm (1:1), acetone/water.
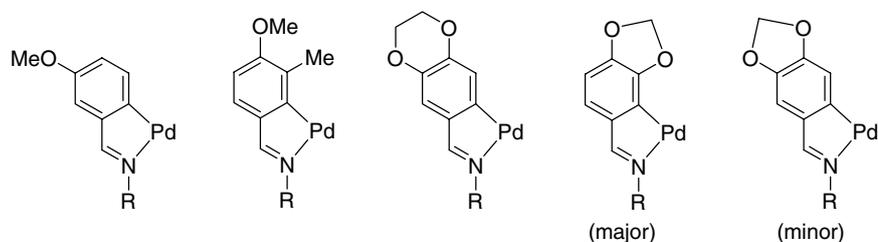

Fig. 1. C–H activation in cyclopalladation reactions.

from activation of the two *ortho*-carbon atoms, with the major isomer being that with a C2–Pd bond [15]. In the present paper, the presence of the 2-Br group in ligand **a** directs metallation by Pd(AcO)$_2$ exclusively towards the C6 atom; in ligand **b** metallation is through the *ortho* carbon to the furane ring.

The C–Br bond in ligand **a** could be activated by treatment with tris(dibenzilideneacetone)palladium(0) in toluene at 80 °C for 24 h. The oxidative addition reaction afforded [Pd{4,5-(OCH$_2$O)C$_6$H$_2$C(H)=N(Cy)-*C2,N*}(μ-Br)]$_2$ **6a**; the ^{1}H NMR spectrum showed two singlets assigned to the H3 and H6 nuclei, and the MS-FAB

spectrum showed, among others, a peak assigned to [(L-H)$_2$-Pd$_2$Br$_2$]$^+$ ion (L-H = cyclometallated ligand), in agreement with a dinuclear nature of the complex [16].

Complexes **1a** and **1b** react with aqueous sodium chloride to give [Pd{2-Br-4,5-(OCH$_2$O)C$_6$HC(H)=N(Cy)-*C6,N*}(μ-Cl)]$_2$ (**2a**) and [Pd{4,5-(OCH$_2$CH$_2$)C$_6$H$_2$C(H)=N-(Cy)-*C6,N*}(μ-Cl)]$_2$ (**2b**), respectively, with exchange of the acetate-bridging groups by chloride-bridging ligands, which were fully characterized (see Section 3). The IR and ^{1}H NMR spectra showed the absence of the acetate ligands and in the IR spectra two v(Pd–Cl) bands were assigned, consistent with an asymmetric Pd$_2$Cl$_2$ bridging unit [17]. The crystal structure of compound **2b** has been determined by X-ray diffraction (*vide infra*).

2.2. Cyclopalladated complexes with phosphines

Treatment of the halide-bridged dinuclear complexes **2a**, **6a** and **2b** with bis(2-diphenylphosphinoethyl)phenylphosphine (triphos) and ammonium hexafluorophosphate in a 1:2 molar ratio in acetone at room temperature yielded the mononuclear complexes [Pd{2-Br-4,5-(OCH$_2$O)C$_6$-HC(H)=N(Cy)-*C6,N*}{(Ph$_2$P-CH$_2$CH$_2$)$_2$PPh-*P,P,P*}][PF$_6$] **3a**, [Pd{4-5-(OCH$_2$O)C$_6$H$_2$C(H)=N(Cy)-*C2,N*}{(Ph$_2$P-CH$_2$CH$_2$)$_2$PPh-*P,P,P*}][PF$_6$] **7a** and [Pd{4,5-(OCH$_2$-CH$_2$)C$_6$H$_2$C(H)=N(Cy)-*C6,N*}{(Ph$_2$PCH$_2$CH$_2$)$_2$PPh-*P,P,P*}][PF$_6$] **3b**, respectively (see Schemes 1–3). The compounds could also be obtained by treatment of **1a** and **1b** with triphos under similar conditions. The microanalytical data and the MS-FAB spectra were consistent with the empirical formula [(L-H)Pd(triphos)][PF$_6$]. The conductivity data (125–150 Ω^{-1} cm^2 mol^{-1} in 10^{-3} mol dm^{-3} solutions in dry acetonitrile) were consistent with 1:1 electrolytes [18].

The absence of v(COO) or v(Pd–Cl) bands in the IR spectra confirmed absence of bridging ligands upon coordination of palladium to the three phosphorus atoms. The shift of the v(C=N) stretching vibration to lower wavenumbers and the upfield shift of the *H*C=N proton resonance in the ^{1}H NMR spectra showed the existence of palladium–nitrogen interaction. The ^{31}P–{^{1}H} NMR spectra showed a triplet (*ca.* 80 ppm, 1P, ^3J(PP) ≈ 25 Hz) and a doublet (*ca.* 40 ppm, 2P), shifted to higher frequency with respect to the free phosphine in agreement with phosphorus coordination to the metal center. This suggested two mutually *trans* phosphorus atoms, with the third phosphorus nearly *trans* to the metallated carbon. The ^{31}P resonance of the central phosphorus nucleus appeared at higher frequency due to the smaller *trans* influence of the carbon atom [19]. The ^{1}H NMR spectrum for compound **7a** showed the resonance for the *ortho* proton to the Pd–C bond as a doublet by coupling phosphorus [δ 5.18, ^4J(PH$_3$) = 7.7 Hz]. This signal was strongly shifted to lower frequency, *ca.* 2 ppm, due to the shielding effect of the phosphine phenyl rings. The ^{13}C–{^{1}H} NMR spectra showed a large coupling constant between the central phosphorus atom and the metallated carbon atom, [d, 1C,

^2J(PC$_6$) = 108.5, **3a**; ^2J(PC$_2$) = 114.9, **7a**; ^2J(PC$_6$) = 109.5, **3b**]. The crystal structure of compounds **3a** and **3b** have been determined by X-ray diffraction (*vide infra*).

Treatment of the halide-bridged dinuclear complexes **2a**, **6a** and **2b** with bis(diphenylphosphino)methane (dppm) in a 1:2 molar ratio in the presence of NH$_4$PF$_6$ gave the mononuclear compounds [Pd{2-Br-4,5-(OCH$_2$O)-C$_6$HC(H)=N(Cy)-*C6,N*}(Ph$_2$PCH$_2$PPh$_2$-*P,P*)][PF$_6$] **4a**, [Pd{4,5-(OCH$_2$O)C$_6$H$_2$C(H)=N(Cy)-*C2,N*}(Ph$_2$PCH$_2$P-Ph$_2$-*P,P*)][PF$_6$] **8a** and [Pd{4,5-(OCH$_2$CH$_2$)C$_6$H$_2$C(H)=N(Cy)-*C6,N*}(Ph$_2$PCH$_2$PPh$_2$-*P,P*)][PF$_6$] **4b**, respectively, as 1:1 electrolytes [18]. The MS-FAB spectra showed, among others, the corresponding peaks assigned to [(L-H)Pd(dppm)]$^+$, which were characteristic clusters of isotopic peaks covering about 10 m/z units, due to the presence of the numerous palladium isotopes (see Section 3). The IR spectrum showed the shift of the C=N stretch towards lower wavenumbers, as compared to the free Schiff base ligand, indicating nitrogen coordination of the C=N group. The ^{31}P–{^{1}H} NMR spectra showed two doublets, for the two non-equivalent phosphorus. The assignment of the doublets was made on the assumption that a ligand of greater *trans* influence shifts the resonance of the phosphorus atoms *trans* to it to lower frequency [19]. The ^{31}P chemical shifts were clearly influenced by the four-membered ring size [20], which gave a negative Δ_R and shifted upfield their resonance. In the ^{1}H NMR spectra the *H*C=N resonance appeared *ca.* δ 8.40 as a doublet by coupling to only the ^{31}P nucleus *trans* to nitrogen. However, for compound **8a**, a doublet of doublets at δ6.19 was assigned to H3, coupled to both phosphorus nuclei; selective decoupling experiments allowed the correct assignment of the corresponding coupling constants [^4J(P$_{trans-C}$H3) = 9.6 Hz, ^4J(P$_{trans-N}$H3) = 7.7 Hz]. In the ^{13}C–{^{1}H} NMR spectra the metallated carbon atom resonance appeared as a doublet of doublets by coupling with the two P atoms ^2J(P$_{trans-C}$C) *ca.* 130 Hz, ^2J(P$_{trans-N}$C) = 4.7–8.7 Hz] and the most of the benzylidene proton signals showed splitting due to the ^{31}P nuclei. The shielding effect of the phenyl phosphine groups *cis* to carbon shifted to lower frequency some proton resonances (OCH$_2$O in **4a**, H3 in **8a** and OCH$_2$CH$_2$ in **4b**). The crystal structure of compounds **4a** and **8a** have been determined by X-ray diffraction (*vide infra*).

Treatment of the halide-bridged dinuclear complexes **2a**, **6a** and **2b** with tertiary diphosphines in 1:1 molar ratio gave the dinuclear compounds [{Pd[2-Br-4,5-(OCH$_2$O)-C$_6$HC(H)=N(Cy)-*C6,N*]}$_2${μ-Ph$_2$PC(H)=C(H)PPh$_2$}] **5a**, [{Pd[4,5-(OCH$_2$O)C$_6$H$_2$C(H)=N(Cy)-*C2,N*]}$_2${μ-Ph$_2$PC(H)=C(H)PPh$_2$}] **9a** and [{Pd[4,5-(OCH$_2$CH$_2$)C$_6$H$_2$C(H)=N(Cy)-*C6,N*]}$_2$(μ-Ph$_2$PCH$_2$PPh$_2$)] **5b**, with the diphosphine in a bridging mode. The MS-FAB spectrum showed peaks assigned to [(L-H)$_2$Pd$_2$X$_2$(diphosphine)]$^+$, [(L-H)$_2$Pd$_2$X-(diphosphine)]$^+$ and [(L-H)$_2$Pd$_2$(diphosphine)]$^+$ (X = Cl, Br), showing a typical way of fragmentation. The ^{31}P–{^{1}H} NMR spectra showed one singlet, in accordance with equivalent phosphorus nuclei, indicating the symmetric

nature of the complexes, shifted to higher frequency from the free phosphine, in agreement with phosphorus coordination to metal center. In the ^{1}H NMR spectra the *H*C=N resonance appeared as a doublet by coupling to phosphorus, in agreement with a P *trans* to N arrangement, within the terms of the "transphobic effect" [21]. The crystal structure of compounds **5a** and **5b** have been determined by X-ray diffraction (*vide infra*).

2.3. X-ray diffraction analysis

Suitable crystals of complexes **3a**, **4a**, **5a**, **8a**, **2b**, **3b** and **5b** were obtained and their molecular structure determined. The labeling schemes for the compounds are shown in Figs. 2–8. The crystals consist of discrete molecules, separated by normal van der Waals distances. Crystallographic data and selected interatomic distances and angles are listed in Tables 1–4.

2.3.1. Molecular structure of complex 2b

Suitable crystals of compound **2b** were grown by slowly evaporating a chloroform solution. The structure comprises a dinuclear molecule (one molecule per asymmetric unit), and may be regarded as a dimeric structure in which two cyclometallated moieties are linked by chlorine-bridging ligands (see Fig. 2). Both cyclometallated moieties have very similar bond distances and angles and discussion will be limited to only one of them.
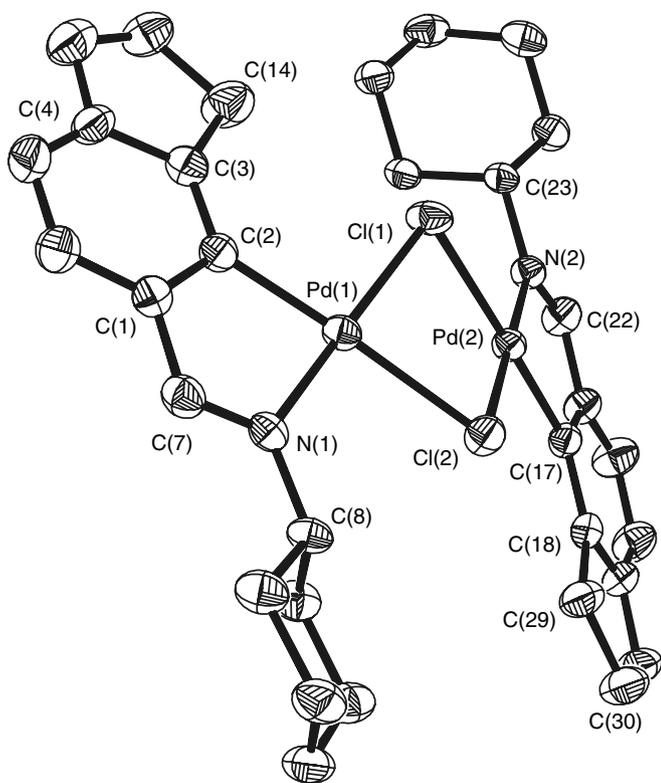

Fig. 3. Molecular structure of the cation for [Pd{2-Br-4,5-(OCH$_2$O)-C$_6$HC(H)=N(Cy)-*C6,N*}{(Ph$_2$PCH$_2$CH$_2$)$_2$PPh-*P,P,P*}][PF$_6$] (**3a**), with labelling scheme. Hydrogen atoms and phosphine phenyl rings have been omitted for clarity.

Fig. 2. Molecular structure of [Pd{4,5-(OCH$_2$CH$_2$)C$_6$H$_2$C(H)=N(Cy)-*C6,N*}(μ-Cl)]$_2$ (**2b**), with labelling scheme. Hydrogen atoms have been omitted for clarity.

Fig. 4. Molecular structure of the cation for [Pd{4,5-(OCH$_2$CH$_2$)-C$_6$H$_2$C(H)=N(Cy)-*C6,N*}{(Ph$_2$PCH$_2$CH$_2$)$_2$PPh-*P,P,P*}][PF$_6$] (**3b**), with labelling scheme. Hydrogen atoms and phosphine phenyl rings have been omitted for clarity.
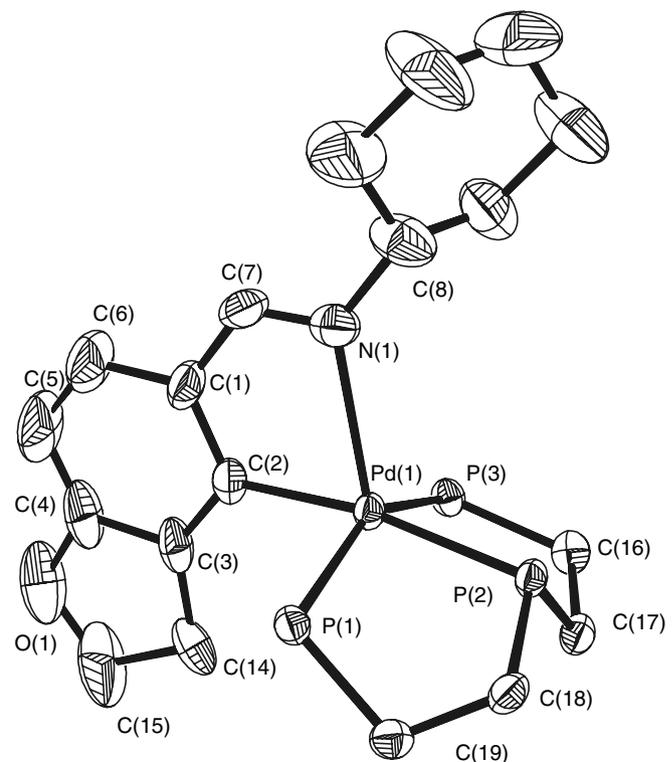
Each palladium atom is bonded to the ligand through the imine nitrogen and the C(2) carbon atom; the coordination sphere is completed by the two bridging chlorine
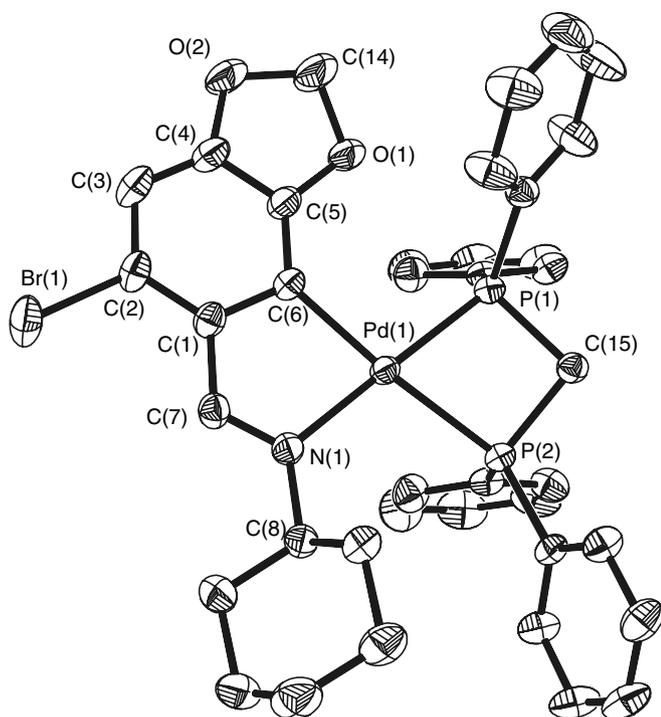
Fig. 5. Molecular structure of the cation for [Pd{2-Br-4,5-(OCH$_2$O)C$_6$HC(H)=N(Cy)-C6,N} (Ph$_2$PCH$_2$PPh$_2$-P,P)][PF$_6$] (**4a**), with labelling scheme. Hydrogen atoms have been omitted for clarity.

Fig. 7. Molecular structure of the cation for [Pd{4,5-(OCH$_2$O)C$_6$H$_2$C(H)=N(Cy)-C2,N}(Ph$_2$PCH$_2$PPh$_2$-P,P)][PF$_6$] (**8a**), with labelling scheme. Hydrogen atoms have been omitted for clarity.

ligands. The sum of angles about the palladium atoms is 360.30°, with the only noteworthy deviation being the somewhat reduced C(2)–Pd(1)–N(1) bond angle of 81.30(17). The geometry around the palladium atoms is planar [mean deviation from the least square plane for plane Pd(1), N(1), C(2), Cl(1), Cl(2) of 0.0825 Å].

The Pd(1)–N(1) bond length, 2.034(3) Å, is accordance with the predicted single bond value of 2.011 Å, based on the sum of covalent radii for nitrogen (sp^2) and palladium, 0.701 and 1.31 Å, respectively [22]. The Pd(1)–C(2) bond length of 1.999(4) Å is shorter than the expected value of 2.081 Å (based on the sum of the covalent radii for carbon (sp^2) and palladium, 0.771 and 1.31 Å, respectively),
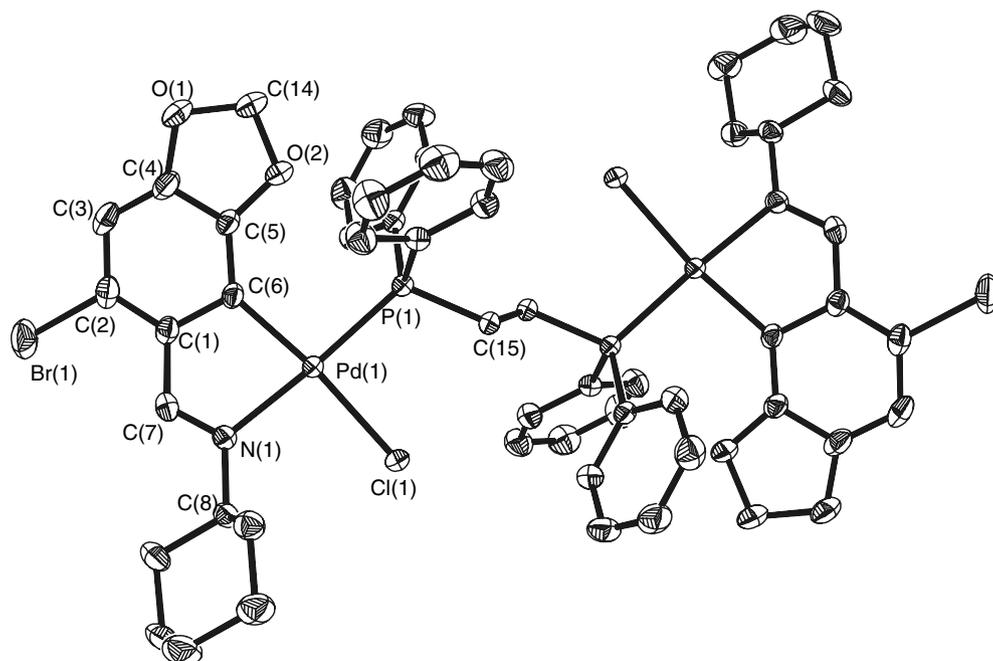
Fig. 6. Molecular structure of [{Pd[2-Br-4,5-(OCH$_2$O)C$_6$HC(H)=N(Cy)-C6,N]}$_2${μ-Ph$_2$PC(H)=C(H)PPh$_2$}] (**5a**), with labelling scheme. Hydrogen atoms have been omitted for clarity.

Fig. 8. Molecular structure of [{Pd[4,5-(OCH₂CH₂)C₆H₂C(H)=N(Cy)-*C6,N*]}₂(μ-Ph₂PCH₂PPh₂)] (**5b**), with labelling scheme. Hydrogen atoms have been omitted for clarity.

Table 1
Crystal and structure refinement data for complexes **3a**, **4a**, **5a** and **8a**

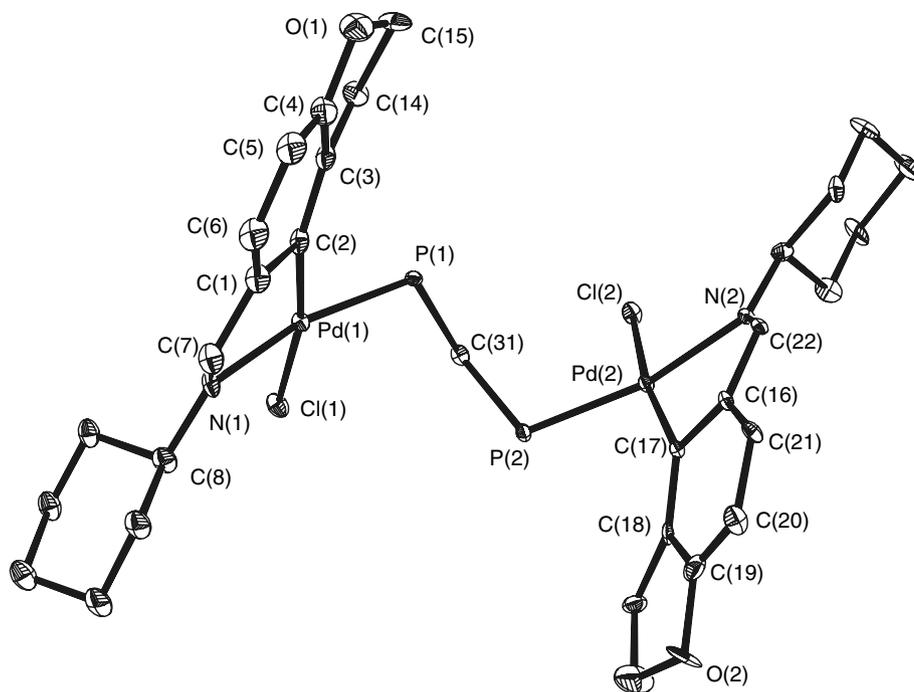|	**3a**	**4a**	**5a · 4CHCl₃**	**8a · CH₃CN**
Empirical formula	$C_{48}H_{48}BrF_6NO_2P_4Pd$	$C_{39}H_{37}BrF_6NO_2P_3Pd \cdot H_2O$	$C_{58}H_{56}Br_2Cl_{14}N_2O_4P_2Pd_2$	$C_{41}H_{41}F_6N_2O_2P_3Pd$
Formula weight	1095.06	962.93	1775.91	907.07
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_{(1)}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions				
a (Å)	11.2440(4)	12.7116(6)	10.4369(9)	9.5731(11)
b (Å)	17.3833(6)	13.9014(7)	12.5983(11)	12.3400(14)
c (Å)	12.7943(5)	13.9784(7)	15.7689(13)	18.203(2)
α (°)	90	77.3320(10)	110.3010(10)	71.243(2)
β (°)	106.9070(10)	68.5880(10)	91.871(2)	82.818(2)
γ (°)	90	63.4860(10)	113.5000(10)	79.435(2)
Z	2	2	1	2
$2\theta_{max}$ (°)	56.60	56.62	58.40	56.66
Independent reflections [R_{int}]	11 824 [0.0786]	10 143 [0.0250]	8519 [0.0363]	9851 [0.1025]
S	1.019	1.084	1.009	1.016
R [F, I > 2σ(I)]	0.0555	0.0406	0.0409	0.0742
wR [F^2, all data]	0.1099	0.1402	0.0961	0.2291
Absolute structure parameter	−0.008(11)			

consistent with those found in related complexes [17,23] and with the five-membered cyclometallated ring having a significant aromatic character [24].

The asymmetric nature of the Pd(μ-Cl)₂P moiety, demonstrated by the Pd–Cl bond distances [Pd(1)–Cl(1), 2.3251(11); Pd(1)–Cl(2), 2.4541(12); Pd(2)–Cl(2), 2.3361(11); Pd(2)–Cl(1), 2.4622(12) Å], results from the differing *trans* influence of the nitrogen and carbon atoms of the Schiff base ligand [17,23,25].

Except for the cyclohexyl and the OCH₂CH₂ groups, the cyclopalladated moiety is nearly planar. The mean deviations from the least squares planes determined for the metallated phenyl ring [C(1), C(2), C(3), C(4), C(5), C(6)] and the metallacycle [Pd(1), C(1), C(2), C(7), N(1)] are 0.0188 and 0.0359 Å, respectively. The angle between planes is 5.7°. The Pd(μ-Cl)₂Pd bridging ring is not planar, but is hinged about the Cl–Cl axis by 37.4°. This situation has been observed in related compounds [23b,26], but contrasts

Table 2
Crystal and structure refinement data for complexes **2b**, **3b** and **5b**

	2b	**3b**	**5b · 3CHCl₃**
Empirical formula	$C_{30}H_{34}Cl_2N_2O_2Pd_2$	$C_{49}H_{51}F_6NOP_4Pd$	$C_{58}H_{61}Cl_{11}N_2O_2P_2Pd_2$
Formula weight	738.29	1014.19	1482.78
Temperature (K)	293(2)	293(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_{(1)}/n$	$P2_{(1)}/n$	$P1n1$
Unit cell dimensions			
a (Å)	13.2638(11)	18.6972(8)	10.603(3)
b (Å)	14.5938(12)	11.1367(5)	15.079(4)
c (Å)	15.1758(13)	22.6435(10)	19.298(5)
α (°)	90	90	90
β (°)	100.327(2)	92.7770(10)	90.659(7)
γ (°)	90	90	90
Z	4	4	2
$2\theta_{max}$ (°)	56.72	56.66	50.00
Independent reflections [R_{int}]	7186 [0.0565]	11701 [0.1541]	10828 [0.1499]
S	1.028	0.979	1.001
R [F, $I > 2\sigma(I)$]	0.0416	0.0649	0.0593
wR [F^2, all data]	0.0996	0.1693	0.1043
Absolute structure parameter			−0.07(3)

Table 3
Selected bond distances (Å) and angles (°) for complexes **3a** and **3b**

	3a	**3b**
Pd(1)–C(6)	2.047(6)	
Pd(1)–C(2)		2.034(5)
Pd(1)–N(1)	2.405(4)	2.497(5)
Pd(1)–P(1)	2.3026(18)	2.3176(14)
Pd(1)–P(2)	2.2993(17)	2.3187(13)
Pd(1)–P(3)	2.3145(17)	2.3318(14)
C(1)–C(6)	1.404(8)	
C(1)–C(2)		1.417(8)
C(1)–C(7)	1.465(8)	1.460(9)
N(1)–C(7)	1.262(7)	1.246(8)
C(6)–Pd(1)–P(2)	173.15(18)	
C(2)–Pd(1)–P(2)		170.02(17)
P(1)–Pd(1)–P(3)	143.53(6)	147.87(5)
P(1)–Pd(1)–N(1)	115.43(14)	105.67(12)
P(2)–Pd(1)–N(1)	110.21(15)	112.48(14)
P(3)–Pd(1)–N(1)	100.97(14)	106.36(12)
P(1)–Pd(1)–P(2)	84.10(5)	84.64(5)
P(2)–Pd(1)–P(3)	85.65(6)	85.54(5)
C(6)–Pd(1)–N(1)	76.1(2)	
C(2)–Pd(1)–N(1)		77.3(2)
C(6)–Pd(1)–P(1)	95.71(16)	
C(2)–Pd(1)–P(1)		90.66(15)
C(6)–Pd(1)–P(3)	90.52(15)	
C(2)–Pd(1)–P(3)		93.90(16)

with the most common planar configuration of the fragment [(C-N)Pd(μ-Cl)₂Pd(C-N)] (C-N = cyclometallated ring) [27].

2.3.2. Molecular structures of complexes 3a and 3b

Suitable crystals of compounds **3a** and **3b** were grown from slowly evaporating dichloromethane/*n*-hexane solutions. The crystal structures of compounds **3a** and **3b** comprise a mononuclear cation (one ion per asymmetric unit)

and a hexafluorophosphate anion. In each structure, the palladium atom is bonded to the adjacent *ortho* carbon of the phenyl ring, C(6) in **3a** and C(2) in **3b**, to a nitrogen atom, and to the three phosphorus atoms of the tridentate phosphine ligand (see Figs. 3 and 4).

The angular structural parameter τ [28] was used to describe the geometry of the above-mentioned complexes [29]. The τ values are 0.49 and 0.37 for compounds **3a** and **3b**, respectively. The geometry of complex **3a** nearly halfway between square-pyramidal (with the palladium, metallated carbon atom and the three phosphorus atoms in the basal plane, and the iminic nitrogen at the apical position) and trigonal-bipyramidal (with the palladium, nitrogen and terminal phosphorus atoms in the equatorial plane, and the metallated carbon atom and the central phosphorus atom at the apical positions); in compound **3b** palladium coordination is closer to a square-pyramidal.

The Pd(1)–N(1) bond distances of 2.405(4) (**3a**) and 2.497(5) (**3b**) are longer than the values of 2.338(3) Å, reported recently by us in a similar complex with a triphos ligand [30b] and 2.23(2) Å found in an "authentic" penta-coordinate Pd(II) complex [31]. However, the Pd–N bond length is shorter than the weak interactions in the range 2.576(4)–2.805(5) Å found in other five-coordinate complexes of palladium with mono- and diphosphines [32].

The Pd–C bond lengths of 2.047(6) and 2.034(5) Å for **3a** and **3b**, respectively, are similar to those found in related cyclometallated complexes [30,33] with C *trans* to phosphorus but longer than Pd–C distances found in cyclometalated complexes with carbon *trans* to nitrogen or chlorine, supporting a phosphine ligand in the *trans* position.

The Pd–P bond lengths are similar to those found in related Pd(II) complexes [30,34] and suggest a slightly

Table 4
Selected bond distances (Å) and angles (°) for complexes **4a**, **5a**, **8a**, **2b** and **5b**

	4a	5a	8a	2b[a]	5b[a]
Pd(1)–C(6)	2.037(3)	2.011(3)			
Pd(1)–C(2)			2.033(7)	1.999(4)	1.991(8)
Pd(1)–N(1)	2.091(3)	2.102(3)	2.082(6)	2.034(3)	2.101(7)
Pd(1)–P(1)	2.2633(9)	2.2728(9)	2.2476(19)		2.265(3)
Pd(1)–P(2)	2.3697(9)		2.3651(18)		
Pd(1)–Cl(1)		2.3744(9)		2.3251(11)	2.382(2)
Pd(1)–Cl(2)				2.4541(12)	
C(1)–C(6)	1.426(5)	1.432(5)			
C(1)–C(2)			1.438(10)	1.404(6)	1.429(12)
C(1)–C(7)	1.465(5)	1.432(5)	1.396(11)	1.435(6)	1.436(12)
N(1)–C(7)	1.283(5)	1.272(4)	1.291(10)	1.280(5)	1.274(10)
C(6)–Pd(1)–P(2)	168.56(10)				
P(1)–Pd(1)–N(1)	177.23(8)	176.34(8)	177.41(19)		164.9(2)
C(6)–Pd(1)–Cl(1)		169.96(10)			
C(2)–Pd(1)–P(2)			171.9(2)		
C(2)–Pd(1)–Cl(2)				177.17(12)	
N(1)–Pd(1)–Cl(1)		93.36(8)		172.37(10)	93.3(2)
C(2)–Pd(1)–Cl(1)				98.54(13)	169.8(3)
C(6)–Pd(1)–N(1)	80.52(13)	80.52(12)			
C(2)–Pd(1)–N(1)			82.2(3)	81.30(16)	80.9(3)
C(6)–Pd(1)–P(1)	100.56(10)	96.02(10)			
C(2)–Pd(1)–P(1)			98.4(2)		98.0(3)
P(1)–Pd(1)–P(2)	71.56(3)		73.50(7)		
N(1)–Pd(1)–P(2)	107.75(8)		105.9(2)		
P(1)–Pd(1)–Cl(1)		90.23(3)			89.73(9)
Cl(1)–Pd(1)–Cl(2)				83.29(4)	
N(1)–Pd(1)–Cl(2)				97.17(10)	

[a] For clarity, the table includes only the observed data for one of the cyclometallated moieties.

partial double bond between the palladium and phosphorus atoms [35].

2.3.3. Molecular structures of complexes 4a, 5a, 8a and 5b

Suitable crystals of the title compounds were grown by slowly evaporating a chloroform (**4a** and **5b**), chloroform/*n*-hexane (**5a**) and acetonitrile (**8a**) solutions.

The crystal structures of **4a** and **8a** comprise a mononuclear molecule (one molecule per asymmetric unit) and a hexafluorophosphate anion, and for compound **8a**, one acetonitrile solvent molecule. The structure of **5a** comprises a dinuclear molecule (half molecule per asymmetric unit, due to an inversion center at the middle point of the CH=CH double bond of the phosphine) and two chloroform solvent molecules. The structure of **5b** comprises a dinuclear molecule (one molecule per asymmetric unit) and three chloroform solvent molecules (see Figs. 5–8).

For compounds **4a** and **8a** the coordination sphere around each palladium atom consists of a nitrogen atom of the imine group, an *ortho* carbon atom of the phenyl ring (C6 in **4a**, C2 in **8a**), and two phosphorus atoms from a chelating dppm (see Figs. 5 and 7). For compounds **5a** and **5b** (see Figs. 6 and 8), the four-coordinated palladium(II) atoms are bonded to an adjacent *ortho* carbon atom (C6 in **4a** and **5a**, C2 in **8a** and **5b**) and to the nitrogen atom of the imine group of the deprotonated Schiff base ligand and to a chlorine atom (*trans* to carbon). A

phosphorus atom from the diphosphine ligand which bridges the two metal centers (*trans*-dppe, **5a**; dppm, **5b**) completes the metal coordination sphere.

The sums of angles at palladium are approximately 360°, with the distortions more noticeable in the somewhat reduced "bite" angles C(2)/C(6)-Pd(1)-N(1) consequent upon chelation [80.52(13), **4a**; 80.52(12), **5a**; 82.2(3), **8a**; 80.9(3), **5b**]. The requirements of the four-membered chelate ring of the phosphine force the bond angles P(1)–Pd(1)–P(2) to 71.56(3) and 73.50(7) for compounds **4a** and **8a**, respectively.

The geometry around the palladium atom is slightly distorted square-planar, the mean deviations from the least squares planes are 0.0900 (**4a**), 0.0767 (**5a**), 0.0212 (**8a**) and 0.1801 (**5b**).

The palladium–nitrogen bond lengths, *ca.* 2.1 Å (see Table 4), are longer than the single bond predicted value of 2.011 Å, and reflects the *trans* influence of the phosphorus atom [23,36]. The palladium–carbon bond lengths, *ca.* 2.0 Å (see Table 4), are within the expected value of 2.081 Å, but longer than those found in related complexes where partial multiple-bond character of the Pd–C bond was proposed [37], suggesting some degree of multiple-bond character in the Pd–C(aryl) linkage. The palladium–phosphorus bond distances are shorter than the sum of the single bond radii for palladium and phosphorus, 2.41 Å, suggesting some partial double bond between both

atoms and are similar to others reported earlier [38]. In compounds **4a** and **8a**, the differing influence of the phenyl carbon and imine nitrogen atoms is clearly illustrated by the Pd–P distance *trans* to carbon, Pd(1)–P(1), and *trans* to nitrogen, Pd(1)–P(2), [2.263(1) *versus* 2.370(1), **4a**; 2.248(2) *versus* 2.365(2), **8a**; respectively]. In compounds **5a** and **5b** the palladium–chloro bond lengths, 2.374(1) and 2.382(2) Å, respectively, are consistent with Pd–Cl distances found in related species [17,38b] but longer than the sum of the covalent radii (2.30 Å) as a consequence of the *trans* influence of the phenyl carbon.

Except for the cyclohexyl and the OCH_2O/OCH_2CH_2 groups, the cyclopalladated moiety is nearly planar. The mean deviations from the least squares planes determined for the metallated phenyl ring [C(1), C(2), C(3), C(4), C(5), C(6); plane 1] and the metallacycle [Pd(1), C(1), C(2)/C(6), C(7), N(1); plane 2] are 0.0089 and 0.0111 (**4a**), 0.0154 and 0.0837 (**5a**), 0.0054 and 0.0222 (**8a**), 0.0139 and 0.0922 Å (**5b**), respectively. The angles between these planes are 1.1 (**4a**), 10.4 (**5a**), 2.9 (**8a**) and 11.7 (**5b**).

In compounds **4a** and **8a** the chelate phosphine ring [Pd(1), P(1), P(2), C(15), plane 3] is almost planar, with a mean deviation from the ideal plane of 0.1754 Å (**4a**) and 0.1029° (**8a**). The angles between plane 3 and the previous planes are as follows: plane 1/plane 3: 10.1 and plane 2/plane 3: 11.0, for complex **4a**; and plane 1/plane 3: 12.1, plane 2/plane 3: 9.2, for complex **8a**.

3. Experimental

3.1. General remarks

3.1.1. Safety note

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.

Solvents were purified by standard methods [39]. Chemicals were reagent grade. The phosphines $Ph_2PCH_2PPh_2$ (dppm), *trans*-$Ph_2P(CH)_2PPh_2$ (dppe), $(Ph_2PCH_2CH_2)_2$-PPh (triphos) were purchased from Aldrich-Chemie. Microanalyses were carried out using a Carlo Erba Elemental Analyser, Model 1108. IR spectra were recorded as Nujol mulls or polythene discs Nujol mulls or KBr discs on a Satellite FTIR. NMR spectra were obtained as $CDCl_3$ solutions and referenced to $SiMe_4$ (^1H, $^{13}C-\{^1H\}$) or 85% H_3PO_4 ($^{31}P-\{^1H\}$) and were recorded on a Bruker AV-300F spectrometer. All chemical shifts were reported downfield from standards. The FAB mass spectra were recorded using a FISONS Quatro mass spectrometer with a Cs ion gun; 3-nitrobenzyl alcohol was used as the matrix.

3.2. Syntheses of the ligands

3.2.1. 2-Br-4,5-(OCH₂O)C₆H₂C(H)=N(Cy) (a)

6-Bromopiperonal (1.000 g, 4.366 mmol) and cyclohexylamine (1.000 g, 6.749 mmol) were added to 50 cm³ of

dry chloroform. The mixture was heated under reflux in a Dean-Stark apparatus for 8 h. After cooling to room temperature, the solvent was evaporated to give a white solid. Yield: 98%. IR: $v(C=N)$ 1624 h cm^{-1}. NMR ^1H (300 MHz, CDCl₃, δ ppm, J Hz): δ = 8.55 [s, 1H, H_i], 7.52 [s, 1H, H_6], 6.98 [s, 1H, H_3], 5.99 [s, 2H, OCH_2O]. NMR $^{13}C-\{^1H\}$ (300 MHz, CDCl₃, δ ppm, J Hz): δ = 157.06 [s, C=N], 150.09 [s, C_4], 147.73 [s, C_5], 128.91 [s, C_1], 116.91 [s, C_2], 112.42 [s, C_3], 107.84 [s, C_6], 101.99 [s, OCH_2O], 69.48 [s, C_7], 34.39 [s, C_8/C_{12}], 25.64 [s, C_{10}], 24.71 [s, C_9/C_{11}].

3.2.2. 4,5-(OCH₂CH₂)C₆H₃C(H)=N(Cy) (b)

Schiff base ligand **b** was prepared similarly to give a brown solid, but using 2,3-dihydrobenzofuran-5-carboxaldehyde as starting material. Yield: 98%. IR: $v(C=N)$ 1638 h cm^{-1}. NMR ^1H (300 MHz, CDCl₃, δ ppm, J Hz): δ = 8.21 [s, 1H, H_i], 7.69 [s, 1H, H_6], 7.37 [d, 1H, H_2, $^3J(H_2H_3)$ = 8.2], 6.77 [d, 1H, H_3], 4.58 [t, 2H, CH_2^a, $^3J(H^aH^b)$ = 8.6], 3.18 [t, 2H, CH_2^b]. NMR $^{13}C-\{^1H\}$ (300 MHz, CDCl₃, δ ppm, J Hz): δ = 162.00 [s, C_4], 158.08 [s, C=N], 129.61 [s, C_3], 129.58 [s, C_5], 127.62 [s, C_1], 123.76 [s, C_6], 108.86 [s, C_2], 71.59 [s, CH_2^a], 69.71 [s, C_7], 34.41 [s, C_8/C_{12}], 29.09 [s, CH_2^b], 25.54 [s, C_{10}], 24.79 [s, C_9/C_{11}].

3.3. Synthesis of the cyclopalladated complexes

3.3.1. [Pd{2-Br-4,5-(OCH₂O)C₆HC(H)=N(Cy)-C6,N}(μ-O₂CMe)]₂ (1a)

A pressure tube containing 2-Br-4,5-(OCH₂O)-C₆H₂C(H)=N(C₆H₁₁) (0.457 g, 1.475 mmol), palladium(II) acetate (0.301 g, 1.341 mmol) and 20 cm³ of dry toluene was sealed under argon. The mixture was heated for 24 h at 60 °C. After cooling to r.t. the solution was filtered through celite to remove the black palladium formed. The solvent was removed under vacuum to give a brown oil, which was chromatographed on a column packed with silica gel. Elution with dichloromethane/ethanol (0.2%) afforded the final product as a yellow solid after solvent removal. Yield: 71%. Anal. Found: C, 40.4; H, 3.7; N, 2.8%; $C_{32}H_{36}N_2O_8Br_2Pd_2$ requires C, 40.5; H, 3.8; N, 2.9%. IR: $v(C=N)$ 1604 h, $v_{as}(COO)$ 1581f, $v_s(COO)$ 1427f cm^{-1}. NMR ^1H (300 MHz, CDCl₃, δ ppm, J Hz): δ = 7.67 [s, 1H, H_i], 6.65 [s, 1H, H_3], 5.94, 5.90 [s, 2H, OCH_2O], 2.02 [s, 3H, O₂CMe]. NMR $^{13}C-\{^1H\}$ (300 MHz, CDCl₃, δ ppm, J Hz): δ = 182.10 [s, CH_3CO_2], 168.63 [s, C=N], 151.03 [s, C_4], 148.89 [s, C_5], 139.90 [s, C_1], 128.86 [s, C_6], 113.47 [s, C_2], 108.31 [s, C_3], 100.99 [s, OCH_2O], 64.89 [s, C_7], 34.61 [s, C_8/C_{12}], 26.01 [s, C_{10}], 25.59, 25.56 [s, C_9, C_{11}], 23.31 [s, CH_3CO_2]. MS-FAB: m/z = 417.8 [{(L-H)Pd}H]$^+$, 890.6 [(L-H)₂Pd₂(OAc)}H]$^+$, 949.6 [{(L-H)₂Pd₂(OAc)₂}H]$^+$.

3.3.2. [Pd{2-Br-4,5-(OCH₂O)C₆HC(H)=N(Cy)-C6,N}(μ-Cl)]₂ (2a)

A solution of **1a** (0.450 g, 0.474 mmol) in 15 cm³ of acetone was treated with an aqueous saturated solution of

NaCl. The pale green precipitate formed was filtered off, washed with water and dried under vacuum. Yield 63%. Anal. Found: C, 37.4; H, 3.4; N, 3.2%; $C_{28}H_{30}N_2O_4Cl_2Br_2Pd_2$ requires C, 37.3; H, 3.3; N, 3.1%. IR: $v(C=N)$ 1597f, $v(Pd–Cl_{trans-N})$ 320m, $v(Pd–Cl_{trans-C})$ 290m cm^{-1}. NMR ^1H (300 MHz, CDCl$_3$, δ ppm, J Hz): δ = 7.98 [s, 1H, H$_i$], 6.68 [s, 1H, H$_3$], 5.91 [s, 2H, OCH_2O]. NMR ^{13}C–{^1H} (300 MHz, CDCl$_3$, δ ppm, J Hz): δ = 169.52 [s, C=N], 150.72 [s, C$_4$], 148.83 [s, C$_5$], 139.58 [s, C$_1$], 127.59 [s, C$_6$], 113.54 [s, C$_2$], 108.76 [s, C$_3$], 100.81 [s, OCH_2O], 66.65 [s, C$_7$], 32.88 [s, C$_8$/C$_{12}$], 29.68 [s, C$_{10}$], 25.36 [s, C$_9$/C$_{11}$]. MS-FAB: m/z = 415.9 [(L-H)PdCl]$^+$, 866.6 [{(L-H)$_2$Pd$_2$Cl}H]$^+$.

3.3.3. [Pd{2-Br-4,5-(OCH$_2$O)C$_6$HC(H)=N(Cy)-C6,N}{(Ph$_2$PCH$_2$CH$_2$)$_2$PPh-P,P,P}][PF$_6$] (3a)

(Ph$_2$PCH$_2$CH$_2$)$_2$PPh (0.024 g, 0.044 mmol) was added to a suspension of **2a** (0.020 g, 0.022 mmol) in acetone (10 cm^3). The mixture was stirred for 30 min, after which an excess of ammonium hexafluorophosphate was added. The mixture was stirred for a further 1 h, after which the complex was precipitated out by addition of water, filtered off and dried *in vacuo*, gave the final compound as a pale yellow solid. Yield: 84%. Anal. Found: C, 52.5; H, 4.6; N, 1.4%; $C_{48}H_{48}NO_2BrF_6P_4Pd$ requires C, 52.6; H, 4.4; N, 1.3%. IR: $v(C=N)$ 1612m cm^{-1}. NMR ^1H (300 MHz, CDCl$_3$, δ ppm, J Hz): δ = 8.54 [s, 1H, H$_i$], 6.59 [s, 1H, H$_3$], 4.53 [s, 2H, OCH_2O]. NMR ^{31}P–{^1H} (300 MHz, CDCl$_3$, δ ppm, J Hz): δ = 84.45 [t, 1P, $^3J(PP)$ = 24.0], 41.96 [d, 2P]. NMR ^{13}C–{^1H} (500 MHz, CDCl$_3$, δ ppm, J Hz): δ = 165.55 [d, C=N, $^3J(PC=N)$ = 4.3], 151.62 [s, C$_4$], 146.80 [d, C$_5$, $^3J(PC_5)$ = 7.0], 140.35 [d, C$_6$, $^2J(PC_6)$ = 108.5], 135.00 [d, C$_1$, $^3J(PC_1)$ = 2.7], 119.14 [d, C$_2$, $^4J(PC_2)$ = 10.2], 109.23 [s, C$_3$], 99.64 [s, OCH_2O], 66.80 [s, C$_7$], 32.92 [s, C$_8$/C$_{12}$], 31.55, 25.69 [m, P(CH$_2$)$_2$P], 25.39 [s, C$_{10}$], 25.10 [s, C$_9$/C$_{11}$]. P-phenyl; 133.03 [ta, C$_i$], 132.81 [ta, C$_o$], 131.99 [ta, C$_o$], 131.73 [s, C$_p$], 131.33 [ta, C$_o$], 131.71 [s, C$_p$], 131.01 [ta, C$_i$], 130.45 [s, C$_p$], 129.54 [ta, C$_i$], 129.50 [d, C$_m$], 128.79 [ta, C$_m$], 128.13 [ta, C$_m$]. MS-FAB: m/z = 737.0 [(L-H-Br)Pd(triphos)]$^+$, 950.1 [{(L-H)Pd(triphos)}H]$^+$. Specific molar conductivity: Λ_m = 122.9 Ω^{-1} cm^2 mol^{-1} (in acetonitrile).

3.3.4. [Pd{2-Br-4,5-(OCH$_2$O)C$_6$HC(H)=N(Cy)-C6,N}(Ph$_2$PCH$_2$PPh$_2$-P,P)][PF$_6$] (4a)

Compounds **4a** was obtained as pale brown, following a similar procedure that **3a** but using the phosphine Ph$_2$PCH$_2$PPh$_2$.

Yield: 81%. Anal. Found: C, 49.7; H, 3.9; N, 1.4%; $C_{39}H_{37}NO_2BrF_6P_3Pd$ requires C, 49.6; H, 3.9; N, 1.5% IR: $v(C=N)$ 1604hd cm^{-1}. NMR ^1H (300 MHz, CDCl$_3$, δ ppm, J Hz): δ = 8.53 [d, 1H, H$_i$, $^4J(P_{trans-N}H_i)$ = 6.4], 6.71 [s, 1H, H$_3$], 5.06 [s, 2H, OCH_2O], 4.29 [t$_{ancho}$, 2H, PCH$_2$P]. NMR ^{31}P–{^1H} (300 MHz, CDCl$_3$, δ ppm, J Hz): δ = –13.97 [d, P$_{trans-N}$, $^2J(PP)$ = 72.2], –35.23 [d, P$_{trans-C}$]. NMR ^{13}C–{^1H} (500 MHz, CDCl$_3$, δ ppm, J Hz): δ = 175.17 [s, C=N], 150.33 [s, C$_5$], 150.15 [dd, C$_4$,

$^4J(P_{trans-C}C_4)$ = 8.1, $^4J(P_{trans-N}C_4)$ = 1.4], 140.17 [s, C$_1$], 137.47 [dd, C$_6$, $^2J(P_{trans-C}C_6)$ = 128.3, $^2J(P_{trans-N}C_6)$ = 4.7], 116.77 [d, C$_2$, $^4J(PC_2)$ = 9.1], 110.62 [s, C$_3$], 99.98 [s, OCH_2O], 69.14 [s, C$_7$], 42.53 [dd, P(CH$_2$)$_2$P, $^1J(P_{trans-C}C)$ = 28.2, $^1J(P_{trans-N}C)$ = 22.1], 33.55 [s, C$_8$/C$_{12}$], 24.97 [s, C$_{10}$], 24.60 [s, C$_9$/C$_{11}$]. P-phenyl; 133.38 [d, C$_o$, $^2J(PC_o)$ = 13.4], 133.22 [d, C$_o$ $^2J(PC_o)$ = 13.3], 132.28 [a, C$_p$], 131.80 [a, C$_p$], 129.79 [d, C$_m$, $^3J(PC_m)$ = 12.3], 129.13 [$^3J(PC_m)$ = 10.8], 127.53 [dd, C$_i$, $^1J(PC_i)$ = 51.8, $^3J(PC_i)$ = 3.9], 126.85 [dd, C$_i$, $^1J(PC_i)$ = 34.9, $^3J(PC_i)$ = 4.3]. MS-FAB: m/z = 799.9 [(L-H)Pd(dppm)]$^+$. Specific molar conductivity: Λ_m = 150.0 Ω^{-1} cm^2 mol^{-1} (in acetonitrile).

3.3.5. [{Pd[2-Br-4,5-(OCH$_2$O)C$_6$HC(H)=N(Cy)-C6,N]}$_2${μ-Ph$_2$PC(H)=C(H)PPh$_2$}] (5a)

Ph$_2$PCH$_2$PPh$_2$ (0.031 g, 0.078 mmol) was added to a suspension of **2a** (0.070 g, 0.078 mmol) in acetone (15 cm^3). The mixture was stirred for 24 h and solvent removed to give a white solid which was recrystallized from chloroform/hexane. Yield: 64%. Anal. Found: C, 49.8; H, 4.1; N, 2.1%; $C_{54}H_{52}N_2O_4Cl_2Br_2P_2Pd_2$ requires C, 49.9; H, 4.0; N, 2.2%. IR: $v(C=N)$ 1615m cm^{-1}. NMR N ^1H (300 MHz, CDCl$_3$, δ ppm, J Hz): δ = 8.45 [m, 1H, H$_i$], 6.98 [ta, 1H, CH=CH, N = 18.9], δ6.52 [s, 1H, H$_3$], 4.83 [s, 2H, OCH_2O]. NMR ^{31}P–{^1H} (300 MHz, CDCl$_3$, δ ppm, J Hz): δ = 28.87 [s]. MS-FAB: m/z = 814.0 [(L-H)PdCl{PPh$_2$C(H)=C(H)}]$^+$, 989.1 [(L-H)Pd$_2$Cl$_2$-(t-dppe)]$^+$.

3.3.6. [Pd{4,5-(OCH$_2$O)C$_6$H$_2$C(H)=N(Cy)-C2,N}(μ-Br)]$_2$ (6a)

A pressure tube containing 4,5-(OCH$_2$CH$_2$)C$_6$H$_3$-C(H)=N(C$_6$H$_{11}$) (0.297 g, 0.958 mmol), tris- (dibenzylideneacetone)dipalladium(0) (0.399 g, 0.436 mmol) and 50 cm^3 of dry toluene was sealed under argon. The mixture was heated for 24 h at 80 °C. After cooling to r.t. the solvent was removed under vacuum to give a green solid. Yield: 71%. Anal. Found: C, 40.3; H, 3.7; N, 3.3%; $C_{28}H_{32}N_2O_4Br_2Pd_2$ requires C, 40.4; H, 3.9; N, 3.4%. IR: $v(C=N)$ 1613d cm^{-1}. NMR ^1H (300 MHz, CDCl$_3$, δ ppm, J Hz): δ = 8.05 [s, 1H, H$_i$], 7.40 [s, 1H, H$_6$], 6.99 [s, 1H, H$_3$], 5.94 [s, 2H, OCH_2O]. MS-FAB: m/z = 752.9 [(L-H)$_2$Pd$_2$Br]$^+$, 832.8 [(L-H)$_2$Pd$_2$Br$_2$]$^+$.

3.3.7. [Pd{4-5-(OCH$_2$O)C$_6$H$_2$C(H)=N(C$_6$H$_{11}$)-C2,N}{(Ph$_2$PCH$_2$CH$_2$)$_2$PPh-P,P,P}][PF$_6$] (7a)

Compound **7a** was obtained as a yellow solid, following a similar procedure that **3a** but using **6a** and as starting material.

Yield: 89%. Anal. Found: C, 56.8; H, 4.8; N, 1.3%; $C_{48}H_{49}NO_2P_4F_6Pd$ requires C, 56.7; H, 4.9; N, 1.4%. IR: $v(C=N)$ 1596d cm^{-1}. NMR ^1H (300 MHz, CDCl$_3$, δ ppm, J Hz): δ = 7.94 [s, 1H, H$_i$], 6.82 [d, 1H, H$_6$], 5.70 [s, 2H, OCH_2O], 5.18 [d, 1H, H$_3$, $^4J(PH_3)$ = 7.7]. NMR ^{31}P–{^1H} (300 MHz, CDCl$_3$, δ ppm, J Hz): δ = 85.45 [d, 2P, $^3J(PP)$ = 26.3], 43.7 [t, 1P]. NMR ^{13}C–{^1H}

(500 MHz, CDCl$_3$, δ ppm, J Hz): δ = 165.12 [d, C=N, ^3J(PC=N) = 5.1], 158.98 [d, C$_2$, ^2J(PC$_2$) = 114.9], 147.99 [d, C$_4$, ^4J(PC$_4$) = 11.7], 145.8 [s, C$_5$], 136.58 [d, C$_1$, ^3J(PC$_1$) = 4.7], 117.54 [s, C$_3$], 110.40 [d, C$_6$, ^4J(PC$_6$) = 7.5], 100.39 [s, OCH$_2$O], 66.75 [s, C$_7$], 33.68 [s, C$_8$/C$_{12}$], 33.23, 26.85 [m, P(CH$_2$)$_2$P], 25.10 [s, C$_{10}$], 24.86 [s, C$_9$/C$_{11}$]. P-phenyl; 132.87 [ta, C$_o$], 132.12 [ta, C$_o$], 131.56 [d, C$_p$], 131.50 [ta, C$_i$], 131.16 [s, C$_p$], 131.12 [d, C$_o$], 130.97 [ta, C$_i$], 130.71 [s, C$_p$], 129.85 [ta, C$_i$], 129.63 [d, C$_m$], 128.73 [m, C$_m$]. MS-FAB: m/z = 426.0 [(L-H)Pd(P(CH$_2$)$_2$P)]$^+$, 870.1 [(L-H)Pd(triphos)]$^+$, 1015.1 [(L-H)Pd(triphos)(PF$_6$)]$^+$. Specific molar conductivity: Λ_m = 112.7 Ω^{-1} cm^2 mol^{-1} (in acetonitrile).

3.3.8. [Pd{4,5-(OCH$_2$O)C$_6$H$_2$C(H)=N(Cy)-C2,N}(Ph$_2$PCH$_2$PPh$_2$-P,P)][PF$_6$] (8a)

Compound **8a** was obtained as a yellow solid, following a similar procedure that **3a** but using **6a** and Ph$_2$PCH$_2$PPh$_2$ as starting materials.

Yield: 89%. Anal. Found: C, 64.8; H, 5.4; N, 1.8%; C$_{39}$H$_{38}$NO$_2$P$_2$Pd requires C, 64.9; H, 5.3; N, 1.9% IR: ν(C=N) 1616hd cm^{-1}. NMR ^{1}H (300 MHz, CDCl$_3$, δ ppm, J Hz): δ = 8.07 [d, 1H, H$_i$, ^4J(P$_{trans\text{-}N}$H$_i$) = 7.7], 6.94 [d, 1H, H$_6$, ^5J(P$_{trans\text{-}C}$H$_6$) = 2.9], 6.19 [dd, 1H, H$_3$, ^4J(P$_{trans\text{-}C}$H$_3$) = 9.6, ^4J(P$_{trans\text{-}N}$H$_3$) = 7.0] 5.86 [s, 2H, OCH$_2$O], 4.27 [dd, 2H, PCH$_2$P, ^2J(P$_{trans\text{-}C}$H) = 8.1, ^2J(P$_{trans\text{-}N}$H) = 11.5]. NMR ^{31}P–{^{1}H} (300 MHz, CDCl$_3$, δ ppm, J Hz): δ = –6.16 [d, P$_{trans\text{-}N}$, ^2J(PP) = 65.6], –29.19 [d, P$_{trans\text{-}C}$]. NMR ^{13}C–{^{1}H} (300 MHz, CDCl$_3$, δ ppm, J Hz): δ = 174.74 [t, C=N, ^3J(PC=N) = 4.8], 157.84 [dd, C$_2$, ^2J(P$_{trans\text{-}C}$C$_2$) = 130.1, ^2J(P$_{trans\text{-}N}$C$_2$) = 8.7], 149.19 [dd, C$_4$, ^4J(P$_{trans\text{-}C}$C$_4$) = 14.7, ^4J(P$_{trans\text{-}N}$C$_4$) = 9.8], 145.89 [d, C$_5$, ^5J(P$_{trans\text{-}C}$C$_5$) = 1.4], 140.95 [d, C$_1$, ^3J(PC$_1$) = 2.0], 117.09 [dd, C$_3$, ^3J(P$_{trans\text{-}C}$C$_3$) = 14.2, ^3J(P$_{trans\text{-}N}$C$_3$) = 4.7], 109.31 [d, C$_6$, ^4J(PC$_6$) = 2.0], 101.14 [s, OCH$_2$O], 69.05 [s, C$_7$], 41.59 [dd, P(CH$_2$)$_2$P, ^1J(P$_{trans\text{-}C}$C) = 27.2, ^1J(P$_{trans\text{-}N}$C) = 21.0], 33.27 [s, C$_8$/C$_{12}$], 24.85 [s, C$_{10}$], 24.47 [s, C$_9$/C$_{11}$]. P-phenyl; 133.72 [d, C$_o$, ^2J(PC$_o$) = 13.5], 133.35 [d, C$_o$, ^2J(P$_{trans\text{-}N}$C$_o$) = 13.2], 132.79 [d, C$_p$, ^4J(PC$_p$) = 2.9], 132.13 [d, C$_p$, ^4J(PC$_p$) = 2.5], 129.78 [d, C$_m$, ^3J(PC$_m$) = 12.0], 129.63 [d, C$_m$, ^3J(PC$_m$) = 10.6], 127.59 [dd, C$_i$, ^1J(PC$_i$) = 48.8, ^3J(PC$_i$) = 4.6]. 124.86 [dd, C$_i$, ^1J(PC$_i$) = 48.8, ^3J(P$_{trans\text{-}N}$C$_i$) = 4.7]. MS-FAB: m/z = 720.1 [(L-H)Pd(dppm)]$^+$. Specific molar conductivity: Λ_m = 118.9 Ω^{-1} cm^2 mol^{-1} (in acetonitrile).

3.3.9. [{Pd[4,5-(OCH$_2$O)C$_6$H$_2$C(H)=N(Cy)-C2,N]}$_2${μ-Ph$_2$PC(H)=C(H)PPh$_2$}] (9a)

To a suspension of **6a** (0.041 g, 0.048 mmol) in acetone (15 cm^3), t-Ph$_2$P(CH$_2$)$_2$PPh$_2$ (0.019 g, 0.048 mmol) was added. The mixture was stirred for 24 h and the resulting grey solid filtered off and dried in vacuo. Yield: 91%. Anal. Found: C, 52.6; H, 4.2; N, 2.1%; C$_{54}$H$_{54}$N$_2$O$_4$Br$_2$P$_2$Pd$_2$ requires C, 52.7; H, 4.4; N, 2.3%. IR: ν(C=N) 1582f cm^{-1}. NMR ^{1}H (300 MHz, CDCl$_3$, δ ppm, J Hz): δ = 6.77 [s, 1H, H$_6$], 6.65 [ta, 1H, CH=CH, N = 21.4],

5.88 [m, H, H$_3$], 5.68 [s, 2H,OCH$_2$O]. NMR ^{31}P–{^{1}H} (300 MHz, CDCl$_3$, δ ppm, J Hz): δ = 35.80 [s]. MS-FAB: m/z = 736.1 [{(L-H)PdBr(PPh$_2$(CH$_2$)$_2$PPh)}H]$^+$, 812.0 [(L-H)PdBr(t-dppe)]$^+$, 918.9 [(L-H)Pd$_2$Br(t-dppe)]$^+$, 1151.0 [(L-H)$_2$Pd$_2$Br$_2$(PPh$_2$(CH$_2$)$_2$PPh)]$^+$, 1229.0 [{(L-H)$_2$Pd$_2$Br$_2$(t-dppe)}H]$^+$.

3.3.10. [Pd{4,5-(OCH$_2$CH$_2$)C$_6$H$_2$C(H)=N(Cy)-C6,N}(μ-O$_2$CMe)]$_2$ (1b)

Compound **1b** was obtained as a yellow solid, following a similar procedure that **1a** but using **b** as starting material.

Yield: 56%. Anal. Found: C, 40.4; H, 3.7; N, 2.8%; C$_{34}$H$_{44}$N$_2$O$_6$Pd$_2$ requires C, 51.7; H, 5.6; N, 3.5%. IR: ν(C=N) 1610h, ν_{as}(COO) 1571f, ν_s(COO) 1412f cm^{-1}. NMR ^{1}H (300 MHz, CDCl$_3$, δ ppm, J Hz): δ = 7.21 [s, 1H, H$_i$], 6.93 [d, 1H, H$_2$, ^3J(H$_2$H$_3$) = 7.9], 6.44 [d, 1H, H$_3$], 4.58, 4.44 [m, 2H, CH$_2$^{a}], 3.46, 2.96 [m, 2H, CH$_2$^{b}], 2.11 [s, 3H, O$_2$CMe]. NMR ^{13}C–{^{1}H} (300 MHz, CDCl$_3$, δ ppm, J Hz): δ = 180.64 [s, CH$_3$CO$_2$], 167.01 [s, C=N], 160.27 [s, C$_4$], 150.25 [s, C$_6$], 140.51 [s, C$_1$], 131.70 [s, C$_5$], 127.58 [s, C$_3$], 104.95 [s, C$_2$], 71.81 [s, CH$_2$^{a}], 64.33 [s, C$_7$], 34.65, 30.57 [s, C$_8$,C$_{12}$], 29.93 [s, CH$_2$^{b}], 26.15, 25.70, 25.52 [s, C$_9$, C$_{10}$, C$_{11}$], 23.52 [s, CH$_3$CO$_2$].

3.3.11. [Pd{4,5-(OCH$_2$CH$_2$)C$_6$H$_2$C(H)=N(Cy)-C6,N}(μ-Cl)]$_2$ (2b)

Compound **2b** was prepared similarly that **2a** as yellow solid, but using **1b** as starting material.

Yield 84%. Anal. Found: C, 48.7; H, 4.8; N, 3.7%; C$_{30}$H$_{36}$N$_2$O$_2$ Cl$_2$Pd$_2$ requires C, 48.7; H, 4.9; N, 3.8%. IR: ν(C=N) 1612f, ν(Pd–Cl$_{trans\text{-}N}$) 325m, ν(Pd–Cl$_{trans\text{-}C}$) 290m cm^{-1}. NMR ^{1}H (300 MHz, CDCl$_3$, δ ppm, J Hz): δ = 7.70 [s, 1H, H$_i$], 7.03 [d, 1H, H$_2$, ^3J(H$_2$H$_3$) = 7.9], 6.49 [d, 1H, H$_3$], 4.51 [t, 2H, CH$_2$^{a}, ^3J(H^{a}H^b) = 8.8], 3.46 [m, 2H, CH$_2$^{b}]. NMR ^{13}C–{^{1}H} (300 MHz, CDCl$_3$, δ ppm, J Hz): δ = 169.85 [s, C=N], 160.65 [s, C$_4$], 148.98 [s, C$_6$], 140.44 [s, C$_1$], 133.74 [s, C$_5$], 128.44 [s, C$_3$], 105.91 [s, C$_2$], 71.75 [s, CH$_2$^{a}], 65.39 [s, C$_7$], 33.19 [s, C$_8$/C$_{12}$], 29.68 [s, CH$_2$^{b}], 25.58 [s, C$_9$/C$_{10}$/C$_{11}$], 23.52 [s, CH$_3$CO$_2$]. MS-FAB: m/z = 334.0 [(L-H)Pd]$^+$, 705.1 [{(L-H)$_2$Pd$_2$Cl}H]$^+$.

3.3.12. [Pd{4,5-(OCH$_2$CH$_2$)C$_6$H$_2$C(H)=N(Cy)-C6,N}{(Ph$_2$PCH$_2$CH$_2$)$_2$PPh-P,P,P}][PF$_6$] (3b)

Compound **3b** was obtained as a yellow solid, following a similar procedure that **3a** but using **2b** as starting material.

Yield: 80%. Anal. Found: C, 58.1; H, 5.1; N, 1.3%; C$_{49}$H$_{51}$NOP$_4$F$_6$Pd requires C, 58.0; H, 5.1; N, 1.4%. IR: ν(C=N) 1617m cm^{-1}. NMR ^{1}H (300 MHz, CDCl$_3$, δ ppm, J Hz): δ = 8.24 [s, 1H, H$_i$], 7.06 [d, 1H, H$_2$, ^3J(H$_2$H$_3$) = 7.9], 6.41 [d, 1H, H$_3$], 3.33 [t, 2H, CH$_2$^{a}, ^3J(H^{a}H^b) = 8.6], 2.99 [m, 2H, CH$_2$^{b}]. NMR ^{31}P–{^{1}H} (300 MHz, CDCl$_3$, δ ppm, J Hz): δ = 79.51 [t, 1P,

$^3J(PP) = 25.8$], 37.90 [d, 2P]. NMR $^{13}C-\{^1H\}$ (500 MHz, CDCl$_3$, δ ppm, J Hz): $\delta = 166.12$ [d, C=N, $^3J(PC=N) = 3.9$], 162.82 [d, C$_6$, $^2J(PC_6) = 109.5$], 161.00 [d, C$_4$, $^4J(PC_4) = 8.2$], 138.16 [d, C$_1$, $^3J(PC_1) = 3.5$], 136.95 [d, C$_5$, $^3J(PC_5) = 2.6$], 133.75 [d, C$_3$, $^5J(PC_3) = 7.8$], 105.01 [s, C$_2$], 71.09 [s, CH_2^a], 65.12 [s, C$_7$], 33.71 [s, C$_8$/C$_{12}$], 31.49, 25.51 [m, P(CH$_2$)$_2$P], 29.69 [s, CH_2^b], 25.64 [s, C$_{10}$], 25.35 [s, C$_9$/C$_{11}$]. P-phenyl; 133.17 [ta, C$_i$], 133.05 [ta, C$_o$], 132.15 [ta, C$_i$], 131.26 [ta, C$_o$], 131.25 [d, C$_o$], 131.18 [s, C$_p$], 130.50 [ta, C$_i$], 130.45 [s, C$_p$], 129.37 [d, C$_m$], 128.83 [ta, C$_m$], 128.76 [ta, C$_m$]. MS-FAB: $m/z = 862.2$ [(L-H)Pd(triphos)]$^+$. Specific molar conductivity: $\Lambda_m = 130.8\ \Omega^{-1}\ cm^2\ mol^{-1}$ (in acetonitrile).

3.3.13. [Pd{4,5-(OCH$_2$CH$_2$)C$_6$H$_2$C(H)=N(Cy)-C6,N}(Ph$_2$PCH$_2$PPh$_2$-P,P)][PF$_6$] (4b)

Compound **4b** was obtained as a yellow solid, following a similar procedure that **3a** but using **2b** and Ph$_2$PCH$_2$PPh$_2$ as starting materials.

Yield: 72%. Anal. Found: C, 55.5; H, 4.8; N, 1.7%; C$_{40}$H$_{40}$NOF$_6$P$_3$Pd requires C, 55.6; H, 4.7; N, 1.6%. IR: ν(C=N) 1613m cm^{-1}. NMR ^1H (300 MHz, CDCl$_3$, δ ppm, J Hz): $\delta = 8.09$ [d, 1 H, H$_i$, $^4J(P_{trans-N}H_i) = 9.0$], 6.56 [d, 1H, H$_3$ $^3J(H_2H_3) = 7.9$], 4.23 [dd, 2H, PCH$_2$P, $^2J(P_{trans-N}H) = 11.0$, $^2J(P_{trans-C}H) = 8.6$] 4.02 [t, 2H, CH$_2^a$, $^3J(H^aH^b) = 8.5$], 2.18 [t, 2H, CH$_2^b$]. NMR $^{31}P-\{^1H\}$ (300 MHz, CDCl$_3$, δ ppm, J Hz): $\delta = -13.84$ [d, P$_{trans-N}$, $^2J(PP) = 73.4$], -34.57 [d, P$_{trans-C}$]. NMR $^{13}C-\{^1H\}$ (500 MHz, CDCl$_3$, δ ppm, J Hz): $\delta = 175.21$ [t, C=N, $^3J(PC=N) = 3.9$], 161.85 [dd, C$_4$, $^4J(P_{trans-C}C_4) = 11.7$, $^4J(P_{trans-N}C_4) = 3.6$], 160.58 [dd, C$_6$, $^2J(P_{trans-C}C_6) = 132.9$, $^2J(P_{trans-N}C_6) = 6.2$] 142.31 [s, C$_1$], 135.62 [dd, C$_5$, $^3J(P_{trans-C}C_5) = 6.7$, $^3J(P_{trans-N}C_5) = 3.9$], 130.99 [d, C$_3$, $^5J(PC_3) = 6.5$], 107.29 [s, C$_2$], 70.79 [CH$_2^a$], 67.59 [d, C$_7$, $^3J(PC_7) = 7.1$], 43.42 [dd, P(CH$_2$)$_2$P, $^1J(P_{trans-C}C) = 29.2$, $^1J(P_{trans-N}C) = 22.1$], 33.17 [s, CH$_2^b$], 33.61 [s, C$_8$/C$_{12}$], 25.10 [s, C$_{10}$], 24.85 [s, C$_9$/C$_{11}$]. P-phenyl; 133.56 [d, C$_o$, $^2J(PC_o) = 13.7$], 133.25 [d, C$_o$, $^2J(PC_o) = 13.2$], 132.86 [d, C$_p$, $^4J(PC_p) = 2.7$], 130.99 [d, C$_p$, $^4J(PC_p) = 2.4$], 129.89 [d, C$_m$, $^3J(PC_m) = 11.9$], 129.80 [d, C$_m$, $^3J(PC_m) = 10.7$], 127.07 [dd, C$_i$, $^1J(PC_i) = 46.1$, $^3J(PC_i) = 5.1$], 126.68 [dd, C$_i$, $^1J(P_{trans-N}C_i) = 33.4$, $^3J(P_{trans-N}C_i) = 4.5$]. MS-FAB: $m/z = 718.2$ [(L-H)Pd(dppm)]$^+$. Specific molar conductivity: $\Lambda_m = 136.0\ \Omega^{-1}\ cm^2\ mol^{-1}$ (in acetonitrile).

3.3.14. [{Pd[4,5-(OCH$_2$CH$_2$)C$_6$H$_2$C(H)=N(Cy)-C6,N]}$_2$(μ-Ph$_2$PCH$_2$PPh$_2$)] (5b)

Compound **5b** was obtained as a pale yellow solid following a similar procedure that **5a** but using **2b** and Ph$_2$PCH$_2$PPh$_2$ as starting materials.

Yield: 63%. Anal. Found: C, 58.6; H, 5.1; N, 2.6%; C$_{55}$H$_{58}$N$_2$O$_2$Cl$_2$P$_2$Pd$_2$ requires C, 58.7; H, 5.2; N, 2.5%. IR: ν(C=N) 1614m cm^{-1}. NMR ^1H (300 MHz, CDCl$_3$, δ ppm, J Hz): $\delta = 7.65$ [d, 1H, H$_i$, $^4J(PH_i) = 6.5$], 6.99 [d, 1H, H$_2$, $^3J(H_2H_3) = 7.89$], 6.31 [d, 1H, H$_3$], 4.99 [t, 2H, PCH$_2$P, $^2J(PH) = 13.5$] 4.32, 3.80 [m, 2H, CH$_2^a$], 3.47,

2.96 [m, 2H, CH$_2^b$]. NMR $^{31}P-\{^1H\}$ (300 MHz, CDCl$_3$, δ ppm, J Hz): $\delta = 26.76$ [s]. MS-FAB: $m/z = 718.2$ [{(L-H)Pd(dppm)}H]$^+$, 1089.1 [{(L-H)$_2$Pd$_2$Cl(dppm)}H]$^+$.

3.4. X-ray crystallographic study

Three-dimensional, room temperature X-ray data were collected on Bruker Smart 1k and AXS CCD diffractometers using graphite-monochromated Mo Kα 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 and refined in riding mode. In **3a** the C(9)–C(13) atoms of the cyclohexyl ring showed elongated thermal ellipsoids, however attempts to treat the disorder were unsuccessful. In complex **4a** The O(1) atom of the water solvent molecule were refined in two complementary positions. The F(3)–F(6) atoms of the hexafluorophosphate ion in **3b** were disordered over two positions (with occupancies of approximately the 65% for the major component). The C(3s) and Cl(8) atoms corresponding to one of the chloroform solvent molecules in complex **5b** were found to be disordered over two positions (with occupancies of approximately 55% for the major component of the disorder). The refinement was carried out taking into account the minor components. Al non-hydrogen atoms were refined anisotropically. The structure solution and refinement were carried out using the program package SHELX-97 [40].

4. Supplementary material

CCDC 655194, 655195, 655196, 655197, 655198, 655199 and 655200 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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