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Synthesis, characterization and crystal structures of cyclometallated palladium (II) compounds containing difunctional ligands with [*P*,*P*], [*As*,*As*], [*N*,*N*], [*P*,*As*], [*P*,*N*] and [*P*,*O*] donor atoms

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ABSTRACT

Treatment of the chloro-bridged dinuclear complex [Pd{3,4-$(MeO)_2C_6H_2C(H)$=N(Cy)-*C*6,*N*}(μ-Cl)]$_2$ (**1**) with homobidentate [*P*,*P*], [*As*,*As*], [*N*,*N*], and heterobidentate [*P*,*As*], [*P*,*N*] ligands in a 1:1 molar ratio gave the dinuclear complexes [{Pd[3,4-$(MeO)_2C_6H_2C(H)$=N(Cy)-*C*6,*N*](Cl)}$_2$(μ-L)] (L = $Ph_2PC_4H_6(NH)CH_2PPh_2$ (**2**); $Ph_2As(CH_2)_2AsPh_2$ (**3**); 1,3-$(NH_2CH_2)_2C_6H_4$ (**4**); $Ph_2P(CH_2)_2AsPh_2$ (**5**); $Ph_2P(CH_2)_2NH_2$ (**6**)), with the bidentate ligands bridging the two cyclometallated fragments.

The reaction with the homobidentate ligands in a 1:2 molar ratio in the presence of $NaClO_4$ afforded the mononuclear compounds [[Pd{3,4-$(MeO)_2C_6H_2C(H)$=N(Cy)-*C*6,*N*}{L-*P*,*P*}][ClO_4] (L = $Ph_2PC_4H_6(NH)CH_2PPh_2$ (**7**); (o-Tol)$_2$P$(CH_2)_2$P(o-Tol)$_2$ (**8**)), [Pd{3,4-$(MeO)_2C_6H_2C(H)$=N(Cy)-*C*6,*N*}{$Ph_2As(CH_2)_2AsPh_2$-*As*,*As*}][ClO_4] (**9**) and [Pd{3,4-$(MeO)_2C_6H_2C(H)$=N(Cy)-*C*6,*N*}{L-*N*,*N*}][ClO_4] (L = $NH_2(CH_2)_3NH_2$ (**10**); $NH_2(C_6H_8)CH_2(C_6H_8)NH_2$ (**11**); 1,3-$(NH_2CH_2)_2C_6H_4$ (**12**); 1,3-$(NH_2)_2C_5H_3N$ (**13**); $NH_2(C_6H_4)O(C_6H_4)NH_2$ (**14**); $NMe_2(CH_2)_2NMe_2$ (**15**)), in which the chloro ligands are absent and the bidentate ligands are chelated to the palladium atom.

Reaction of **1** with $Ph_2P(CH_2)_2AsPh_2$ in 1:2 molar ratio in acetone in the presence of NH_4PF_6 afforded the analogous mononuclear compound [Pd{3,4-$(MeO)_2C_6H_2C(H)$=N(Cy)-*C*6,*N*}{$Ph_2P(CH_2)_2AsPh_2$-*P*,*As*}][PF_6] (**16**); whereas reaction with $Ph_2P(CH_2)_3NH_2$ gave [Pd{3,4-$(MeO)_2C_6H_2C(H)$=N(Cy)-*C*6,*N*}{$Ph_2P(CH_2)_3N(C{=}Me_2)$-*P*,*N*}][PF_6] (**17**), derived from intermolecular condensation between the aminophosphine and acetone. Condensation of the NH_2 group was precluded by change of solvent, using dichloromethane.

Iminophoshines also reacted with **1** in 1:2 molar ratio in acetone to give a new series of mononuclear cyclometallated complexes: [Pd{3,4-$(MeO)_2C_6H_2C(H)$=N(Cy)-*C*6,*N*}{L-*P*,*N*}][ClO_4] (L = $Ph_2PC_6H_4C(H)$=NCy (**20**); $Ph_2PC_6H_4C(H)$=$NC(CH_3)_3$ (**21**); $Ph_2PC_6H_4C(H)$=$NNMe_2$ (**22**); $Ph_2PC_6H_4C(H)$=NNHMe (**23**); $Ph_2PC_6H_4C(H)$=NNHPh (**24**)). Analogous complexes with a stable *P*,*O*-chelate were obtained using bidentate [*P*,*O*] donor ligands: [Pd{3,4-$(MeO)_2C_6H_2C(H)$=N(Cy)-*C*6,*N*}{L-*P*,*O*}][Cl] (L = 2-$(Ph_2P)C_6H_4CHO$ (**25**); $Ph_2PN(Me)C(=O)Me$ (**26**)).

The crystal structures of compounds **1**, **5**, **15**, **16**, **18**, **20** have been determined by X-ray crystallography.

1. Introduction

Cyclometallated compounds have been widely studied over the last decades especially due to their numerous applications in catalytic and synthetic processes [1], in medicine and biology [2], and to their interesting mesogenic [3], luminiscent and electronic properties [4].

In the past we have researched the reactivity of cyclometallated compounds with diphosphines, due to the versality of the electronic and steric properties of the latter [5–9]; more recently we have prepared a series of related complexes with diarsines [10]. We were now interested in looking further into the chemistry of cyclopalladated complexes when they react with other bidentate group 15 donor atom ligands such as diamines. Furthermore, there has been recent interest in the chemistry of polydentate ligands, especially those which combine "soft" and "hard" donor atoms [11–18]. These ligands show a characteristic behaviour when binding to soft metal centers giving complexes that are good catalysts in numerous processes [19–23]. Thus, in the present paper we also describe the synthesis and characterization of new cyclometallated compounds derived from heterobidentate [*P*,*N*], [*P*,*As*] and [*P*,*O*] ligands, amongst which are the widely studied iminophosphines [24–27]. Accordingly, we have prepared a series of iminophosphine

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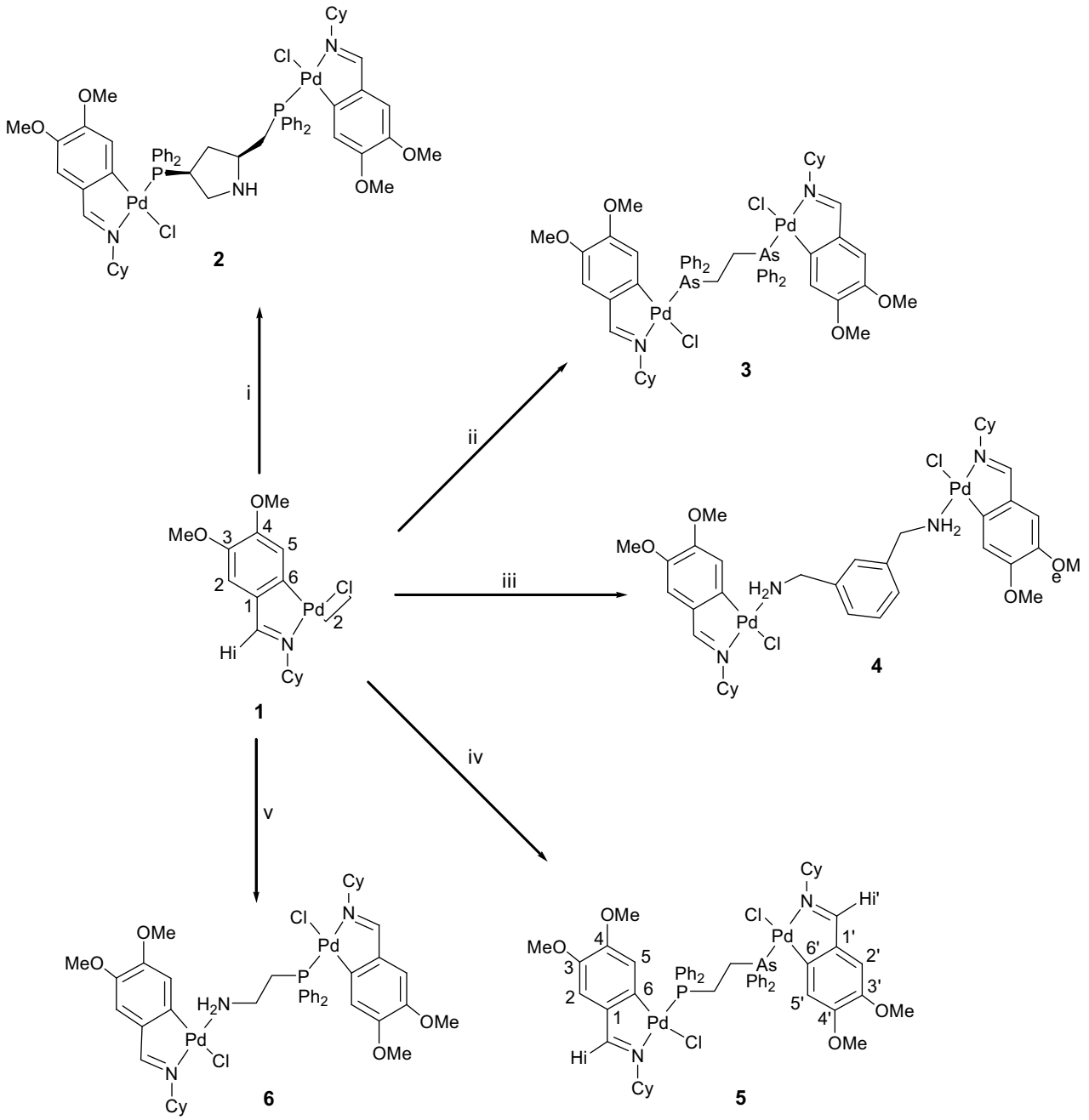
ligands *via* condensation between amines or hydrazines and *o*-(diphenylphosphino)benzaldehyde; the latter being one of the simplest bidentate *P*,*O*-chelating agents [28–33], for which we have also explored its coordination chemistry, as well as that of the related *N*-methyl acetamido phosphine: $Ph_2PN(Me)C(O)Me$ [34,35].

These homo- and heterofunctional ligands have been reacted with the chloro-bridged dinuclear complex [Pd{3,4-$(MeO)_2C_6H_2$C-(H)=N(Cy)-*C6,N*}(μ-Cl)]$_2$ (**1**) previously synthetized by us [36], and herein we report the synthesis and characterization of the resulting species, inclusive of the crystal structures of **1** and of some of its derivatives.

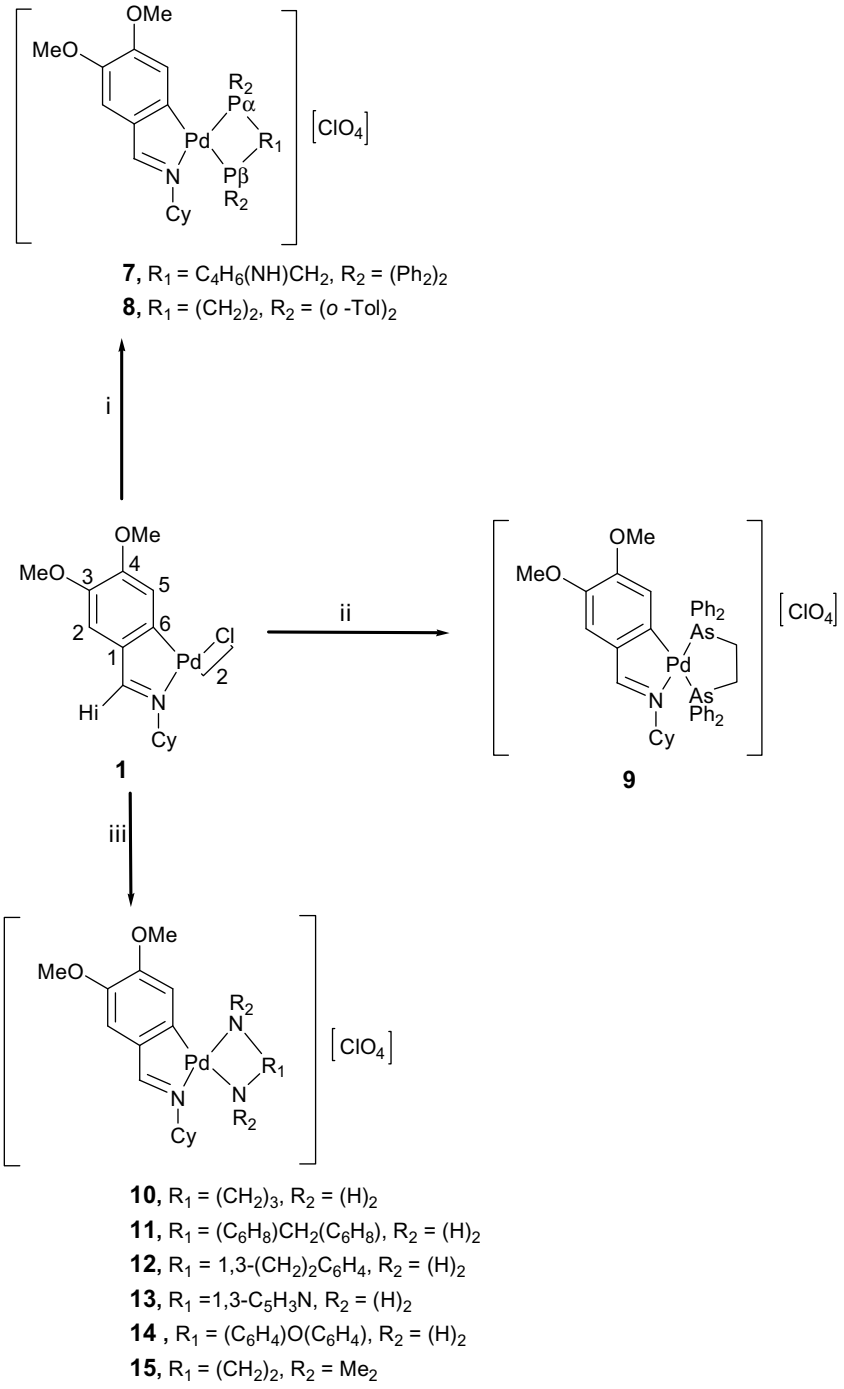
2. Results and discussion

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 ^{1}H, ^{31}P-{^{1}H} and (in part) ^{13}C-{^{1}H} NMR spectroscopy (data in Section 3).

Treatment of the chloro-bridged dinuclear complex [Pd{3,4-$(MeO)_2C_6H_2$C(H)=N(Cy)-*C6,N*}(μ-Cl)]$_2$ (**1**) with $Ph_2PC_4H_6(NH)CH_2PPh_2$ in a complex/phosphine 1:1 molar ratio gave the dinuclear complex [{Pd[3,4-$(MeO)_2C_6H_2$C(H)=N(Cy)-*C6,N*](Cl)}$_2${μ-$Ph_2PC_4H_6$(NH)CH_2PPh_2}] (**2**) which was fully characterized.



Scheme 1. (i) $Ph_2PC_4H_6(NH)CH_2PPh_2$ (1:1), dichloromethane; (ii) $Ph_2As(CH_2)_2AsPh_2$ (1:1), dichloromethane; (iii) 1,3-$(CH_2NH_2)C_6H_4$ (1:1), dichloromethane; (iv) $Ph_2As(CH_2)_2PPh_2$ (1:1), dichloromethane; (v) $H_2N(CH_2)_2PPh_2$ (1:1), dichloromethane.



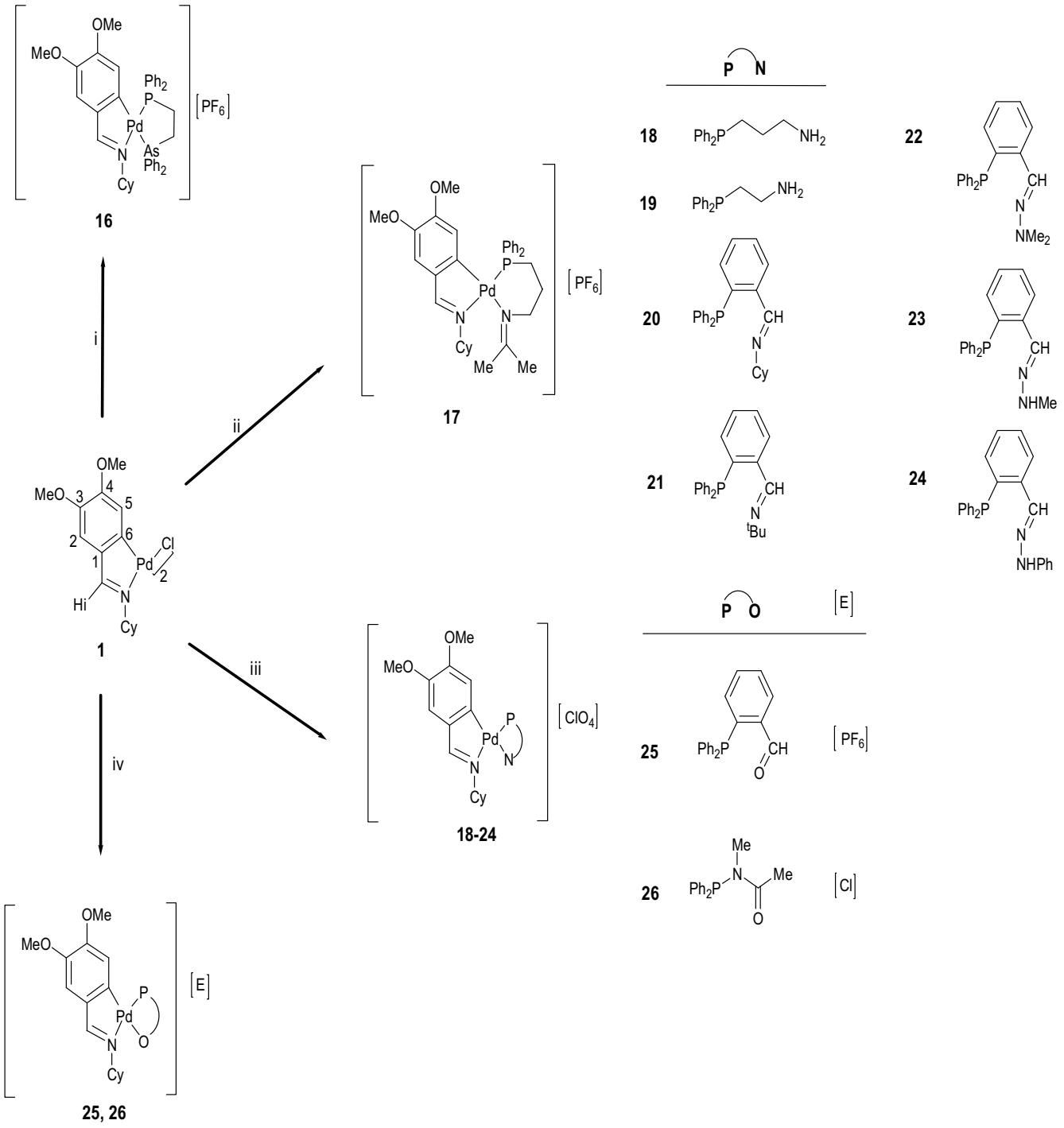
Scheme 2. (i) $R_2PR_1PR_2$ (1:2), $NaClO_4$, dichloromethane; (ii) $Ph_2As(CH_2)_2AsPh_2$ (1:2), $NaClO_4$, dichloromethane; (iii) $R_2NR_1NR_2$ (1:2), $NaClO_4$, dichloromethane.

The IR spectrum showed the shift of the C=N stretch towards lower wavenumbers, as compared to the free Schiff base ligand (*ca.* 1614 vs. 1644 cm^{-1}), indicating nitrogen coordination of the C=N group.[37] The MS-FAB spectrum showed peaks assigned to $[M-Cl]^+$ and $[LPd(PP)]^+$ (L = cyclometallated ligand), which were characteristic clusters of isotopic peaks covering about 10 *m*/*z* units, due to the presence of the numerous palladium isotopes [38,39].

The $^{31}P-\{^1H\}$ NMR spectrum showed two singlets at δ39.26 and δ41.02 assigned to the two non-equivalent phosphorus atoms, consequent on the asymmetric structure of the diphosphine. The singlets were shifted to higher frequency from the free phosphine, suggesting coordination of both phosphorus atoms to the metal center [40].

The ^1H NMR spectrum showed two doublets at δ5.78 and δ5.96, assigned to the H5/H5′ protons, coupled to the ^{31}P nucleus, and two singlets at δ2.83 and δ2.99 assigned to the two 4-MeO groups, thus putting forward the asymmetry of the diphosphine. These resonances were shifted to lower frequency from the starting product due to the shielding effect of the phosphine phenyl rings, in agreement with a P *trans* to N arrangement, typical of these reactions and within the terms of the "transphobic effect" as coined by Vicente et al. [41].

Reaction of **1** with the diarsine $Ph_2As(CH_2)_2AsPh_2$ or with the diamine 1,3-$(NH_2CH_2)C_6H_4$ in 1:1 molar ratio afforded the dinuclear complexes [{Pd[3,4-$(MeO)_2C_6H_2C(H)$=N(Cy)-C6,*N*](Cl)}$_2${μ-$Ph_2As(CH_2)_2AsPh_2$}] (**3**) and [{Pd[3,4-$(MeO)_2C_6H_2C(H)$=N(Cy)-



Scheme 3. (i) $Ph_2P(CH_2)_2AsPh_2$ (1:2), NH_4PF_6, acetone/water; (ii) $Ph_2P(CH_2)_3NH_2$ (1:2), NH_4PF_6, acetone/water; (iii) [*P*,*N*] (1:2), $NaClO_4$, toluene, **18**, **19**; dichloromethane, **20**–**24**; (iv) $Ph_2P(C_6H_4)CHO$ (1:2), NH_4PF_6, acetone/water (**25**), $Ph_2PN(CH_3)C(=O)CH_3$ (1:2), dichloromethane (**26**).

*C*6,*N*](Cl)}$_2${μ-1,3-$(NH_2CH_2)_2C_6H_4$}] (**4**), respectively. The IR and the FAB-mass spectra were similar to those for complex **2**. In the ^{1}H NMR spectra of **3** and **4**, the multiplicity of some of the signals was simplified due to the absence of the phosphorus atoms. Thus, the *H*C=N resonance appeared as a singlet at *ca.* δ8.00. A singlet *ca.* δ6.02 (**3**) δ6.27 (**4**) was assigned to the H5 resonance, putting forward the centrosymmetric nature of the complexes. In the spectrum of **3** these resonances were shifted to higher field due to the shielding effect of the diarsine phenyl rings, in agreement with a As *trans* to N arrangement. This shielding also influenced the 4-MeO signal at δ2.76 (**3**), which was also shifted to higher field from the starting material by 1 ppm upon arsenic coordination to the metal.

Reaction of **1** with the heterobidentate [*P*,*As*] and [*P*,*N*] ligands $Ph_2P(CH_2)_2AsPh_2$ and $Ph_2P(CH_2)_2NH_2$ in 1:1 molar ratio gave the dinuclear complexes [{Pd[3,4-$(MeO)_2C_6H_2C$(H)=N(Cy)-*C*6,*N*](Cl)}$_2$ {μ-$Ph_2P(CH_2)_2AsPh_2$}] (**5**) and [{Pd[3,4-$(MeO)_2C_6H_2C$(H)=N(Cy)-*C*6,*N*](Cl)}$_2${μ-$Ph_2P(CH_2)_2NH_2$}] (**6**). A singlet at δ39.50 (**5**) δ52.58 (**6**) in the ^{31}P-{^{1}H} NMR spectrum confirmed phosphorus coordination of the heterobidentate ligand to the metal center. Thus, in the ^{1}H NMR spectrum of **5** the H5 and H5′ protons gave rase to a doublet at δ5.91, by coupling to the phosphorus nucleus, and a singlet

at δ6.00, respectively. In the ^{1}H NMR spectrum of **6** two singlets at δ7.97 and δ6.78 were assigned to the H′C=N and the H5′ protons, respectively, and two doublets at δ8.03 and δ6.10 were assigned to the *H*C=N and the H5 protons, also, respectively. The H5 resonance was upfield shifted with respect to H5′ in agreement with the shielding effect of the phosphine phenyl rings, absent in the case of the amino group.

In the ^{13}C-{^{1}H} NMR spectrum of **6** a doublet and a singlet *ca.* δ170 and a doublet and a singlet *ca.* δ150 were assigned to the C=N/C′=N and C6/C6′ carbon atoms, respectively, downfield shifted from the spectrum of the free ligand (δ158, C=N; δ122.7, C6) thereby confirming metallation. The C4 and the C5 resonances appeared as two doublets at δ149.7 and δ121.2, respectively, by coupling to the phosphorus nucleus. However, the C4′ and C5′ resonances appeared as singlets at δ149.8 and δ125.0. These findings reflected the asymmetry of the bidentate ligands.

Treatment of the chloro-bridged complex **1** with diphosphines or with the diarsine $Ph_2As(CH_2)_2AsPh_2$ in a 1:2 molar ratio in the presence of $NaClO_4$ gave the mononuclear compounds [[Pd{3,4-$(MeO)_2C_6H_2C(H)$=N(Cy)-*C6,N*}{$Ph_2PC_4H_6(NH)CH_2PPh_2$-*P,P*}][ClO_4] (**7**), [Pd{3,4-$(MeO)_2C_6H_2C(H)$=N(Cy)-*C6,N*}{*o*-$Tol)_2P(CH_2)_2P$(*o*-$Tol)_2$-*P,P*}][ClO_4] (**8**) and [Pd{3,4-$(OMe)_2C_6H_2C(H)$=N(Cy)-*C6,N*}{$Ph_2As(CH_2)_2AsPh_2$-*As,As*}][ClO_4] (**9**). An analogous reaction with different diamines gave [Pd{3,4-$(MeO)_2C_6H_2C(H)$=N(Cy)-*C6,N*}{L-*N,N*}][ClO_4] [L = $NH_2(CH_2)_3NH_2$ (**10**); $NH_2(C_6H_8)CH_2(C_6H_8)NH_2$ (**11**); 1,3-$(NH_2CH_2)_2C_6H_4$ (**12**); 1,3-$(NH_2)_2C_5H_3N$ (**13**); $NH_2(C_6H_4)O(C_6H_4)NH_2$ (**14**); $NMe_2(CH_2)_2NMe_2$ (**15**)].

The MS-FAB spectra showed the corresponding peaks assigned to $[M]^+$ (see Section 3). The IR spectra exhibited the characteristic absorptions of the ClO_4^- anion *ca.* 1100 and 600 cm^{-1} and the molar conductivity measurements (125–150 Ω^{-1} cm^2 mol^{-1} in 10^{-3} mol dm^{-3} solutions in dry acetonitrile) were in agreement with 1:1 electrolytes [42].

The ^{31}P-{^{1}H} NMR spectra of **7** and **8** showed two doublets for the two non-equivalent phosphorus. 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 [40].

The ^{31}P chemical shifts were clearly influence by ring size [43]. Thus, compared to an analogous compound where the P_α phosphorous of the chelated diphosphine is a triphenylphosphine ligand [36], the five-membered ring compound, **8**, gave a positive Δ_{ring} (11.64), whereas the four-membered ring compound **7** gave a negative Δ_{ring} (−3.65).

In the ^{1}H NMR spectra of the diphosphine compounds a doublet of doublets *ca.* δ6.00 was assigned to H5, coupled to both phosphorus nuclei [$^4J(P_\alpha H5)$ ca. 5 Hz, $^4J(P_\beta H5)$ ca.8 Hz]. However, the *H*C=N resonance appeared *ca.* δ8.00 as a doublet by coupling to only the ^{31}P nucleus *trans* to nitrogen; this was confirmed by selective irradiation experiments. In the ^{1}H NMR spectra of the remaining the compounds, **9**–**15**, absence of the phosphorus nuclei was reflected in the simplification of signal multiplicity and in the position of the H5 and 4-OMe resonances (see Section 3).

The ^{13}C-{^{1}H} NMR spectrum of **15** was very similar to that for **1**; two singlets at δ51.5 and δ48.5 were ascribed to the diamine methyl groups of the non-equivalent nitrogen atoms.

Reaction of **1** with $Ph_2P(CH_2)_2AsPh_2$ or $Ph_2P(CH_2)_3NH_2$ in 1:2 molar ratio in acetone in the presence of NH_4PF_6 afforded [Pd{3,4-$(MeO)_2C_6H_2C(H)$=N(Cy)-*C6,N*}{$Ph_2P(CH_2)_2AsPh_2$-*P,As*}][PF_6] (**16**) and [Pd{3,4-$(MeO)_2C_6H_2C(H)$=N(Cy)-*C6,N*}{$Ph_2P(CH_2)_3N(C$=Me_2)-*P,N*}][PF_6] (**17**), after intermolecular condensation between the aminophosphine and the acetone.

The ^{31}P-{^{1}H} NMR spectra showed a singlet at δ28.61 in agreement with phosphorus coordination. In the ^{1}H NMR spectra the 4-MeO and H5 resonances were high-field shifted with respect to those of **1** (*vide supra*). The IR spectra showed the characteristic absorptions of the PF_6^- anion *ca.* 840 and 558 cm^{-1}. The IR spectrum of **17** showed two bands at 1616 and 1648 cm^{-1} consistent with the presence of two different imino groups: the HC=N group in the cyclometallated ring and the Me_2C=N group in the chelating [*P,N*] ligand after condensation. Furthermore, the ^{1}H NMR spectrum showed the presence of two singlets at δ2.28 and δ2.04 assignable to the non-equivalent N=C*Me*$_2$ methyl groups.

Condensation of the NH_2 group was precluded by change of solvent. Thus, reaction of **1** with $Ph_2P(CH_2)_nNH_2$, in dichloromethane, in the presence of $NaClO_4$, afforded compounds [Pd{3,4-$(MeO)_2C_6H_2C(H)$=N(Cy)-*C6,N*}{$Ph_2P(CH_2)_3NH_2$-*P,N*}][ClO_4] (**18**) and [Pd{3,4-$(MeO)_2C_6H_2C(H)$=N(Cy)-*C6,N*}{$Ph_2P(CH_2)_2NH_2$-*P,N*}][ClO_4] (**19**). The analytical and mass data were in agreement with the proposed structures. The conductivity measurements, (130–165 Ω^{-1} cm^2 mol^{-1} in 10^{-3} mol dm^{-3} solutions in dry acetonitrile) showed them to be 1:1 electrolytes, confirming the presence of the aminophosphine ligand in its neutral form. The IR and NMR data were similar to that observed for compound **17**. In the ^{13}C-{^{1}H} NMR spectrum of **18**, the C4, C5, C6 and the C=N, resonances appeared as four doublets at δ149.4, δ121.2, δ149.6 and δ172.0, respectively, by coupling to the phosphorus nucleus.

Treatment of **1** with different iminophoshines in 1:2 molar ratio in dichloromethane in the presence of $NaClO_4$ gave [Pd{3,4-$(MeO)_2C_6H_2C(H)$=N(Cy)-*C6,N*}{*L-P,N*}][ClO_4] (L = $Ph_2PC_6H_4C(H)$=NCy (**20**); $Ph_2PC_6H_4C(H)$=$NC(Me)_3$ (**21**); $Ph_2PC_6H_4C(H)$=$NNMe_2$ (**22**); $Ph_2PC_6H_4C(H)$=NNHMe (**23**); $Ph_2PC_6H_4C(H)$=NNHPh (**24**)).

A strong band at 1628–1648 cm^{-1} was assigned to the C=N stretch, at lower frequency than in the free ligand, in accordance with coordination of the iminophosphine ligand. The ^{1}H NMR spectra showed the corresponding aromatic signals of the neutral ligands, with a typical imine doublet resonance (Hi′) at 7.9–8.8 ppm [^4J(PHi′) = 2.0–3.5 Hz].

The ^{13}C-{^{1}H} NMR spectrum of **21** showed two singlets at δ29.7 and δ30.9 for the methyl groups of the *ter*-butyl fragment, suggesting the hindered rotation of the CMe_3 substituent around the C=N bond.

Finally, treatment of **1** with $Ph_2P(C_6H_4)CHO$ or $Ph_2PN(Me)C(=O)Me$ in a 1:2 molar ratio gave the mononuclear compounds [Pd{3,4-$(MeO)_2C_6H_2C(H)$=N(Cy)-*C6,N*}{2-$(Ph_2P)C_6H_4$-CHO-*P,O*}][PF_6] (**25**) and [Pd{3,4-$(MeO)_2C_6H_2C(H)$=N(Cy)-*C6,N*} {$Ph_2PN(Me)$-C(=O)Me-*P,O*}][Cl] (**26**) as 1:1 electrolytes with the ligand chelated to the metal center.

Bonding of the *P,O*-chelate to the Pd centre resulted in ν(C=O) bands at 1647 (**25**) and 1584 cm^{-1} (**26**) (*cf.* free ligand ν(C=O) 1700 and 1669 cm^{-1}, respectively), and low-field shifted ^{31}P-{^{1}H} NMR resonances at δ35.90 (**25**) and δ94.81 (**26**) (*cf.* free ligand δ *−11.2* and δ55.1, respectively). The ^{1}H NMR data was in agreement with P-*trans*-N and O-*trans*-C(phenyl ring) coordination.

In the ^{1}H NMR spectra of compound **25**, a doublet at δ10.15 was assigned to the CHO group of the [*P,O*] ligand [^4J(P*H*) = 1.5 Hz], upfield shifted *ca.* 0.35 ppm from the spectrum of the free ligand confirming oxygen coordination to the metal center [44].

Along with **25** an additional compound was obtained prior to the addition of $NaClO_4$, which was separated by filtration. The spectroscopic data was in agreement with a species bearing a monocoordinated phosphine-*P*. The IR spectrum exhibited an absorption band at 1696 cm^{-1}, characteristic of a non coordinated formyl group. The ^{1}H NMR spectrum showed a doublet at δ10.44 (d, PC*H*O, ^4J(PH) = 2.4 Hz) close to the free ligand value of 10.5 ppm. A singlet resonance at δ38.86, in the ^{31}P-{^{1}H} NMR spectrum, was in accordance with phosphorus coordination to the metal center (see Section 3).

For the mononuclear compounds with chelated heterobidentate ligands the ^{31}P chemical shifts were influenced by ring size; the data for (**16**–**26**) are summarized in Table 1. With respect to a non-chelated complex [36], 6-membered rings are shielded

Table 1
^{31}P parameters

	P_α	Δ_{ring}[a]
16	60.67	17.17
17	29.69	−13.81
18	29.22	−14.28
19	51.83	8.33
20	39.81	−3.69
21	40.08	−3.42
22	39.50	−4.00
23	40.40	−3.10
24	36.55	−6.95
25	35.90	−7.60
26	94.81	51.31

[a] Difference respect to an equivalent phosphorus in a non-chelated analogue [Pd{3,4-$(MeO)_2C_6H_2C(H)$=N(Cy)-C6,N}(Cl)(PPh_3)] (P *trans* to nitrogen δ 43.50) [36].

whereas 5-membered rings (**16**, **19** and **26**) are deshielded. The presence of the more electronegative nitrogen heteroatom in the phosphine backbone gives an unusually large value of Δ_{ring} for compound **26**, similar to that described in related complexes [45].

2.1. X-ray diffraction analysis

Suitable crystals were grown by slowly evaporating chloroform/n-hexane (**1**, **5**, **15**, **16**) or dichloromethane/n-hexane (**18**, **20**) solutions of the complexes.

The labeling schemes for all the compounds are shown in Figs. 1–6.

All crystals consist of discrete molecules, separated by normal van der Waals distances. Crystallographic data and selected interatomic distances and angles are listed in Tables 2–5.

2.1.1. Molecular structures of [Pd{3,4-$(MeO)_2C_6H_2C(H)$=N(Cy)-C6,N}(μ-Cl)]$_2$ (**1**) and [{Pd[3,4-$(MeO)_2C_6H_2C(H)$=N(Cy)-C6,N](Cl)}$_2${μ-$Ph_2P(CH_2)_2AsPh_2$}] (**5**)

The crystal structure comprises a centrosymmetric dinuclear molecule (half molecule per asymmetric unit) and two, **1**, or four, **5**, $CHCl_3$ solvent molecules.

Table 3
Crystal and structure refinement data for complexes **18**, **20**

	18 · 0.5H_2O	20 · 2CH_2Cl_2
Fórmula	$C_{30}H_{39}ClN_2O_{6.5}PPd$	$C_{42}H_{50}Cl_5N_2O_6PPd$
M_r	704.45	993.46
Temperature (K)	293(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space Group	$P\bar{1}$	$P\bar{1}$
Cell dimensions		
a (Å)	13.695(3)	13.0763(7)
b (Å)	14.508(3)	13.4561(7)
c (Å)	17.253(3)	15.1561(8)
α (°)	98.405(3)	102.497(10)
β (°)	94.019(4)	106.676(10)
γ (°)	100.332(4)	113.146(10)
V (Å^3)	3319.8(12)	2178.8(2)
Z	4	2
$D_{calc.}$ (mg/m^3)	1.409	1.514
μ (mm^{-1})	0.731	0.818
Crystal size (mm)	0.31 × 0.25 × 0.12	0.43 × 0.35 × 0.12
$2\theta_{max}$ (°)	57.78	56.64
Independent reflections [$R_{(int)}$]	1498 (0.0503)	10386 (0.0166)
S	0.910	1.044
R [F, $I > 2\sigma(I)$]	0.0626	0.0210
wR [F^2, all data]	0.1858	0.0525
max ρ (e Å^3)	0.998	0.436

For both complexes the four-coordinated palladium(II) is bonded to an adjacent *ortho*-carbon atom (C1) of the deprotonated Schiff base ligand, to the nitrogen atom of the imine group and to a chlorine atom (*trans* to C1), with the fourth coordination position occupied by another chlorine atom, **1** (Fig. 1), or by a P/As atom, **5** (Fig. 2) thus completing the metal coordination sphere. Note that in **5**, even though the bridging ligand is asymmetric, the dinuclear molecule is crystallographically centrosymmetric; this is caused by the disordered distribution of the P and As atoms (population parameters 50%) and the *quasi* centrosymmetric nature of the compound, which gives similar environments for both P and As atoms. This behaviour has been observed in other complexes derived from the arsino-phosphine ligand [17,46]; however, in compound **16**

Table 2
Crystal and structure refinement data for complexes **1**, **5**, **15** and **16**

	1 · 2$CHCl_3$	5 · 4$CHCl_3$	15 · 2$CHCl_3$	16 · 0.5$CHCl_3$
Fórmula	$C_{32}H_{42}Cl_8N_2O_4Pd_2$	$C_{60}H_{68}AsCl_{14}N_2O_4PPd_2$	$C_{23}H_{38}Cl_7N_3O_6Pd$	$C_{41.5}H_{44.5}Cl_{1.5}F_6NO_2P_2Pd$
M_r	1015.08	1696.15	807.11	999.72
Temperature (K)	293(2)	293(2)	100(2)	293(2)
Wavelength (A)	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/c$
Cell dimensions				
a (Å)	7.789(10)	13.669(5)	10.185(2)	12.787(9)
b (Å)	9.103(10)	12.817(5)	13.779(2)	12.653(9)
c (Å)	14.780(10)	20.175(5)	13.828(2)	28.61(2)
α (°)	96.487(10)	90	60.130(2)	90
β (°)	91.392(10)	90.122(5)	77.721(3)	100.592(13)
γ (°)	102.430(10)	90	82.864(3)	90
V (Å^3)	1015.6(18)	3535(2)	1643.9(5)	4550(6)
Z	1	2	2	4
$D_{calc.}$ (mg/m^3)	1.660	1.594	1.631	1.459
μ (mm^{-1})	1.448	1.570	1.174	1.346
Crystal size (mm)	0.55 × 0.50 × 0.45	0.24 × 0.18 × 0.03	0.39 × 0.34 × 0.10	0.50 × 0.39 × 0.30
$2\theta_{max}$ (°)	56.58	56.64	56.61	57.32
Independent reflections [$R_{(int)}$]	4792 (0.0143)	8458 (0.0889)	7481 (0.0121)	10806 (0.0427)
S	1.063	0.991	1.055	1.016
R [F, $I > 2\sigma(I)$]	0.0333	0.0646	0.0209	0.0525
wR [F^2, all data]	0.0943	0.1621	0.0561	0.1704
max ρ (e Å^3)	0.881	0.987	0.702	1.356

Table 4
Selected bond distances (A) and angles (°) for complexes **1**, **5**, **15** and **16**

	1	5	15	16
Pd(1)–C(1)	1.973(3)	2.031(6)	2.032(1)	2.055(4)
Pd(1)–N(1)	2.038(2)	2.111(4)	2.078(1)	2.108(4)
Pd(1)–N(2)			2.105(1)	
Pd(1)–N(3)			2.209(1)	
Pd(1)–Cl(1)	2.329(1)	2.403(2)		
Pd(1)–Cl(1A)	2.463(1)			
Pd(1)–P(1)				2.262(2)
Pd(1)–As(1)		2.313(1)		2.425(1)
C(1)–C(6)	1.392(3)	1.406(8)	1.405(2)	1.400(6)
C(6)–C(7)	1.445(4)	1.429(8)	1.442(2)	1.442(6)
N(1)–C(7)	1.281(4)	1.289(7)	1.287(2)	1.290(6)
C(1)–Pd(1)–N(1)	81.33(10)	81.3(2)	81.17(5)	80.89(16)
C(1)–Pd(1)–Cl(1)	94.31(8)			
Cl(1)–Pd(1)–Cl(1A)	85.81(3)			
N(1)–Pd(1)–Cl(1A)	98.71(6)			
C(1)–Pd(1)–P(1)				98.12(13)
C(1)–Pd(1)–As(1)		93.31(17)		
C(1)–Pd(1)–N(2)			97.81(5)	
N(2)–Pd(1)–N(3)			83.71(5)	
P(1)–Pd(1)–As(1)				83.42(5)
As(1)–Pd(1)–Cl(1)		91.27(5)		
N(1)–Pd(1)–Cl(1)		93.92(14)		
N(1)–Pd(1)–P(1)				
N(1)–Pd(1)–N(3)			98.00(5)	
N(1)–Pd(1)–As(1)				97.64(10)
C(7)–N(1)–Pd(1)	113.83(18)	111.9(4)	112.97(10)	112.4(3)
N(1)–C(7)–C(6)	117.1(2)	118.4(6)	118.44(13)	118.7(4)
C(1)–C(6)–C(7)	114.7(2)	117.7(6)	115.94(13)	117.1(4)
C(6)–C(1)–Pd(1)	112.91(18)	110.5(4)	111.35(10)	110.8(3)

Table 5
Selected bond distances (A) and angles (°) for complexes **18**, **20**

	18	20
Pd(1)–C(1)	2.013(6)	2.022(1)
Pd(1)–N(1)	2.117(5)	2.120(1)
Pd(1)–P(1)	2.246(2)	2.218(4)
Pd(1)–N(2)	2.176(5)	2.131(1)
Pd(1)–As(1)		
Pd(1)–As(2)		
Pd(1)–Cl(1)		
Pd(1)–Cl(2)		
C(1)–C(6)	1.401(9)	1.408(2)
C(6)–C(7)	1.444(9)	1.453(2)
N(1)–C(7)	1.268(8)	1.284(2)
C(1)–Pd(1)–N(1)	80.9(2)	81.16(5)
C(1)–Pd(1)–P(1)	95.0(2)	99.19(4)
P(1)–Pd(1)–N(2)	91.47(17)	85.41(3)
N(1)–Pd(1)–N(2)	92.4(2)	96.51(4)
C(7)–N(1)–Pd(1)	112.3(4)	112.28(9)
N(1)–C(7)–C(6)	118.4(6)	117.93(12)
C(1)–C(6)–C(7)	116.7(6)	116.70(12)
C(6)–C(1)–Pd(1)	111.4(5)	111.39(9)
As(1)–Pd(1)–As(2)		
As(2)–Pd(1)–Cl(2)		
Cl(2)–Pd(1)–Cl(1)		
Cl(1)–Pd(1)–As(1)		

(*vide infra*) where the P and the As atoms are in different chemical surroundings, the technique clearly distinguishes both atoms.

The Pd–C and Pd–N bond lengths for both palladium complexes are similar to those reported for related compounds [16,47–49]. The differing Pd–Cl(1)$_{trans\text{-}N}$ [2.329(1)] and PdCl(1A)$_{trans\text{-}C}$ [2.463 (1)] bond lengths in compound **1** and PdCl(1)$_{trans\text{-}C}$ [2.403(2)] for **5** reflect the higher *trans* influence of the aryl carbon as compared to the imine nitrogen atom of the organic ligand [50].

For complex **1** the mean deviation from the least-squares planes of the Pd1 C1 N1 Cl1 Cl1A plane (plane 1), the cyclometallated ring (plane 2) and the metallated phenyl ring (plane 3) are 0.0153, 0.0124 and 0.0026 Å. The angles between planes are as follows: 1/2: 0.5°, 1/3: 1.5 *y* 2/3: 1.6°. Thus, apart from the MeO groups and the cyclohexyl rings, the other five rings in the complex are near coplanar, as observed in other halide-bridged cyclometallated complexes [47–49], and in contrast with the situation in similar non-planar Pd_2X_2 bridging units [51,52].

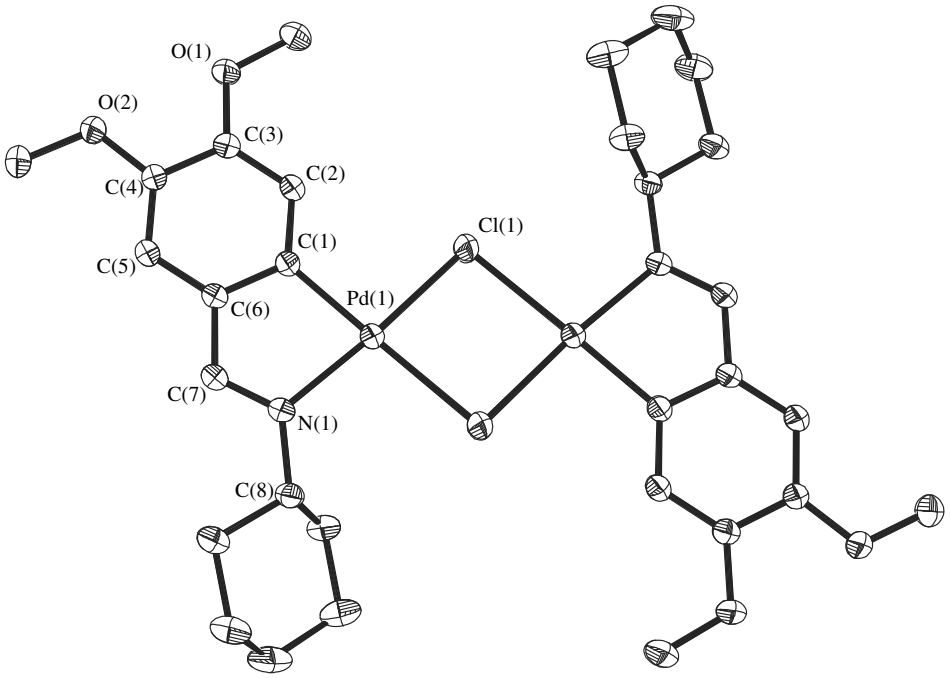


Fig. 1. Molecular structure of [Pd{3,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-C6,*N*}(μ-Cl)]$_2$ (**1**), with labelling scheme. Hydrogen atoms have been omitted for clarity.

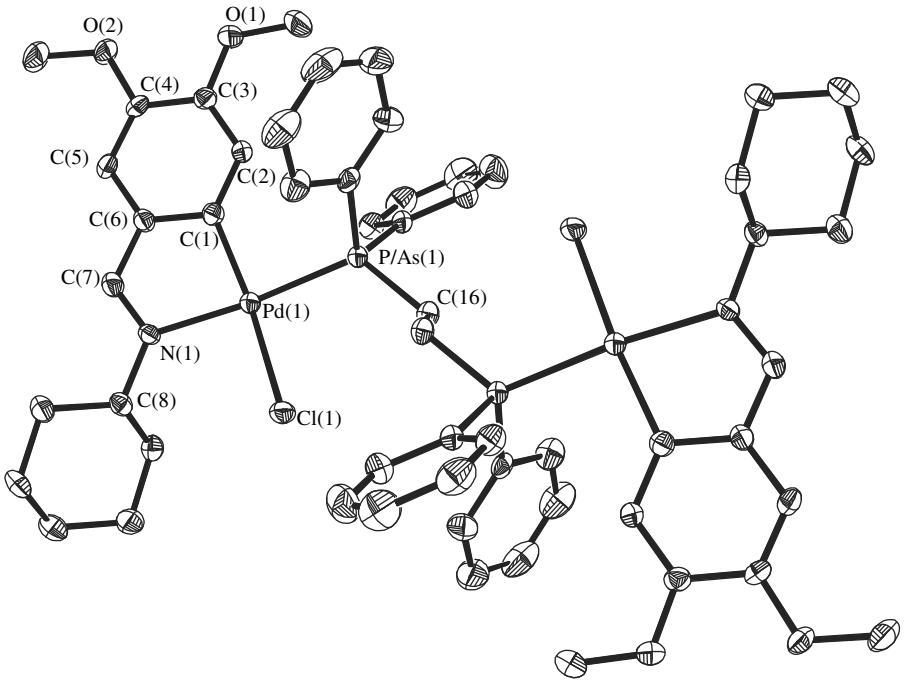


Fig. 2. Molecular structure of [{Pd[3,4-$(MeO)_2C_6H_2C(H)$=N(Cy)-*C6,N*](Cl)}$_2$ {μ-$Ph_2P(CH_2)_2AsPh_2$}] (**5**), with labelling scheme. Hydrogen atoms have been omitted for clarity.

*2.1.2. Molecular structures of [Pd{3,4-$(MeO)_2C_6H_2C(H)$=N(Cy)-C6,N}{$NMe_2(CH_2)_2NMe_2$-N,N}][ClO_4] (**15**), [Pd{3,4-$(MeO)_2C_6H_2C(H)$=N(Cy)-C6,N}{$Ph_2P(CH_2)_2AsPh_2$-P,As}][PF_6] (**16**), [Pd{3,4-$(MeO)_2C_6H_2C(H)$=N(Cy)-C6,N}{$Ph_2P(CH_2)_3NH_2$-P,N}][ClO_4] (**18**), [Pd{3,4-$(MeO)_2C_6H_2C(H)$=N(Cy)-C6,N}{$Ph_2PC_6H_4C(H)$=NCy-P,N}][ClO_4] (**20**)*

The crystal structures of compounds **15**, **16** and **20** comprise a mononuclear cation (one molecule per asymmetric unit), a perclorate or a hexafluorophosphate (**16**) anion and two $CHCl_3$ (**15**), one half $CHCl_3$ (**16**) or two CH_2Cl_2 (**20**) solvent molecules.

The crystal structure of **18** consists of a mononuclear cation, a perclorate anion and half molecule of H_2O; in this case, the asymmetric unit comprises two cations with similar structures, of which only one will be discussed.

For the mononuclear complex **15** the palladium(II) atom is bonded to the C1 atom and to three nitrogen atoms, one from the Schiff base ligand and two from the diamine chelating ligand (see Fig. 3). In compounds **16**, **18** and **20** the palladium(II) atom

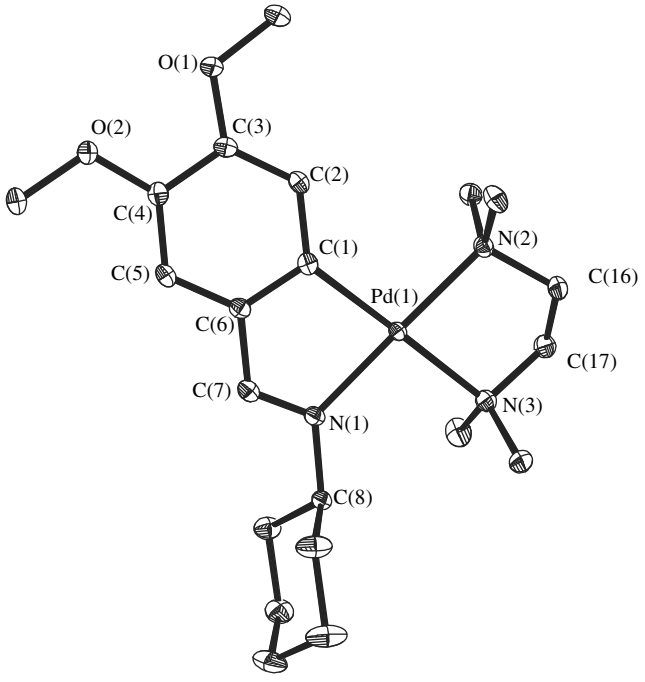


Fig. 3. Molecular structure of the cation for [Pd{3,4-$(MeO)_2C_6H_2C(H)$=N(Cy)-*C6,N*}{$NMe_2(CH_2)_2NMe_2$-*N,N*}][ClO_4] (**15**), with labelling scheme. Hydrogen atoms have been omitted for clarity.

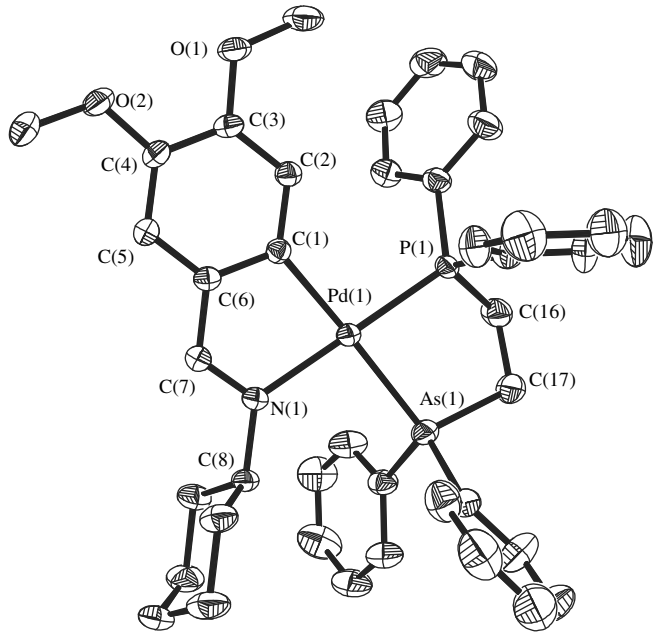


Fig. 4. Molecular structure of the cation for [Pd{3,4-$(MeO)_2C_6H_2C(H)$=N(Cy)-*C6,N*}{$Ph_2P(CH_2)_2AsPh_2$-*P,As*}][PF_6] (**16**), with labelling scheme. Hydrogen atoms have been omitted for clarity.

is bonded to an *ortho*-carbon of the phenyl ring, to a nitrogen atom of the benzylidene ligand, and to the phosphorus and arsenic (**16**) or nitrogen (**18**, **20**) atoms of the chelating arsino-phosphine or phosphinoamine ligand, giving a five- or a six-membered chetale ring, respectively (see Figs. 4–6).

The sum of angles about palladium is approximately 360° as expected for a square-planar geometry. The angles between adjacent atoms in the coordination sphere are close to 90°; the most noticeable distortion corresponds to the C(1)–Pd(1)–N(1) angle in the cyclometallated ring, of 81.17(5)° (**15**), 80.89(16)° (**16**), 80.9(2)° (**18**), 81.16(5)° (**20**), consequent upon chelation. The geometry around the palladium atom is slightly distorted square-planar, the mean deviations from the least-squares plane (plane 1: Pd1, C1, N1, N2, N3, **15**; Pd1, C1, N1, P1, As1, **16**; Pd1, C1, N1, P1, N2, **18**, **20**) are 0.0925, 0.0320, 0.0541 and 0.1622 Å, respectively.

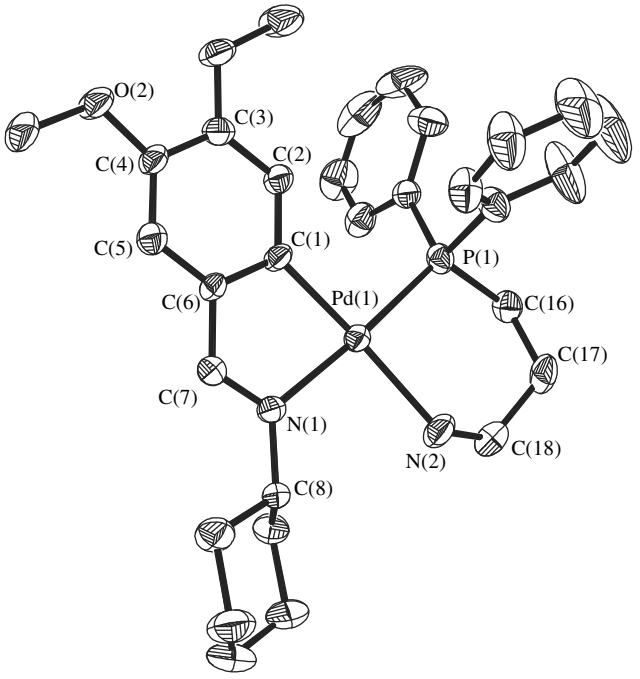


Fig. 5. Molecular structure of the cation for [Pd{3,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-*C6,N*}{Ph$_2$P(CH$_2$)$_3$NH$_2$-*P,N*}][ClO$_4$] (**18**), with labelling scheme. Hydrogen atoms have been omitted for clarity.

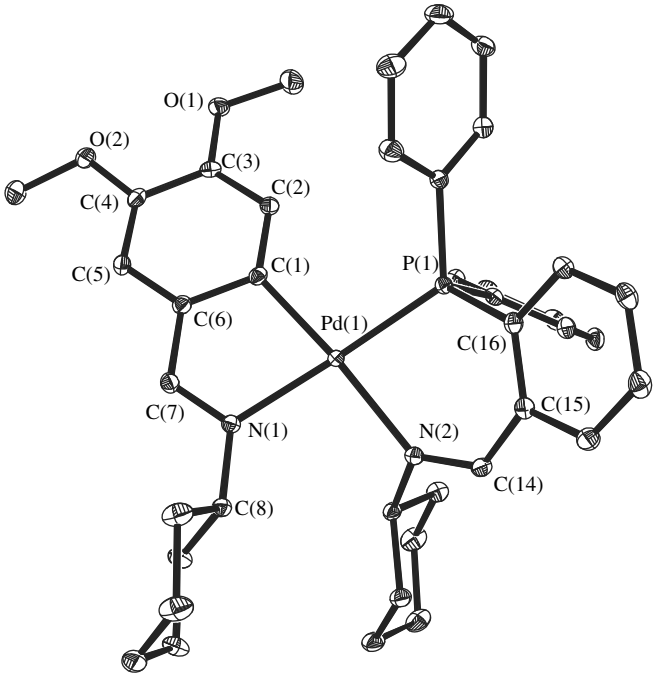


Fig. 6. Molecular structure of the cation for [Pd{3,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-*C6,N*}{Ph$_2$PC$_6$H$_4$C(H)=N(Cy)-*P,N*}][ClO$_4$] (**20**), with labelling scheme. Hydrogen atoms have been omitted for clarity.

The mean deviations from the least-squares planes determined for the metallacycle (plane 2: Pd1, C1, C6, C7, N1) and the metallated phenyl ring (plane 3: C1, C2, C3, C4, C5, C6) are 0.134 and 0.0083 Å (**15**), 0.0188 and 0.0062 Å (**16**), 0.0230 and 0.0078 Å (**18**), 0.0253 and 0.0094 Å (**20**), respectively. The angle between these planes are as follows: 3.7°, 2.9°, 4.8° and 10.5°, also respectively. The angles between plane 1 and the previous planes are: plane 1/plane 2: 5.5°(**15**), 2.1°(**16**), 5.9°(**18**), 10.5°(**20**) and plane 1/plane 3: 9.0°(**15**), 3.1°(**16**), 10.6°(**18**), 20.2°(**20**), with the most noticeable distortion in compound **20** with the P1 and N2 of the iminophosphine ligand lying in a different side in relation to the Pd1 C1 N1 plane (+0.38 and −0.49 Å, respectively). The torsion angles of 1.0° for C14 C15 C16 P1 and 42.2° for the Pd1 P1 C16 C15 units points to a perturbed envelop conformation of the six-membered ring of the iminophosphine, similar to that described in other related complexes [53,54].

The palladium–carbon bond lengths, (2.032(1) Å (**15**), 2.055(4) Å (**16**), 2.013(6) Å (**18**), 2.022(1) Å (**20**)), are somewhat 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) [55].

The palladium-nitrogen bond lengths in the cyclometallated ring (Pd–N1), (2.078(1) Å (**15**), 2.108(4) Å (**16**), 2.117(5) Å (**18**), 2.120(1) Å (**20**)), are longer than 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), and reflect the influence of the atom in *trans* position. In **15** the distinct palladium–nitrogen bond lengths with the diamine chelating ligand (Pd–N2 = 2.105(1) Å and Pd–N3 = 2.209(1) Å) reflect the differing *trans* influence of the metallated carbon and the nitrogen atoms of the Schiff base ligand.

The Pd–P (2.262(2) Å (**16**), 2.246(2) Å (**18**), 2.218(4) Å (**20**), and Pd–As (2.425(1) (**16**)) bond distances, similar those found in related palladium complexes [17,56,57], are shorter than the sum of the single bond radii for palladium and the corresponding atoms (2.41 Å for Pd–P and 2.55 Å for Pd–As), suggesting partial double bond character between the palladium and the donor atom.

3. Experimental

CAUTION (safety note): 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.

3.1. General remarks

All solvents were distilled prior to use from appropriate drying agents [58]. Chemicals were used as supplied from commercial sources. Elemental analyses (C, H, N) were carried out in a Carlo-Erba 1108 elemental analyser. IR spectra were recorded as KBr pellets or Nujol mulls on a Perkin–Elmer 1330 spectrophotometer. Mass spectra were obtained in a QUATRO mass spectrometer with Cs ion-gun and 3-NBA matrix. NMR spectra were obtained as $CDCl_3$ solutions and referenced to $SiMe_4$ (^{1}H, ^{13}C-{^{1}H}) or 85% H_3PO_4 (^{31}P-{^{1}H}); and were recorded on a Bruker AC-200F spectrometer (200.0 MHz for ^{1}H, 50.3 MHz for ^{13}C-{^{1}H}, 81.0 MHz for ^{31}P-{^{1}H}). Conductivity measurements were made on a Crison GLP 32 con-

ductivimeter using 10^{-3} M solutions in dry acetonitrile at room temperature (298 K). The ligand $Ph_2PN(Me)C(=O)Me$ was prepared as described previously in the literature [34]. The syntheses of the heteroligands $Ph_2PC_6H_4C(H)=NCy$, $Ph_2PC_6H_4C(H)=NCMe_3$, $Ph_2PC_6H_4C(H)=NNMe_2$, $Ph_2PC_6H_4C(H)=NNHMe$, $Ph_2PC_6H_4C(H)=NNHPh$ were performed by heating chloroform solutions of the appropriate quantities of *o*-(diphenylphosphino)benzaldehyde and the corresponding amine or hydrazine in a Dean–Stark apparatus under reflux.

3.2. Syntheses

3.2.1. [Pd{3,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-C6,N}(μ-Cl)]$_2$ (**1**)

The synthesis of **1** has been reported previously from this laboratory [36].

^{13}C-{^{1}H} NMR: δ = 24.8 (s, C9, C11), 25.4 (s, C10), 32.9 (s, C8, C12), 55.9, 56.2 (s, OMe), 63.5 (s, C7), 109.9 (s, C5), 115.8 (s, C2), 138.0 (s, C1), 146.5 (s, C3), 147.7 (s, C6), 148.0 (s, C4), 169.4 (s, C=N).

3.2.2. [{Pd[3,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-C6,N](Cl)}$_2${μ-Ph$_2$PC$_4$H$_6$(NH)CH$_2$PPh$_2$}] (**2**)

To a suspension of **1** (40.00 mg, 0.052 mmol) in dichloromethane (*ca.* 10 mL), $Ph_2PC_4H_6(NH)CH_2PPh_2$ (21.22 mg, 0.047 mmol) was added. The mixture was stirred for 12 h at room temperature, after which the precipitate formed was filtered off, dried *in vacuo*, and recrystallized from chloroform/n-hexane to yield the desired product as a yellow solid.

Yield: 67%. Anal. Calc. for $C_{59}H_{65}Cl_2N_3O_4P_2Pd_2$: C, 57.8; H, 5.3; N 3.4. Found: C, 57.5; H, 5.3; N, 3.1%. IR: ν(C=N): 1614m. FAB-Mass: 1190 [M-Cl]$^+$, 801 [LPd(PP)]$^+$. ^{1}H NMR: δ = 2.83, 2.99 (s, 4-OMe), 3.76 (s, 3-OMe), 5.78, 5.96 (d, H5, ^4J(PH5) = 6.4, 5.9 Hz), 6.83, 6.84 (s, H2). ^{31}P-{^{1}H} NMR: δ = 39.26 (s), 41.02 (s).

3.2.3. [{Pd[3,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-C6,N](Cl)}$_2${μ-Ph$_2$As(CH$_2$)$_2$AsPh$_2$}] (**3**)

Complex **3** was synthesized with a procedure similar to that described for complex **2**, but using $Ph_2As(CH_2)_2AsPh_2$.

Yield: 51%. Anal. Calc. for $C_{56}H_{64}Cl_2N_2O_4As_2Pd_2$: C, 53.3; H, 5.1; N, 2.2. Found: C, 53.6; H, 5.0; N, 2.1%. IR: ν(C=N): 1616m. FAB-Mass: 838 [LPd(AsAs)]$^+$, 352 [LPd]$^+$, 246 [L]$^+$. ^{1}H NMR: δ = 2.76 (s, 4-OMe), 3.75 (s, 3-OMe), 6.02 (s, H5), 6.82 (s, H2), 7.95 (s, Hi).

3.2.4. [{Pd[3,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-C6,N](Cl)}$_2${μ-1,3-(NH$_2$CH$_2$)$_2$C$_6$H$_4$}] (**4**)

Complex **4** was synthesized with a procedure similar to that described for complex **2**, but using 1,3-$(NH_2CH_2)C_6H_4$.

Yield: 67%. Anal. Calc. for $C_{38}H_{52}Cl_2N_4O_4Pd_2$: C, 50.0; H, 5.7; N, 6.1. Found: C, 49.9; H, 5.6; N, 6.1%. IR: ν(C=N): 1607m. FAB-Mass: 488 [LPd(NN)]$^+$, 352 [LPd]$^+$, 246 [L]$^+$. ^{1}H NMR: δ = 3.89, 3.90 (s, OMe), 6.27 (s, H5), 6.84 (s, H2), 8.03 (s, Hi).

3.2.5. [{Pd[3,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-C6,N](Cl)}$_2${μ-Ph$_2$P(CH$_2$)$_2$AsPh$_2$}] (**5**)

Complex **5** was synthesized with a procedure similar to that described for complex **2**, but using $Ph_2P(CH_2)_2AsPh_2$.

Yield: 30%. Anal. Calc. for $C_{56}H_{64}Cl_2N_2O_4AsPPd_2$: C, 55.1; H, 5.3; N, 2.3. Found: C, 55.1; H, 5.1; N, 2.2%. IR: ν(C=N): 1619m. FAB-Mass: 795 [LPd(PAs)]$^+$. ^{1}H NMR: δ = 2.73, 2.84 (s, 4-OMe), 3.75 (s, 3-OMe), 5.91 (d, H5, ^4J(PH5) = 6.4 Hz), 6.00 (s, H5′), 6.81 (s, H2). ^{31}P-{^{1}H} NMR: δ = 39.50 (s).

3.2.6. [{Pd[3,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-C6,N](Cl)}$_2${μ-Ph$_2$P(CH$_2$)$_2$NH$_2$}] (**6**)

Complex **6** was synthesized with a procedure similar to that described for complex **2**, but using $Ph_2P(CH_2)_2NH_2$.

Yield: 75%. Anal. Calc. for $C_{44}H_{56}Cl_2N_3O_4PPd_2$: C, 52.5; H, 5.6; N, 4.1. Found: C, 52.2; H, 5.6; N, 3.9%. IR: ν(C=N): 1608m. FAB-Mass: 581 [LPd(PN)]$^+$, 352 [LPd]$^+$ 581, 246 [L]$^+$. ^{1}H NMR: δ = 3.10 (s, 4-OMe), 3.80, 3.81 (s, OMe), 6.10 (d, H5, ^4J(PH5) = 5.4 Hz), 6.78 (s, H5′), 6.80 (s, H2), 7.97 (s, Hi′), 8.03 (d, Hi, ^4J(PHi) = 6.8 Hz). ^{13}C-{^{1}H} NMR: δ = 25.3 (s, C9, C11), 25.7 (s, C10), 29.6 (s, *C*H$_2$CH$_2$P), 33.7 (s, C8, C12), 41.0 (d, *C*H$_2$P, ^1J(PC) 8 3.9 Hz), 65.0 (s, C7), 55.4, (s, 4-OMe), 55.9, 56.0, 56.1 (s, OMe), 111.6 (s, C2), 121.2 (d, C5, ^3J(PC5) 8 11.4 Hz), 125.0 (s, C5′), 127.2 (d, C$_i$, ^1J(PC$_i$) = 49.7 Hz), 129.3 (d, C$_m$, ^3J(PC$_m$) = 10.6 Hz), 132.0 (d, C$_p$, ^4J(PC$_p$) = 2.8 Hz), 134.2 (d, C$_o$, ^2J(PC$_o$) = 12.8 Hz), 140.5 (s, C1), 146.0 (s, C3), 149.7(d, C4, ^4J(PC4) = 5.6 Hz), 149.8 (s, C4′), 151.1(d, C6, ^2J(PC6) = 2.8 Hz), 151.2 (s, C6′), 171.3 (s, C=N′), 171.3 (d, C=N, ^3J(PC=*N*) = 3.6 Hz). ^{31}P-{^{1}H} NMR: δ 8 52.58 (s).

3.2.7. [Pd{3,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-C6,N}{Ph$_2$PC$_4$H$_6$(NH)CH$_2$PPh$_2$-P,P}]-[ClO$_4$] (**7**)

To a suspension of **1** (20.00 mg, 0.026 mmol) in dichloromethane (*ca.* 15 mL), $Ph_2PC_4H_6(NH)CH_2PPh_2$ (23.57 mg, 0.052 mmol) was added. The mixture was stirred for 2 h at room temperature, after which an estequiometric amount of sodium perclorate was added and the resultant solution stirred for a further 1 h. Then the solvent was removed under reduced pressure, and the residue triturated with hexane to yield a solid, which was filtered off and dried *in vacuo*. The desired complex was recrystallized from chloroform/*n*-hexane as yellow microcrystals.

Yield: 66%. Anal. Calc. for $C_{44}H_{49}ClN_2O_6P_2Pd$: C, 58.3; H, 5.4; N, 3.1. Found: C, 58.3; H, 5.1; N, 3.3%. IR: ν(C=N): 1612m. FAB-Mass: 805 [M]$^+$, 291 [(L-2MeO)Pd]$^+$. ^{1}H NMR: δ = 2.99 (s, 4-OMe), 3.79 (s, 3-OMe), 5.94 (dd, H5, ^4J(P$_\beta$H5) = 8.4 Hz, ^4J(P$_\alpha$H5) = 5.4 Hz), 6.89 (s, H2), 8.11 (d, Hi, ^4J(PHi) = 6.4 Hz). ^{31}P-{^{1}H} NMR: δ = 1.59 (d, P$_\beta$, ^5J(PP) = 115.1 Hz), 39.85 (d, P$_\alpha$).

3.2.8. [Pd{3,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-C6,N}{(*o*-Tol)$_2$P(CH$_2$)$_2$P(*o*-Tol)$_2$-P,P}] [ClO$_4$] (**8**)

Complex **8** was synthesized with a procedure similar to that described for complex **7**, using (*o*-Tol)$_2$P(CH$_2$)$_2$P(*o*-Tol)$_2$.

Yield: 51%. Anal. Calc. for $C_{45}H_{52}ClNO_6P_2Pd$: C, 59.6; H, 5.8; N, 1.5. Found: C, 59.9; H, 5.7; N, 1.8%. IR: ν(C=N): 1618m. FAB-Mass: 806 [M]$^+$. ^{1}H NMR: δ = 2.97 (s, 4-OMe), 3.82 (s, 3-OMe), 6.17 (dd, H5, ^4J(P$_\beta$H5) = 8.3 Hz, ^4J(P$_\alpha$H5) = 5.9 Hz), 7.13 (s, H2), 8.31 (d, Hi, ^4J(PHi) = 8.3 Hz). ^{31}P-{^{1}H} NMR: δ = 41.91 (d, P$_\beta$, ^3J(PP) = 17.2 Hz), 55.14 (d, P$_\alpha$).

3.2.9. [Pd{3,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-C6,N}{Ph$_2$As(CH$_2$)$_2$AsPh$_2$-As,As}][ClO$_4$] (**9**)

Complex **9** was synthesized using a procedure similar to that described for complex **7**, but using $Ph_2As(CH_2)_2AsPh_2$.

Yield: 78%. Anal. Calc. for $C_{41}H_{44}ClNO_6As_2Pd$: C, 52.5; H, 4.7; N, 1.5. Found: C, 53.1; H, 5.0; N, 1.4%. IR: ν(C=N): 1626m. FAB-Mass: 838 [M]$^+$. ^{1}H NMR: δ = 2.96 (s, 4-OMe), 3.84 (s, 3-OMe), 6.32 (s, H5), 7.19 (s, H2), 8.29 (s, Hi).

3.2.10. [Pd{3,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-C6,N}{NH$_2$(CH$_2$)$_3$NH$_2$-N,N}][ClO$_4$] (**10**)

Complex **10** was synthesized with a procedure similar to that described for complex **7**, but using $NH_2(CH_2)_3NH_2$.

Yield: 45%. Anal. Calc. for $C_{18}H_{30}ClN_3O_6Pd$: C, 41.1; H, 5.7; N, 8.0. Found: C, 41.0; H, 5.9; N, 7.7%. IR: ν(C=N): 1611m. FAB-Mass: 426 [M]$^+$, 352 [LPd]$^+$, 248 [L+H]$^+$. ^{1}H NMR: δ = 3.66, 3.80 (s, OMe), 6.53 (s, H5), 7.11 (s, H2), 8.12 (s, Hi).

3.2.11. 3.2.11.[Pd{3,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-C6,N}{NH$_2$(C$_6$H$_8$)CH$_2$(C$_6$H$_8$)NH$_2$-N,N}][ClO$_4$] (**11**)

Complex **11** was synthesized with a procedure similar to that described for complex **7**, but using $NH_2(C_6H_8)CH_2(C_6H_8)NH_2$.

Yield: 49%. Anal. Calc. for $C_{28}H_{46}ClN_3O_6Pd$: C, 50.8; H, 7.0; N, 6.3. Found: C, 50.3; H, 7.4; N, 6.5%. IR: ν(C=N): 1609m. FAB-Mass: 352 [LPd]$^+$, 291 [(L−2OMe)Pd]$^+$, 248 [L+H]$^+$. ^{1}H NMR: δ = 3.83, 3.92 (s, OMe), 6.36 (s, H5), 6.88 (s, H2), 7.76 (s, Hi).

*3.2.12. [Pd{3,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-C6,N}{1,3-(NH$_2$CH$_2$)$_2$C$_6$H$_4$-N,N}][ClO$_4$] (**12**)*

Complex **12** was synthesized with a procedure similar to that described for complex **7**, but using 1,3-(NH$_2$CH$_2$)$_2$C$_6$H$_4$.

Yield: 34%. Anal. Calc. for $C_{23}H_{32}ClN_3O_6Pd$: C, 47.0; H, 5.5; N, 7.1. Found: C, 46.9; H, 5.4; N, 7.3%. IR: ν(C=N): 1617m. FAB-Mass: 488 [M]$^+$, 352 [LPd]$^+$, 248 [L+H]$^+$. ^{1}H NMR: δ = 3.85, 3.94 (s, OMe), 6.53 (s, H5), 6.92 (s, H2), 7.89 (s, Hi).

*3.2.13. [Pd{3,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-C6,N}{1,3-(NH$_2$)$_2$C$_5$H$_3$N-N,N}][ClO$_4$] (**13**)*

Complex **13** was synthesized with a procedure similar to that described for complex **7**, using 1,3-(NH$_2$)$_2$C$_5$H$_3$N.

Yield: 31%. Anal. Calc. for $C_{20}H_{27}ClN_4O_6Pd$: C, 42.8; H, 4.9; N, 10.0. Found: C, 42.7; H, 4.9; N, 10.2%. IR: ν(C=N): 1607m. FAB-Mass: 461 [M]$^+$, 352 [LPd]$^+$, 248 [L+H]$^+$. ^{1}H NMR: δ = 3.57, 3.80 (s, OMe), 5.64 (s, H5), 6.86 (s, H2), 7.85 (s, Hi).

*3.2.14. [Pd{3,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-C6,N}{NH$_2$(C$_6$H$_4$)O(C$_6$H$_4$)NH$_2$-N,N}] [ClO$_4$] (**14**)*

Complex **14** was synthesized with a procedure similar to that described for complex **7**, but using NH$_2$(C$_6$H$_4$)O(C$_6$H$_4$)NH$_2$.

Yield: 38%. Anal. Calc. for $C_{27}H_{32}ClN_3O_7Pd$: C, 49.7; H, 5.0; N, 6.4. Found: C, 49.4; H, 5.0; N, 6.6%. IR: ν(C=N): 1615m. FAB-Mass: 552 [M]$^+$, 352 [LPd]$^+$, 248 [L+H]$^+$. ^{1}H NMR: δ = 3.81, 3.91 (s, OMe), 6.67 (s, H5), 6.80 (s, H2), 7.72 (s, Hi).

*3.2.15. [Pd{3,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-C6,N}{NMe$_2$(CH$_2$)$_2$NMe$_2$-N,N}][ClO$_4$] (**15**)*

Complex **15** was synthesized with a procedure similar to that described for complex **7**, but using NMe$_2$(CH$_2$)$_2$NMe$_2$.

Yield: 50%. Anal. Calc. for $C_{21}H_{36}ClN_3O_6Pd$: C, 44.4; H, 6.4; N, 7.4. Found: C, 44.6; H, 6.4; N, 7.2%. IR: ν(C=N): 1618m. FAB-Mass: 468 [M]$^+$, 352 [LPd]$^+$. ^{1}H NMR: δ = 3.82, 3.96 (s, OMe), 6.68 (s, H5), 6.94 (s, H2), 7.91 (s, Hi).

^{13}C-{^{1}H} NMR: δ = 25.2 (s, C9, C11), 25.8 (s, C10), 34.0 (s, C8, C12), 48.5, 51.5 (s, N*C*H$_3$), 56.2, 56.4 (s, OMe), 60.7, 64.6 (s, CH$_2$*C*H$_2$N), 63.5 (s, C7), 111.6 (s, C2), 115.0 (s, C5), 139.2 (s, C1), 147.4, 147.9 (s, C3, C6), 149.8 (s, C4), 174.9 (s, C=N).

*3.2.16. [Pd{3,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-C6,N}{Ph$_2$P(CH$_2$)$_2$AsPh$_2$-P,As}][PF$_6$] (**16**)*

To a suspension of **1** (20.00 mg, 0.026 mmol) in acetone (*ca.* 15 mL), Ph$_2$P(CH$_2$)$_2$AsPh$_2$ (23.00 mg, 0.052 mmol) was added. The mixture was stirred for 2 h at room temperature, after which ammonium hexafluorophosphate in estequiometric amount was added and the resulting solution stirred for a further 1 h. Then, water (*ca.* 40 cm^3) was added dropwise and the resulting mixture stirred for 2 h. The precipitate formed was filtered off, washed with water (2 × 5 mL) and dried *in vacuo*. The desired complex was recrystallized from chloroform/*n*-hexane.

Yield: 46%. Anal. Calc. for $C_{41}H_{44}F_6NO_2AsP_2Pd$: C, 52.4; H, 4.7; N, 1.5. Found: C, 52.5; H, 4.5; N, 1.4%. IR: ν(C=N): 1611m. FAB-Mass: 794 [M]$^+$, 291 [(L−2OMe)Pd]$^+$, 248 [L+H]$^+$. ^{1}H NMR: δ = 2.97 (s, 4-OMe), 3.83 (s, 3-OMe), 6.11 (d, H5, ^4J(PH5) = 5.8 Hz), 7.07 (s, H2), 8.25 (d, Hi, ^4J(PHi) = 8.8 Hz). ^{31}P-{^{1}H} NMR: δ = 60.67 (s).

*3.2.17. [Pd{3,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-C6,N}{Ph$_2$P(CH$_2$)$_3$N(C=Me$_2$)-P,N}][PF$_6$] (**17**)*

Complex **17** was synthesized with a procedure similar to that described for complex **7**, albeit in acetone, using PPh$_2$(CH$_2$)$_3$NH$_2$.

Yield: 40%. Anal. Calc. for $C_{33}H_{42}F_6N_2O_2P_2Pd$: C, 50.7; H, 5.4; N, 3.6. Found: C, 51.2; H, 5.7; N, 3.9%. IR: ν(C=N): 1616m, 1648m. FAB-Mass: 635 [M]$^+$, 352 [LPd]$^+$, 291 [(L-2OMe)Pd]$^+$. ^{1}H NMR: δ = 2.04, 2.28 (s, N(C=Me$_2$)), 2.91 (s, 4-OMe), 3.81 (s, 3-OMe), 5.92 (d, H5, ^4J(PH5) = 5.9 Hz), 6.95 (s, H2), 8.11 (d, Hi, ^4J(PHi) = 7.3 Hz). ^{31}P-{^{1}H} NMR: δ = 29.69 (s).

*3.2.18. [Pd{3,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-C6,N}{Ph$_2$P(CH$_2$)$_3$NH$_2$-P,N}][ClO$_4$] (**18**)*

Complex **18** was synthesized with a procedure similar to that described for complex **7**, using PPh$_2$(CH$_2$)$_3$NH$_2$ in dichloromethane.

Yield: 52%. Anal. Calc. for $C_{30}H_{38}ClN_2O_6PPd$: C, 51.8; H, 5.5; N, 4.0. Found: C, 51.5; H, 5.6; N, 4.0%. IR: ν(C=N): 1618m. FAB-Mass: 595 [M]$^+$, 352 [LPd]$^+$, 291 [(L−2OMe)Pd]$^+$, 248 [L+H]$^+$. ^{1}H NMR: δ = 2.89 (s, 4-OMe), 3.79 (s, 3-OMe), 5.91 (d, H5, ^4J(PH5) = 6.4 Hz), 6.92 (s, H2), 8.09 (d, Hi, ^4J(PHi) = 7.8 Hz).

^{13}C-{^{1}H} NMR: δ = 29.7 (s, *C*H$_2$CH$_2$P), 23.5 (s, NC*H*$_2$), 25.7 (s, C10), 25.1 (s, C9, C11), 33.6 (s, C8, C12), 42.2 (d, *C*H$_2$P, ^1J(PC) = 5.0 Hz), 55.2, (s, 4-OMe) 55.9 (s, 3-OMe), 62.0 (s, C7), 111.8 (s, C2), 121.2 (d, C5, ^3J(PC5) = 12.8 Hz), 127.2 (d, C$_i$, ^1J(PC$_i$) = 49.7 Hz), 129.3 (d, C$_m$, ^3J(PC$_m$) = 10.6 Hz), 132.0 (d, C$_p$, ^4J(PC$_p$) = 2.8 Hz), 134.2 (d, C$_o$, ^2J(PC$_o$) = 12.8 Hz), 140.3 (s, C1), 146.2 (s, C3), 149.4 (d, C4, ^4J(PC4) = 6.3 Hz), 149.6 (d, C6, ^2J(PC6) = 2.1 Hz), 172.0 (d, C=N, ^3J(PC=*N*) = 3.5 Hz). ^{31}P-{^{1}H} NMR: δ = 29.22 (s).

*3.2.19. [Pd{3,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-C6,N}{Ph$_2$P(CH$_2$)$_2$NH$_2$-P,N}][ClO$_4$] (**19**)*

Complex **19** was synthesized with a procedure similar to that described for complex **7**, using PPh$_2$(CH$_2$)$_2$NH$_2$ in dichloromethane.

Yield: 62%. Anal. Calc. for $C_{29}H_{36}ClN_2O_6PPd$: C, 51.1; H, 5.3; N, 4.1. Found: C, 50.9; H, 5.3; N, 4.0%. IR: ν(C=N): 1615m. FAB-Mass: 581 [M]$^+$, 291 [(L−2OMe)Pd]$^+$. ^{1}H NMR: δ = 3.05 (s, 4-OMe), 3.80 (s, 3-OMe), 6.07 (d, H5, ^4J(PH5) = 5.4 Hz), 6.92 (s, H2), 8.06 (d, Hi, ^4J(PHi) = 8.8 Hz). ^{31}P-{^{1}H} NMR: δ = 51.83 (s).

*3.2.20. [Pd{3,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-C6,N}{Ph$_2$PC$_6$H$_4$C(H)=NC$_6$H$_{11}$-P,N}] [ClO$_4$] (**20**)*

Complex **20** was synthesized with a procedure similar to that described for complex **7**, using Ph$_2$PC$_6$H$_4$C(H)=NCy.

Yield: 21%. Anal. Calc. for $C_{40}H_{46}ClN_2O_6PPd$: C, 58.3; H, 5.6; N, 3.4. Found: C, 58.1; H, 5.4; N, 3.1%. IR: ν(C=N): 1617m, 1648m. FAB-Mass: 723 [M]$^+$, 352 [LPd]$^+$, 291 [(L-2OMe)Pd]$^+$. ^{1}H NMR: δ = 3.05 (s, 4-OMe), 3.83 (s, 3-OMe), 6.03 (d, H5, ^4J(PH5) = 6.3 Hz), 6.96 (s, H2), 8.27 (d, Hi, ^4J(PHi) = 7.8 Hz), 8.68 (d, Hi′, ^4J(PHi′) = 2.4 Hz). ^{31}P-{^{1}H} NMR: δ = 39.81 (s).

*3.2.21. [Pd{3,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-C6,N}{Ph$_2$PC$_6$H$_4$C(H)=NC(CH$_3$)$_3$-P,N}] [ClO$_4$] (**21**)*

Complex **21** was synthesized with a procedure similar to that described for complex **7**, using Ph$_2$PC$_6$H$_4$C(H)=NCMe$_3$.

Yield: 35%. Anal. Calc. for $C_{38}H_{44}ClN_2O_6PPd$: C, 57.2; H, 5.6; N, 3.5. Found: C, 57.3; H, 5.8; N, 3.6%. IR: ν(C=N): 1615m, 1628m. FAB-Mass: 697 [M]$^+$, 291 [(L-2OMe)Pd]$^+$. ^{1}H NMR: δ = 1.26, 1.33 (s, C(*CH*$_3$)$_3$), 3.08 (s, 4-OMe), 3.82 (s, 3-OMe), 5.99 (d, H5, ^4J(PH5) = 6.0 Hz), 6.97 (s, H2), 8.14 (d, Hi, ^4J(PHi) = 7.8 Hz) 8.82 (d, Hi′, ^4J(PHi′) = 3.5 Hz). ^{13}C-{^{1}H} NMR: δ = 25.4 (s, C9, C11), 25.6 (s, C10), 29.7, 30.9 (s, NC(*CH*$_3$)$_3$), 55.0, (s, 4-OMe) 56.0 (s, 3-OMe), 64.2 (s, C7), 64.2, 64.6 (s, N*C*(CH$_3$)$_3$), 111.2 (s, C2), 121.5 (d, C5, ^3J(PC5) = 12.8 Hz), 123.0 (d, C$_i$, ^1J(PC$_i$) = 49.1 Hz), 130.1 (d, C$_m$, ^3J(PC$_m$) = 11.4 Hz), 132.6 (d, C$_p$, ^4J(PC$_p$) = 2.3 Hz), 133.1 (d, C$_o$, ^2J(PC$_o$) = 12.7 Hz), 140.1 (d, C1, ^3J(PC1) = 1.4 Hz), 146.6 (s, C3), 149.8 (d, C4, ^4J(PC4) = 7.1 Hz), 153.1 (d, C6, ^2J(PC6) = 2.7 Hz), 167.9 (d, C=N′, ^3J(PC=*N*) = 4.8 Hz), 171.4 (d, C=N, ^3J(PC=*N*) = 4.0 Hz). ^{31}P-{^{1}H} NMR: δ = 40.08 (s).

*3.2.22. [Pd{3,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-C6,N}{Ph$_2$PC$_6$H$_4$C(H)=NNMe$_2$-P,N}] [ClO$_4$] (**22**)*

Complex **22** was synthesized with a procedure similar to that described for complex **7**, using Ph$_2$PC$_6$H$_4$C(H)=NNMe$_2$.

Yield: 59%. Anal. Calc. for $C_{36}H_{41}ClN_3O_6PPd$: C, 55.1; H, 5.3; N, 5.4. Found: C, 55.0; H, 5.1; N, 5.2%. IR: ν(C=N): 1617m, 1642m. FAB-Mass: 684 [M]$^+$, 291 [(L-2OMe)Pd]$^+$. ^{1}H NMR: δ = 3.02 (s, N(CH_3)$_2$), 3.08 (s, 4-OMe), 3.82 (s, 3-OMe), 5.96 (d, H5, ^4J(PH5) = 6.3 Hz), 6.95 (s, H2), 7.90 (d, Hi′, ^4J(PHi′) = 2.4 Hz), 8.08 (d, Hi, ^4J(PHi) = 7.3 Hz). ^{31}P-{^{1}H} NMR: δ = 39.50 (s).

*3.2.23. [Pd{3,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-C6,N}{Ph$_2$PC$_6$H$_4$C(H)=NNHMe-P,N}] [ClO$_4$] (**23**)*

Complex **23** was synthesized with a procedure similar to that described for complex **7**, using Ph$_2$PC$_6$H$_4$C(H)=NNHMe.

Yield: 36%. Anal. Calc. for $C_{35}H_{39}ClN_3O_6PPd$: C, 54.6; H, 5.1; N, 5.5. Found: C, 54.2; H, 4.9; N, 5.6%. IR: ν(C=N): 1620m, 1640m. FAB-Mass: 670 [M]$^+$, 291 [(L-2OMe)Pd]$^+$. ^{1}H NMR: δ = 2.90 (d, NHCH_3, ^3J(HCH$_3$) = 4.3 Hz), 2.98 (s, 4-OMe), 3.90 (s, 3-OMe), 5.85 (d, H5, ^4J(PH5) = 6.3 Hz), 6.79 (s, H2), 8.07 (d, Hi, ^4J(PHi) = 7.8 Hz). ^{31}P-{^{1}H} NMR: δ = 40.40 (s).

*3.2.24. [Pd{3,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-C6,N}{Ph$_2$PC$_6$H$_4$C(H)=NNHPh-P,N}] [ClO$_4$] (**24**)*

Complex **24** was synthesized with a procedure similar to that described for complex **7**, using Ph$_2$PC$_6$H$_4$C(H)=NNHPh.

Yield: 35%. Anal. Calc. for $C_{40}H_{41}ClN_3O_6PPd$: C, 57.7; H, 5.0; N, 5.0. Found: C, 57.5; H, 4.8; N, 4.9%. IR: ν(C=N): 1610m, 1639m. FAB-Mass: 732 [M]$^+$, 291 [(L−2OMe)Pd]$^+$. ^{1}H NMR: δ = 3.06 (s, 4-OMe), 3.78 (s, 3-OMe), 6.05 (d, H5, ^4J(PH5) = 6.8 Hz), 6.74 (s, H2), 8.70 (d, Hi′, ^4J(PHi′) = 2.0 Hz), 9.82 (s, NH). ^{31}P-{^{1}H} NMR: δ = 36.55 (s).

*3.2.25. [Pd{3,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-C6,N}{2-(Ph$_2$P)C$_6$H$_4$CHO-P,O}][PF$_6$] (**25**)*

Complex **25** was synthesized with a procedure similar to that described for complex **16**, using Ph$_2$P(C$_6$H$_4$)CHO.

Yield: 32%. Anal. Calc. for $C_{34}H_{35}F_6NO_3P_2Pd$: C, 51.8; H, 4.5; N, 1.8. Found: C, 52.0; H, 4.8; N, 1.6%. IR: ν(C=O): 1647s, ν(C=N): 1620m. FAB-Mass: 642 [M]$^+$, 291 [(L−2OMe)Pd]$^+$, 248 [L+H]$^+$. ^{1}H NMR: δ = 2.95 (s, 4-OMe), 3.82 (s, 3-OMe), 5.93 (d, H5, ^4J(PH5) = 5.8 Hz), 6.95 (s, H2), 8.08 (d, Hi, ^4J(PHi) = 8.8 Hz), 10.15 (d, PCHO, ^4J(P*H*) = 1.5 Hz). ^{31}P-{^{1}H} NMR: δ = 35.90 (s).

During the synthesis of compound **25**, an additional compound was obtained previously to the addition of the NaClO$_4$ which was separated by filtration:

[Pd{3,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-*C6,N*}(Cl){2-(Ph$_2$P)C$_6$H$_4$CHO-*P*}]

Yield: 33%. Anal. Calc. for $C_{34}H_{35}ClNO_3PPd$: C, 60.2; H, 5.2; N, 2.0. Found: C, 60.4; H, 5.4; N, 1.7%. IR: ν(C=O): 1696s, ν(C=N): 1614m. FAB-Mass: 642 [M-Cl]$^+$, 352 [LPd]$^+$, 291 [(L−2OMe)Pd]$^+$, 248 [L+H]$^+$. ^{1}H NMR: δ = 2.92 (s, 4-OMe), 3.82 (s, 3-OMe), 6.04 (d, H5, ^4J(PH5) = 6.4 Hz), 6.88 (s, H2), 10.44 (d, PCHO, ^4J(P*H*) = 2.4 Hz). ^{31}P-{^{1}H} NMR: δ = 38.86 (s).

*3.2.26. [Pd{3,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-C6,N}{Ph$_2$PN(CH$_3$)C(=O)CH$_3$-P,O}][Cl] (**26**)*

To a suspension of **1** (20.00 mg, 0.026 mmol) in dichloromethane (*ca.* 10 mL), Ph$_2$PN(CH$_3$)C(=O)CH$_3$ (13.36 mg, 0.052 mmol) was added. The mixture was stirred for 12 h at room temperature, after which the solvent was removed to yield the desired product as a yellow solid.

Yield: 48%. Anal. Calc. for $C_{30}H_{36}ClN_2O_3PPd$: C, 55.8; H, 5.6; N, 4.3. Found: C, 55.6; H, 5.4; N, 4.2%. IR: ν(C=O): 1584s, ν(C=N): 1614m. FAB-Mass: 609 [M]$^+$. ^{1}H NMR: δ = 2.57 (s, C(=O)CH_3), 3.18 (d, NCH_3, ^3J(PNCH_3) = 5.9 Hz), 3.14 (s, 4-OMe), 3.77 (s, 3-OMe), 5.97 (d, H5, ^4J(PH5) = 7.3 Hz), 6.89 (s, H2). ^{31}P-{^{1}H} NMR: δ = 94.81 (s).

3.2.27. X-ray crystallographic study

Three-dimensional X-ray data were collected on a Bruker Smart 1K and Bruker 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.

Of the two CH_2Cl_2 solvent molecules in compound **20** one was found to be disordered over two positions (76% and 24% occupancy) while in the other one only one of the chloride atoms, Cl4, was disordered occupying two positions, with each component having approximately 50% occupancy (0.58% and 0.42%).

Hydrogen atoms were included in calculated positions and refined in riding mode. All non-hydrogen atoms were refined anisotropically. The structure solution and refinement were carried out using the program package SHELX-97 [59].

Supplementary material

CCDC 655186, 655187, 655188, 655189, 655190 and 655191 contains the supplementary crystallographic data for **1**, **5**, **15**, **16**, **18** and **20**. 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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