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New developments in the studies of the reactivity of cyclometallated palladium(II) compounds with homo- ([P,P],[As,As]) and heterobidentate ([P,N],[P,O]) ligands

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Abstract

Treatment of the chloro-bridged dinuclear compounds $[\{Pd[RC_6H_3C(H)=NCy\text{-}C2,N]\}(\mu\text{-}Cl)]_2$ (R = 4-(COH), **1**; R = 5-(COH), **2**) with bidentate phosphorus or arsenic diphosphines or diarsine ligands in 1:1 molar ratio gave the dinuclear complexes $[\{Pd[RC_6H_3C(H)=NCy\text{-}C2,N](Cl)\}_2\{\mu\text{-}(o\text{-}Tol)_2P(CH_2)_2P(o\text{-}Tol)_2\}]$ (R = 4-(COH), **3**; R = 5-(COH), **4**), $[\{Pd[RC_6H_3C(H)=NCy\text{-}C2,N](Cl)\}_2\{\mu\text{-}Ph_2PC_4H_2(NH)CH_2PPh_2\}]$ (R = 4-(COH), **5**; R = 5-(COH), **6**) and $[\{Pd[RC_6H_3C(H)=NCy\text{-}C2,N](Cl)\}_2\{\mu\text{-}Ph_2As(CH_2)_2AsPh_2\}]$ (R = 4-(COH), **7**; R = 5-(COH), **8**) with the homobidentate [*P*,*P*] and [*As*,*As*] ligands in a bridging mode. Treatment of **1** and **2** with the aminophosphine $Ph_2P(CH_2)_2NH_2$ yields the dinuclear complexes $[\{Pd[RC_6H_3C(H)=NCy\text{-}C2,N](Cl)\}_2\{\mu\text{-}Ph_2P(CH_2)_2NH_2\}]$ (R = 4-(COH), **9**; R = 5-(COH), **10**). The analogous reactions carried out in a 1:2 molar ratio, in the presence of NH_4PF_6 or $NaClO_4$, gave the mononuclear compounds $[Pd\{RC_6H_3C(H)=NCy\text{-}C2,N\}\{(o\text{-}Tol)_2P(CH_2)_2P(o\text{-}Tol)_2\text{-}P,P\}][PF_6]$ (R = 4-(COH), **11**; R = 5-(COH), **12**), $[Pd\{RC_6H_3C(H)=NCy\text{-}C2,N\}\{Ph_2PC_4H_2(NH)CH_2PPh_2\text{-}P,P\}][ClO_4]$ (R = 4-(COH), **13**; R = 5-(COH), **14**) and $[Pd\{RC_6H_3C(H)=NCy\text{-}C2,N\}\{Ph_2As(CH_2)_2AsPh_2\text{-}As,As\}][ClO_4]$(R = 4-(COH), **15**; R = 5-(COH), **16**), with the [*P*,*P*] and [*As*,*As*] ligands chelated to the palladium atom.

Treatment of **2** with $Ph_2P(CH_2)_3NH_2$in a 1:2 molar ratio in acetone in the presence of NH_4PF_6 afforded the mononuclear compound $[Pd\{5\text{-}(COH)C_6H_3C(H)=NCy\text{-}C2,N\}\{Ph_2P(CH_2)_3N(=Me_2)\text{-}P,N\}][PF_6]$, **17**, *via* intermolecular condensation between the aminophosphine and the solvent. Condensation was precluded using toluene as solvent to give $[Pd\{RC_6H_3C(H)=NCy\text{-}C2,N\}\{Ph_2P(CH_2)_nNH_2\text{-}P,N\}][PF_6]$, ($n = 3$, R = 5-(COH), **18**; $n = 2$, R = 4-(COH), **19**; $n = 2$, R = 5-(COH), **20**). Treatment of **1** and **2** with $Ph_2P(C_6H_4)CHO$ in a 1:2 molar ratio in the presence of NH_4PF_6 gave the mononuclear complexes $[Pd\{RC_6H_3C(H)=NCy\text{-}C2,N\}\{2\text{-}(Ph_2P)C_6H_4CHO\text{-}P,O\}][PF_6]$ (R = 4-(COH), **21**; R = 5-(COH), **22**) with the palladium atom bonded to four different atoms (C, N, P, O) and a chelating [*P*,*O*] ligand. The crystal structures of compounds **7**, **11**, **15** and **21** have been determined by X-ray crystallography.

Keywords: Palladium; Metallation; Diphosphines; Diarsines; [*P*,*N*] ligands; [*P*,*O*] ligands; X-ray diffraction

1. Introduction

In the last decades much attention has been devoted to the study of cyclometallation compounds [1–5]. In particular, cyclometallation of Schiff-base ligands with a wide range of transition metals has been extensively investigated. Tetradentate [*C*,*N*,*C*,*N*] Schiff bases generally undergo double metallation to give compounds with two metal atoms per organic ligand [6–16], however, as we have reported previously, in the case of the potentialy tetradentate ligands derived from isophthalaldehyde, 1,3-$(CyN{=}CH)_2C_6H_4$, and terephthalaldehyde, 1,4-$(CyN{=}CH)_2C_6H_4$, they may be mono- or dimetallated depending on the reaction

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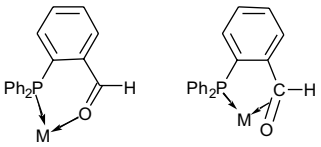
conditions [17–19]. Thus, treatment with palladium(II) acetate in acetic acid gave the monocyclometallated complexes **1** and **2** after cleavage of one C=N double bond, and we have studied the reactivity of these cyclometallated complexes towards different mono and bidentate ligands [20–24]. Herein, we present further developments of our investigations regarding the reactivity of **1** and **2** with the new group 15 donor atom bidentate ligands: the diphosphines, 1,2-bis(di-*o*-tolylphosphino)ethane and 4-(diphenylphosphino)-2-(diphenylphosphinomethyl)pyrrol, as well the diarsine: 1,2-bis(diphenylarsino)ethane.

Furthermore, there is a great interest in metal complexes with diphosphines due to the versatility of their electronic and steric properties [25–28], and there has also been a growing interest in bidentate ligands which combine both hard and soft donor atoms [29–34]. Among these are the heterofunctionalized phosphines with phosphorus (soft) and oxygen or nitrogen (hard) donor atoms. These ligands exhibit partial lability making them particularly interesting in homogeneous catalysis [35–39], with coordination alternating between bidentate and monodentate, which generates vacant sites on the metal ion for potential substrate binding. Consequently, we decided to study the behavior of cyclometallated complexes **1** and **2** towards heterofunctionalized [*P*,*N*] and [*P*,*O*] phosphines: 2-(diphenylphosphino)ethylamine, 2-(diphenylphosphino)-1-propylamine and 2-(diphenylphosphino)benzaldehyde. The latter is one of the simplest bidentate [*P*,*O*] ligands and it exhibits two binding modes when the PCHO group acts as a chelating ligand [40], with the aldehyde moiety bonded to the metal in a σ-fashion through the oxygen atom [41–43], or in a π-fashion through the carbon–oxygen double bond [44,45].



The coordination mode of the aldehyde is dependent on the transition metal, the oxidation state and the other ligands present in the compound. Herein we report a detailed description of this chemistry together with the crystal structure of the first cyclometallated palladium PCHO complex containing a σ-bonded aldehyde group.

2. Results and discussion

For the convenience of the reader the compounds and reactions are shown in Schemes 1 and 2. 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 complexes $[\{Pd[RC_6H_3C(H)=NCy\text{-}C2,N]\}(\mu\text{-}Cl)]_2$ (R = 4-(COH), **1**; R = 5-(COH), **2**) with tertiary diphosphines in 1:1 molar ratio gave the dinuclear compounds $[\{Pd[RC_6H_3C(H)=NCy\text{-}C2,N](Cl)\}_2\{\mu\text{-}(o\text{-}Tol)_2P(CH_2)_2P(o\text{-}Tol)_2\}]$ (R = 4-(COH), **3**; R = 5-(COH), **4**); and $[\{Pd[RC_6H_3C(H)=NCy\text{-}C2,N](Cl)\}_2\{\mu\text{-}Ph_2PC_4H_2(NH)CH_2PPh_2\}]$ (R = 4-(COH), **5**; R = 5-(COH), **6**) with the diphosphine in a bridging mode.

The IR spectrum showed the shift of the C=N stretch towards lower wavenumbers, as compared to the free Schiff-base ligand (*ca.* 1620 vs. 1630 cm^{-1}), indicating nitrogen coordination of the C=N group [46]. A band *ca.* 1690 cm^{-1} was assigned to the uncoordinated formyl group [47]. The MS-FAB spectrum showed peaks assigned to $[LPd(PP)]^+$ and $[(L\text{-}CHO)Pd]^+$ (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 [48,49].

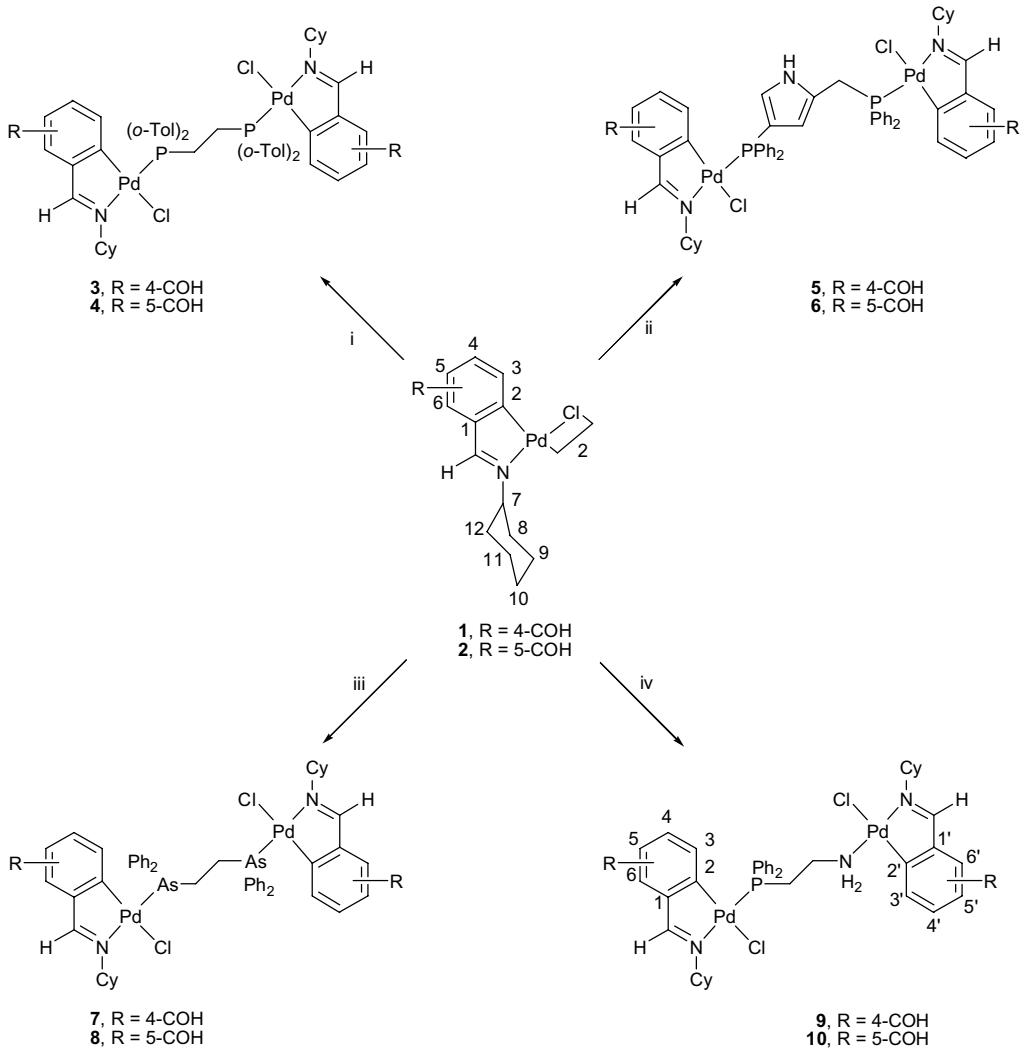
The ^{31}P–$\{^{1}H\}$ NMR spectrum of **3** and **4** showed only one singlet at δ 28.50, in accordance with equivalent phosphorus nuclei, indicating the symmetric nature of the complexes. The singlet was shifted to higher frequency from the free phosphine, in agreement with phosphorus coordination to metal center [50]. However, the ^{31}P–$\{^{1}H\}$ NMR spectrum of **5** and **6** showed two singlets *ca.* δ 40, assigned to the two non-equivalent phosphorus atoms, consequent on the asymmetric structure of the diphosphine, $Ph_2\underline{P}C_4H_2(NH)CH_2PPh_2$. This was also reflected in the ^{1}H NMR spectrum (*vide infra*).

A singlet resonance in the ^{1}H NMR spectrum at δ 9.04 (**3**) and δ 9.81 (**4**), respectively, was assigned to the C*H*O proton. In the former case the resonance was shifted to lower frequency from the starting product by 0.94 ppm, due to the shielding effect of the phosphine tolyl rings, in agreement with a P *trans* to N arrangement, typical of these reactions and within the terms of the "transphobic effect" coined by Vicente et al. [51]. A broad signal *ca.* δ 6.60 was assigned to the H3 proton, coupled to the phosphorus atom and shifted to lower frequency from the starting product *ca.* 1.3 and 1.0 ppm, respectively, due to the shielding effect of the phosphine tolyl rings.

The ^{1}H NMR spectrum for **5** and **6** showed two COH resonances as singlets, δ 9.10, δ 9.33 (**5**) and δ 9.72, δ 9.79 (**6**), as well as to two doublets, *ca.* δ 6.60 and δ 6.90, ascribed to the H3/H3′ protons coupled to the ^{31}P nucleus; thus putting forward the asymmetry of the diphosphine.

The ^{13}C–$\{^{1}H\}$ NMR spectrum of **5** showed two doublets at δ 170.6 and δ 172.5 and two singlets at δ 153.9 and δ 154.3 were assigned to the C = N/C′ = N and the C2/C2′ carbon atoms, respectively, downfield shifted from the spectrum of the free ligand (*ca.* 25 and 14 ppm, also respectively) thereby confirming cyclometallation. The C3/C3′ and C4/C4′ resonances appeared as four doublets at δ 139.4, δ 139.8 $[^{3}J(PC3/PC3') = 9.6, 9.8\ Hz]$, and δ 135.8, δ 136.2 $[^{4}J(PC4/PC4') = 4.2, 4.3\ Hz]$ by coupling to the phosphorus nuclei.

Reaction of **1** and **2** with the diarsine $Ph_2As(CH_2)_2AsPh_2$ in 1:1 molar ratio afforded the dinuclear complexes $[\{Pd[RC_6H_3C(H)=NCy\text{-}C2,N](Cl)\}_2(\mu\text{-}Ph_2As(CH_2)_2As\text{-}$



Scheme 1. (i) $(o\text{-Tol})_2P(CH_2)_2P(o\text{-Tol})_2$ (1:1), dichloromethane; (ii) $Ph_2PC_4H_2(NH)CH_2PPh_2$ (1:1), dichloromethane (**5**), chloroform (**6**); (iii) $Ph_2As(CH_2)_2AsPh_2$ (1:1), dichloromethane; (iv) $Ph_2P(CH_2)_2NH_2$ (1:1), acetone.

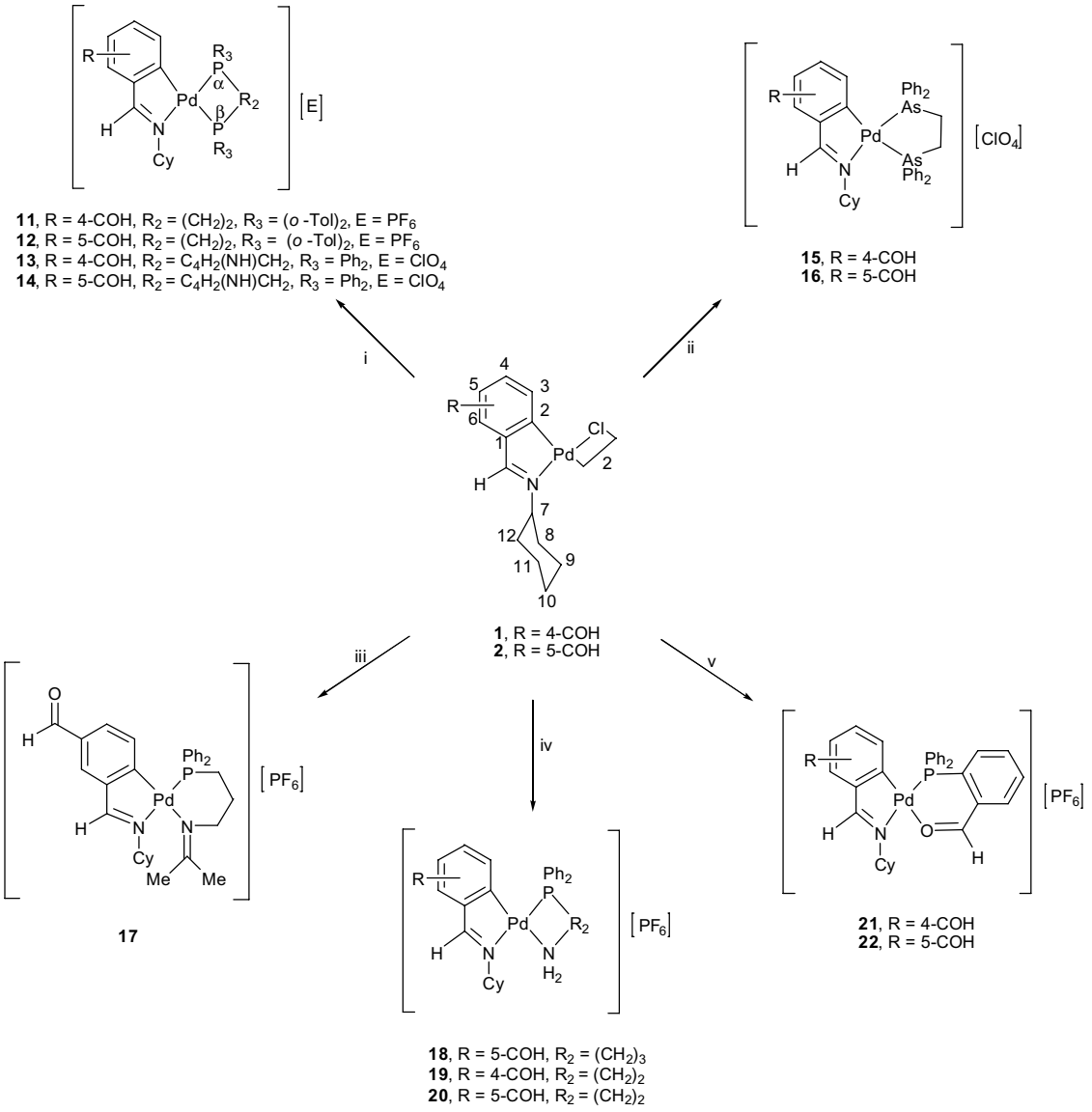
$Ph_2)]$ (R = 4-(COH), **7**; R = 5-(COH), **8**) which were fully characterized (see Section 3.2).

The ^1H NMR spectra of **7** and **8** were similar to those described for **3** and **4**. A singlet at δ 6.89 (**7**) and a doublet at δ 6.70 [^3J(H4H3) = 8.0 Hz] (**8**) were assigned to the H3 resonance, shifted to lower frequency due to the shielding effect of the diarsine phenyl rings, in agreement with a As *trans* to N arrangement. This was confirmed by the formyl group resonance in the spectrum of complex **7** (derived from **1**, R = 4-COH), shifted to lower frequency from the starting material by 0.85 ppm.

In the ^{13}C–{^1H} NMR spectrum of **8** three singlets at δ 170.5, δ 166.0 and δ 149.9 were assigned to the C=N, C1 and C2 carbons, downfield shifted from the spectrum of the free ligand in agreement with metallation at C2. The As*C*H_2 resonance was a singlet at δ 29.7.

Reaction of **1** and **2** with the heterobidentate [*P*,*N*] ligand $Ph_2P(CH_2)_2NH_2$ in 1:1 molar ratio gave the dinuclear complexes $[\{Pd[RC_6H_3C(H)=NCy\text{-}C2,N](Cl)\}_2\text{-}\{\mu\text{-}Ph_2P(CH_2)_2NH_2\}]$ (R = 4-(COH), **9**; R = 5-(COH), **10**). A singlet at δ 53.01 in the ^{31}P–{^1H} NMR spectrum confirmed phosphorus coordination to the metal center. In the ^1H NMR spectrum of **10** two singlets at δ 9.80 and δ 9.88 were assigned to the COH and the COH′ protons. In the ^1H NMR spectrum of **9** the resonances at δ 9.43, upfield shifted due to the shielding effect of the phosphine phenyl rings, and at δ 9.97, were ascribed to the CHO and CHO′ protons, respectively. Two doublets of doublets at δ 7.06 and δ 8.22 were assigned to H3 and HC=N protons, respectively, and two doublets at δ 7.21 and δ 8.19 were assigned to H3′ and HC = N′, also respectively.

Treatment of the chloro-bridged complexes **1** and **2** with diphosphines or diarsines in a 1:2 molar ratio in the presence of NH_4PF_6 and $NaClO_4$ gave the mononuclear compounds $[Pd\{RC_6H_3C(H)=NCy\text{-}C2,N\}\{(o\text{-Tol})_2P(CH_2)_2P(o\text{-Tol})_2\text{-}P,P\}][PF_6]$ (R = 4-(COH), **11**; R = 5-(COH), **12**), $[Pd\{RC_6H_3C(H)=NCy\text{-}C2,\ N\}\{Ph_2PC_4H_2(NH)CH_2PPh_2\text{-}$



Scheme 2. (i) (*o*-Tol)$_2$P(CH$_2$)$_2$P(*o*-Tol)$_2$(1:2), NH_4PF_6, acetone/water (**11**, **12**); $Ph_2PC_4H_2(NH)CH_2PPh_2$ (1:2), $NaClO_4$, dichloromethane (**13**, **14**) (ii) $Ph_2As(CH_2)_2AsPh_2$ (1:2), $NaClO_4$, dichloromethane; (iii) $Ph_2P(CH_2)_2NH_2$ (1:2), NH_4PF_6, acetone/water. (iv) $Ph_2P(CH_2)_nNH_2$ (1:2), NH_4PF_6, toluene; (v) $Ph_2P(C_6H_4)CHO$ (1:2), NH_4PF_6, acetone/water.

P, *P*}][ClO$_4$] (R = 4-(COH), **13**; R = 5-(COH), **14**) and [Pd{RC$_6$H$_3$C(H)=NCy-*C*2, *N*}{Ph$_2$As(CH$_2$)$_2$AsPh$_2$-*As*, *As*}][ClO$_4$] (R = 4-(COH), **15**; R = 5-(COH), **16**). The conductivity data (125–150 Ω^{-1} cm^2 mol^{-1} in 10^{-3} mol dm^{-3} solutions in dry acetonitrile) showed them to be 1:1 electrolytes [52]. The MS-FAB spectra showed, among others, the corresponding peaks assigned to $[M]^+$, $[M-COH]^+$ and/or $[M-Cy]^+$ (see Section 3). The $^{31}P-\{^1H\}$ 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 [50]. In the ^1H NMR spectrum a multiplet at δ 6.55–6.90 was assigned to H3, coupled to both phosphorus nuclei, e.g. for compound **14**, selective decoupling experiments allowed the correct assignment of the corresponding coupling constants, $^4J(P_\alpha H3) = 4.4$ Hz, $^4J(P_\beta H3) = 4.9$ Hz. However, the HC=N resonance appeared *ca.* δ 8.40 as a doublet by coupling to only the ^{31}P nucleus *trans* to nitrogen. The ^1H NMR spectra for compounds **11** and **12** showed the COH and H3 resonances shifted to lower frequency from the starting product due to the shielding effect of the phosphine tolyl groups *cis* to carbon.

Reaction of **2** with $Ph_2P(CH_2)_3NH_2$ in 1:2 molar ratio in acetone in the presence of NH_4PF_6 afforded [Pd{5-(COH)C$_6$H$_3$C(H)=NCy-*C*2,*N*}{Ph$_2$P(CH$_2$)$_3$N(=CMe$_2$)-P,*N*}][PF$_6$] (**17**), with a chelating [*P*,*N*] ligand derived from intermolecular condensation between the aminophosphine and acetone. The IR spectrum showed two bands at 1621 and 1647 cm^{-1} consistent with the presence of two different imino groups, the HC=N group in the cyclometallated ring and the Me$_2$C=N group in the chelating [*P*,*N*] ligand after

condensation. The $^{31}P–\{^1H\}$ NMR spectra showed a singlet at δ 28.61 in agreement with phosphorus coordination. In the ^1H NMR spectrum the shift of the *H*C=O and *H*3 resonances with respect to those of **2**, were in accordance with a P *trans* to N arrangement in the palladium environment. Furthermore, the spectrum showed the presence of two singlets at δ 2.30 and δ 2.02 assignable to the non-equivalent Me_2C=N methyl groups.

Condensation of the NH_2 group was precluded by change of solvent. Thus, reaction of **1** and **2** with $Ph_2P(CH_2)_nNH_2$ in toluene afforded compounds $[Pd\{RC_6H_3C(H)=NCy\text{-}C2,N\}\{Ph_2P(CH_2)_nNH_2\text{-}P,N\}][PF_6]$ ($n = 3$, R = 5-(COH), **18**; $n = 2$, R = 4-(COH), **19**; $n = 2$, R = 5-(COH), **20**). The analytical and the mass data were in agreement with the proposed structures. The conductivity measurements between 130 and 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**. No condensation of the phosphine amine group to the (*COH*)C_6H_3-group was observed.

Treatment of **1** and **2** with $Ph_2P(C_6H_4)CHO$ in a 1:2 molar ratio in the presence of NH_4PF_6 gave the mononuclear compounds $[Pd\{RC_6H_3C(H)=NCy\text{-}C2,N\}\{2\text{-}(Ph_2P)C_6H_4CHO\text{-}P,O\}][PF_6]$ (R = 4-(COH), **21**; R = 5-(COH), **22**) as 1:1 electrolytes with the ligand chelated to the metal center to give a six-membered ring. The IR spectrum showed two bands *ca.* 1645 and 1695 cm^{-1} consistent with two different C=O groups. The former was shifted to lower frequency as compared with the free [*P*,*O*] ligand in agreement with oxygen coordination to the metal center. The $^{31}P–\{^1H\}$ NMR spectra showed singlets at δ 34.71 (**21**) and δ 34.44 (**22**). The ^1H NMR data was in agreement with the P-*trans*-N and O-*trans*-C(phenyl ring) coordination. A doublet at δ 10.15 was assigned to the CHO group of the [*P*,*O*] ligand [$^4J(PH) = 1.5$ Hz]. This signal was upfield shifted 0.35 ppm from the spectrum of the free ligand confirming oxygen coordination to the metal center, and consistent with a σ-bound aldehyde [53].

2.1. Molecular structures of complexes 7, 11, 15 and 21

Suitable crystals were grown by slowly evaporating dichloromethane/*n*-hexane (**7**, **15**, **21**) or chloroform/*n*-hexane (**11**) solutions of the complexes. The labeling schemes for the compounds are shown in Figs. 1–4.

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 1 and 2.

For compound **7**, the crystal structure comprises a dinuclear molecule (half molecule per asymmetric unit) and two CH_2Cl_2 solvent molecule. The crystal structures of compounds **11**, **15** and **21** comprise a mononuclear cation (one molecule per asymmetric unit), a perchlorate (**15**) or a hexafluorophosphate (**11**, **21**) anion, 1.25$CHCl_3$ for **11**, and half molecule of CH_2Cl_2 for **15**.

In compound **7** the four-coordinated palladium(II) is bonded to an adjacent *ortho*-carbon atom (C1) and to the nitrogen atom of the imine group of the deprotonated

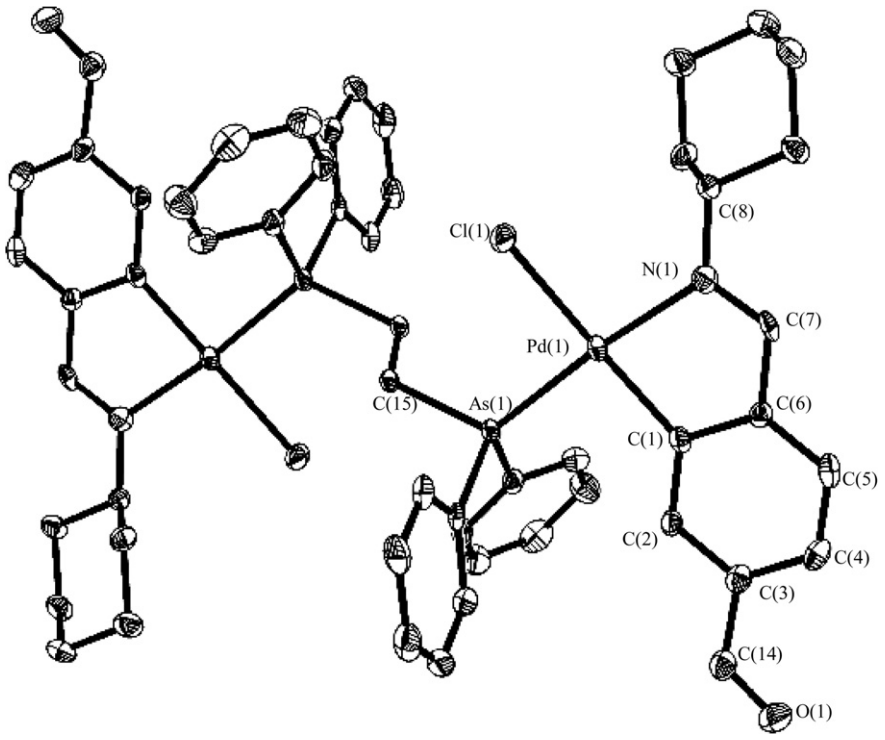


Fig. 1. Molecular structure of $[\{Pd[4\text{-}(COH)C_6H_3C(H)=NCy\text{-}C2,N](Cl)\}_2\{\mu\text{-}Ph_2As(CH_2)_2AsPh_2\}]$ (**7**), with labelling scheme. Hydrogen atoms have been omitted for clarity.

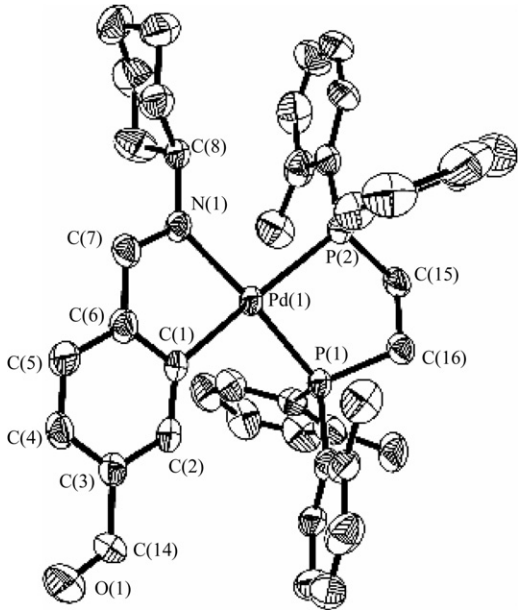


Fig. 2. Molecular structure of the cation for [Pd{4-(COH)C_6H_3-C(H)=NCy-C2,x N}{(*o*-Tol)$_2$P(CH$_2$)$_2$P(*o*-Tol)$_2$-P,P}][PF_6] (**11**), with labelling scheme. Hydrogen atoms have been omitted for clarity.

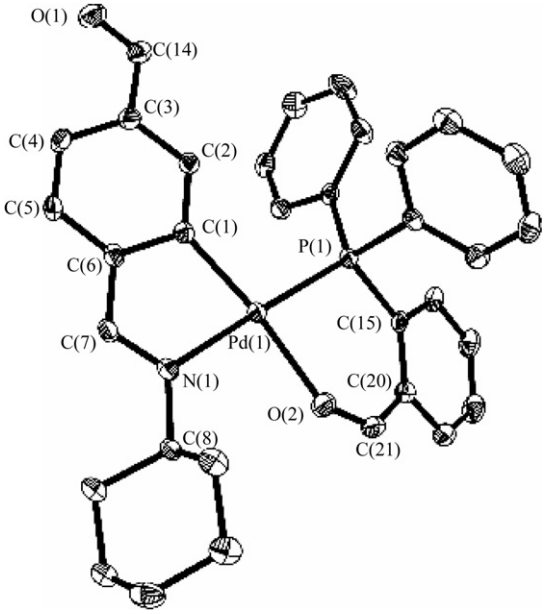


Fig. 4. Molecular structure of the cation for [Pd{4-(COH)C_6H_3-C(H)=NCy-*C2,N*}{2-(Ph_2P)C_6H_4CHO-*P,O*}][PF_6] (**21**), with labelling scheme. Hydrogen atoms have been omitted for clarifty.

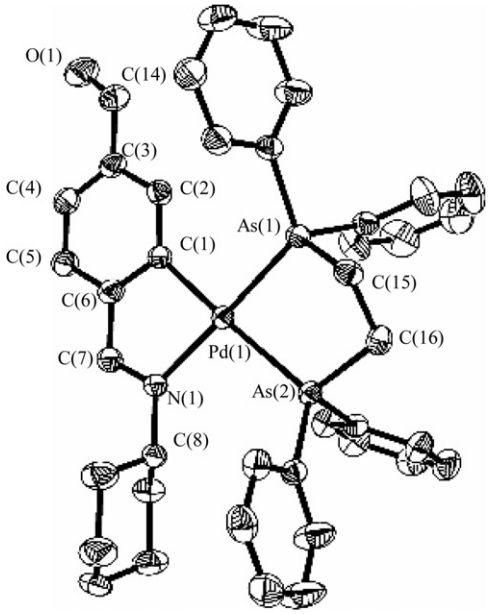


Fig. 3. Molecular structure of the cation for [Pd{4-(COH)C_6H_3-C(H)=NCy-C2,N}{$Ph_2As(CH_2)_2AsPh_2$-*As,As*}][ClO_4] (**15**), with labelling scheme. Hydrogen atoms have been omitted for clarity.

Schiff-base ligand and to a chlorine atom (*trans* to C1). An arsenic atom from the diarsine ligand which bridges the two metal centers, completes the metal coordination sphere.

For mononuclear complexes **11** and **15** the palladium(II) is bonded to the C1 and the nitrogen atoms of the Schiff-base ligand and to the phosphorous (**11**) or arsenic (**15**) atoms of the homobidentate chelating ligand. In compound **21** the palladium(II) is bonded to four different atoms: and ortho-carbon of the phenyl ring and a nitrogen atom of the benzylidene ligand, and the oxygen and phosphorous atoms of the 2-(diphenylphosphino)benzaldehyde forming a six-membered ring chelate.

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 80.9(3)° (**7**), 80.7(3)° (**11**), 81.4(1)° (**15**), 81.6(1)° (**21**), 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, As1, Cl1, **7**; Pd1, C1, N1, P1, P2, **11**; Pd1, C1, N1, As1, As2, **15**; Pd1, C1, N1, P1, O2, **21**;) are 0.1034, 0.0959, 0.0771 and 0.0233 Å, respectively.

The palladium–carbon bond lengths, (2.004(7) Å (**7**), 2.080(8) Å (**11**), 2.044(4) Å (**15**), 1.996(3) Å (**21**)), are somewhat shorter than the expected value of 2.081 A (based on the sum of the covalent radii for carbon(sp^2) and palladium, 0.771 and 1.31 A, respectively) [54]. However, the palladium–nitrogen bond lengths in the metallacycle, (2.098(6) Å (**7**), 2.113(7) Å (**11**), 2.086(4) Å (**15**), 2.087(2) Å (**21**)), 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 reflects the influence of the atom in *trans* position. The Pd–P (2.267(2) and 2.376(2) Å (**11**), 2.2508(10) Å (**21**)), Pd–As (2.350(10) (**7**) and 2.359(5) and 2.4671(5) (**15**)) bond distances, 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 similar to others reported earlier [23,55,56].

Table 1
Crystal and structure refinement data for complexes **7**, **11**, **15** and **21**

	7 · $2CH_2Cl_2$	**11** · $1.25CHCl_3$	**15** · $0.5CH_2Cl_2$	**21**
Formula	$C_{56}H_{60}As_2Cl_6N_2O_2Pd_2$	$C_{45.25}H_{49.25}Cl_{3.75}F_6NOP_3Pd$	$C_{40.5}H_{42}As_2Cl_2NO_5Pd$	$C_{33}H_{31}F_6NO_2P_2Pd$
M_r	1368.4	1069.35	949.89	755.93
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C1c1$	$P\bar{1}$	$P21/c$
Cell dimensions				
a (A)	9.800(3)	13.343(4)	12.655(10)	16.405(5)
b (A)	12.853(4)	27.302(8)	13.614(10)	11.449(4)
c (A)	13.175(4)	14.721(4)	13.888(10)	18.108(6)
α (°)	101.536(6)	90	99.093(10)	90
β (°)	106.900(7)	104.768(5)	116.113(10)	111.705(2)
γ (°)	112.224(6)	90	101.010(10)	90
V (Å^3)	1377.0(7)	5185.6(26)	2027.8(3)	3159.9(18)
Z	1	4	2	4
D_{calc} (Mg/m^3)	1.445	1.370	1.556	1.589
μ (mm^{-1})	2.180	0.698	2.252	0.756
Crystal size (mm)	$0.29 \times 0.07 \times 0.05$	$0.44 \times 0.21 \times 0.20$	$0.34 \times 0.30 \times 0.17$	$0.36 \times 0.11 \times 0.10$
$2\theta_{max}$ (°)	56.72	56.98	56.54	56.74
Independent reflections	6285 ($R_{int} = 0.0566$)	5802 ($R_{int} = 0.0327$)	9197 ($R_{int} = 0.0198$)	7512 ($R_{int} = 0.0459$)
S	0.948	1.082	1.018	0.981
R [F, $I > 2\sigma(I)$]	0.0662	0.0627	0.0436	0.0386
wR [F^2, all data]	0.1404	0.1849	0.1209	0.0861
max ρ (e Å^3)	0.880	1.131	1.061	0.403
Absolute structure parameter		0.00(4)		

Table 2
Selected bond distances (A) and angles (°) for complexes **7**, **11**, **15** and **21**

	7	**11**	**15**	**21**
Pd(1)–C(1)	2.004(7)	2.080(8)	2.044(4)	1.996(3)
Pd(1)–N(1)	2.098(6)	2.113(7)	2.086(4)	2.087(2)
Pd(1)–P(1)		2.267(2)		2.2508(10)
Pd(1)–P(2)		2.376(2)		
Pd(1)–O(2)				2.106(2)
Pd(1)–Cl(1)	2.383(2)			
Pd(1)–As(1)	2.350(10)		2.359(5)	
Pd(1)–As(2)			2.4671(5)	
C(1)–C(6)	1.405(9)	1.414(13)	1.393(6)	1.423(4)
C(6)–C(7)	1.443(9)	1.439(15)	1.458(7)	1.447(4)
N(1)–C(7)	1.272(8)	1.276(11)	1.284(6)	1.278(4)
O(1)–C(14)	1.201(8)	1.201(15)	1.192(6)	1.212(3)
C(1)–Pd(1)–N(1)	80.9(3)	80.7(3)	81.4(15)	81.62(10)
C(1)–Pd(1)–P(1)		95.9(2)		100.02(8)
C(1)–Pd(1)–P(2)		171.6(2)		
C(1)–Pd(1)–As(1)	93.8(2)		97.2(12)	
C(1)–Pd(1)–As(2)			173.2(12)	
C(1)–Pd(1)–O(2)				171.67(10)
P(1)–Pd(1)–P(2)		84.6(8)		
As(1)–Pd(1)–As(2)			82.2(18)	
P(1)–Pd(1)–O(2)				88.16(6)
As(1)–Pd(1)–Cl(1)	90.6(6)			
N(1)–Pd(1)–Cl(1)	95.4(18)			
N(1)–Pd(1)–P(1)		175.2(2)		
N(1)–Pd(1)–P(2)		99.3(2)		
N(1)–Pd(1)–As(1)			177.5(10)	
N(1)–Pd(1)–As(2)			99.4(10)	
N(1)–Pd(1)–O(2)				90.24(9)
C(7)–N(1)–Pd(1)	111.8(2)	112.9(7)	113.1(3)	113.4(2)
N(1)–C(7)–C(6)	119.7(6)	118.6(9)	117.7(4)	117.3(3)
C(1)–C(6)–C(7)	114.6(6)	117.7(8)	117.1(4)	116.5(3)
C(6)–C(1)–Pd(1)	112.5(5)	109.1(6)	110.7(3)	111.2(2)

For compound **21** the Pd–O(2) bond distance, 2.106(2) Å, is longer than the expected value of 1.97 Å and shows the *trans* influence of the aryl carbon atom.

The distinct Pd–P and Pd–As bond distances in the mononuclear compounds **11** and **15** also reflects the differing *trans* influence of the metallated carbon and the nitrogen atoms of the Schiff-base ligand (see Table 2).

For compound **7** the Pd–Cl bond length, 2.383(2) Å, is consistent with Pd–Cl distances found in related species [24,56] but longer than the sum of the covalent radii (2.30 Å) also as a consequence of the *trans* influence of the C(phenyl) carbon.

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 0.0368 and 0.0063 Å (**7**), 0.0472 and 0.0117 Å (**11**), 0.0137 and 0.0052 Å (**15**), 0.0115 and 0.0138 Å (**21**), respectively. The angle between these planes are as follows: 3.9°, 5.4°, 1.4° and 1.6°, also respectively. The angles between plane 1 and the previous planes are: plane 1/plane 2: 8.0°(**7**), 8.1°(**11**), 5.9°(**15**), 1.6°(**21**) and plane 1/plane 3: 10.4°(**7**), 10.1°(**11**), 6.1°(**15**), 3.0°(**21**).

The crystal structure of **11** confirms that the bigger steric requirement of the phosphine tolyl rings makes them to be nearest of the H3 and the formyl group in the C4 position of the metallated ring, with the consequences we have seen in the ^{1}H NMR spectrum.

In compound **21** the C(21)–O(2) distance (1.219(4) Å) of the aldehyde group is indicative of the greater double-bond character typical of a σ-bonded aldehyde group. This bond length lies in the range reported for transition metal complexes with aldehydes bonded in a σ-fashion [57–59]. The O(2) shows a displacement from the plane formed by the phosphorous atom and the carbon atoms of the benzaldehyde group (P(1), C(15)–C(21), r.m.s. = 0.0156 Å) of 0.24 Å, which reflects the deviation from the planarity of the aldehyde unit upon coordination to the metal center.

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 [60]. 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 conductivimeter using 10^{-3} M solutions in dry acetonitrile at room temperature (298 K). The synthesis of [Pd{4-(COH)C_6H_3-C(H)=NCy-*C*2,*N*}(μ-Cl)]$_2$ (**1**) and [Pd{5-(COH)C_6H_3-C(H)=NCy-*C*2,*N*}(μ-Cl)]$_2$ (**2**) has been reported previously from this laboratory [17,18]. The phosphine (*o*-Tol)$_2$P(CH$_2$)$_2$P(*o*-Tol)$_2$ was prepared as described previously in the literature [61].

3.2. Syntheses

3.2.1. [{Pd[4-(COH)C_6H_3C(H)=NCy-C2,N](Cl)}$_2$-{μ-(*o*-Tol)$_2$P(CH$_2$)$_2$P(*o*-Tol)$_2$}] (**3**)

To a suspension of **1** (25.00 mg, 0.035 mmol) in dichloromethane (*ca.* 10 mL), (*o*-Tol)$_2$P(CH$_2$)$_2$P(*o*-Tol)$_2$ (13.57 mg, 0.032 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: 41%. Anal. Calc. for $C_{58}H_{64}Cl_2N_2O_2P_2Pd_2$: C, 59.7; H, 5.5; N, 2.4. Found: C, 59.5; H, 5.1; N, 2.2%; IR: *ν*(C=N): 1621m, *ν*(C=O): 1694 s. FAB-Mass: 775 [LPd(PP)]$^+$, 291 [(L-CHO)Pd]$^+$. ^{1}H NMR: $\delta = 4.58$ (t, CH_2P, $^2J(PH) = 10.8$), 6.59 (br, H3), 7.07 (d, H5, $^3J(H5H6) = 7.6$ Hz), 9.04 (s, Ha). ^{31}P–{^{1}H} NMR: $\delta = 28.58$ (s).

3.2.2. [{Pd[5-(COH)C_6H_3C(H)=NCy-C2,N](Cl)}$_2$-{μ-(*o*-Tol)$_2$P(CH$_2$)$_2$P(*o*-Tol)$_2$}] (**4**)

To a suspension of **2** (25.00 mg, 0.035 mmol) in dichloromethane (*ca.* 10 mL), (*o*-Tol)$_2$P(CH$_2$)$_2$P(*o*-Tol)$_2$ (13.57 mg, 0.032 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: 81%. Anal. Calc. for $C_{58}H_{64}Cl_2N_2O_2P_2Pd_2$: C, 59.7; H, 5.5; N, 2.4. Found: C, 59.4; H, 5.2; N, 2.1%. IR: *ν*(C=N): 1614 m, *ν*(C=O): 1693 s. FAB-Mass: 774 [LPd(PP)]$^+$. ^{1}H NMR: $\delta = 4.58$ (t, CH_2P, $^2J(PH) = 10.8$), 6.61 (br, H3), 7.10 (dd, H4, $^3J(H6H4) = 1.7$ Hz, $^3J(H4H3) = 8.0$ Hz), 9.81 (s, Ha). ^{31}P–{^{1}H} NMR: $\delta = 28.50$ (s).

3.2.3. [{Pd[4-(COH)C_6H_3C(H)=NCy-C2,N](Cl)}$_2$(μ-$Ph_2PC_4H_2$(NH)CH_2PPh_2)] (**5**)

Complex **5** was synthesized with a procedure similar to that described for complex **3**, but using $Ph_2PC_4H_2$-(NH)CH_2PPh_2.

Yield: 78%. Anal. Calc. for $C_{57}H_{57}Cl_2N_3O_2P_2Pd_2$: C, 58.9; H, 4.9; N, 3.6. Found: C, 58.5; H, 5.7; N, 3.5%. IR: *ν*(C=N): 1619m, *ν*(C=O): 1693s. FAB-Mass: 778 [LPd(PP)]$^+$.

^{1}H NMR: $\delta = 6.54$, 6.90 (d, H3, $^4J(PH3) = 6.3$, 5.4 Hz), 9.10, 9.33 (s, Ha). ^{13}C NMR: $\delta = 24.7$ (s, C10), 25.5, 25.7

(s, C9, C11), 33.3, 33.6 (s, C8, C12), 62.0, 64.4 (s, C7), 124.0 (s, C6), 127.4 (s, C5), 129.0, 129.6 (d, C_m, $^3J(PC_m) = 11.3$ Hz), 130.8, 131.2 (d, C_p, $^4J(PC_p) = 2.8, 2.1$ Hz), 134.0, 134.8 (d, C_o, $^2J(PC_o) = 13.5, 12.0$ Hz), 135.8, 136.2 (d, C4, $^4J(PC4) = 4.2, 4.3$ Hz), 139.4, 139.8 (d, C3, $^3J(PC3) = 9.6, 9.8$ Hz), 153.9, 154.3 (s, C2), 157.6 (s, C1), 170.6, 172.5 (d, C=N, $^3J(PC = N) = 2.8, 3.6$ Hz), 191.8, 191.9 (s, COH). $^{31}P–\{^1H\}$ NMR: $\delta = 39.08$ (s), 41.36 (s).

3.2.4. [{Pd[5-(COH)C_6H_3C(H)=NCy-C2,N](Cl)}$_2$-(μ-$Ph_2PC_4H_2(NH)CH_2PPh_2$)] (6)

To a suspension of **2** (25.00 mg, 0.035 mmol) in chloroform (*ca.* 10 mL), $Ph_2PC_4H_2(NH)CH_2PPh_2$ (13.38 mg, 0.032 mmol) was added. The mixture was stirred for 12 h at room temperature, after which solvent was removed under reduced pressure, and the residue triturated with diethylether to yield a yellow solid, which was filtered off and dried *in vacuo*.

Yield: 59%. Anal. Calc. for $C_{57}H_{57}Cl_2N_3O_2P_2Pd_2(Et_2O)_3$: C, 62.0; H, 6.5; N, 3.1. Found: C, 61.9; H, 6.2; N, 3.1%. IR: *ν*(C=N): 1620m, *ν*(C=O): 1690s. FAB-Mass: 779 [(L-CHO)Pd(PP)]$^+$, 291 [(L-CHO)Pd]$^+$. ^{1}H NMR: $\delta = 6.66$, 6.95 (dd, H3, $^4J(PH3) = 4.9$, 5.8 Hz), 7.13 (dd, H4, $^4J(H4H6) = 1.6$ Hz) 9.72, 9.79 (s, Ha). $^{31}P–\{^1H\}$ NMR: $\delta = 40.88$ (s), 41.82 (s).

3.2.5. [{Pd[4-(COH)C_6H_3C(H)=NCy-C2,N](Cl)}$_2$-{μ-$Ph_2As(CH_2)_2AsPh_2$}] (7)

Complex **7** was synthesized with a procedure similar to that described for complex **3**, but using $Ph_2As(CH_2)_2AsPh_2$.

Yield: 79%. Anal. Calc. for $C_{54}H_{56}As_2Cl_2N_2O_2Pd_2$: C, 54.1; H, 4.7; N, 2.3. Found: C, 54.2; H, 4.6; N, 2.1%. IR: *ν*(C=N): 1620 m, *ν*(C=O): 1693s. FAB-Mass: 807 [LPd(AsAs)]$^+$, 291 [(L-CHO)Pd]$^+$. ^{1}H NMR: $\delta = 4.48$ (m, CH_2As), 6.89 (s, H3), 8.12 (d, Hi, $^5J(HiH7) = 1.0$ Hz), 9.13 (s, Ha).

3.2.6. [{Pd[5-(COH)C_6H_3C(H)=NCy-C2,N](Cl)}$_2$-{μ-$Ph_2As(CH_2)_2AsPh_2$}] (8)

Complex **8** was synthesized with a procedure similar to that described for complex **4**, but using $Ph_2As(CH_2)_2AsPh_2$.

Yield: 90%. Anal. Calc. for $C_{54}H_{56}As_2Cl_2N_2O_2Pd_2$: C, 54.1; H, 4.7; N, 2.3. Found: C, 53.9; H, 5.0; N, 2.2%. IR: *ν*(C=N): 1624m,*ν*(C=O): 1693s. FAB-Mass: 807 [LPd(AsAs)]$^+$. ^{1}H NMR: $\delta = 4.48$ (m, CH_2As), 6.70 (d, H3, $^3J(H4H3) = 8.0$ Hz), 7.00 (dd, H4, $^6J(H6H4) = 1.9$ Hz), 8.17 (s, Hi), 9.75 (s, Ha). ^{13}C NMR: $\delta = 29.7$ (s, CH_2As), 25.4 (s, C9, C11), 25.7 (s, C10), 33.5 (s, C8, C12), 62.8 (s, C7), 126.8 (s, C6), 128.8 (s, C_m), 131.1 (s, C_p), 133.4 (s, C_o), 138.1 (s, C3), 149.9 (s C2), 166.0 (s, C1), 170.5 (s, C=N), 191.2 (s, COH).

3.2.7. [{Pd[4-(COH)C_6H_3C(H)=NCy-C2,N](Cl)}$_2${μ-$Ph_2P(CH_2)_2NH_2$}] (9)

Complex **9** was synthesized with a procedure similar to that described for complex **3**, but using acetone.

Yield: 51%. Anal. Calc. for $C_{42}H_{48}Cl_2N_3O_2PPd_2$: C, 53.6; H, 5.1; N, 4.5. Found: C, 53.4; H, 4.9; N, 4.1%. IR: *ν*(C=N): 1616m, *ν*(C=O): 1698s. FAB-Mass: 551 [LPd(PN)]$^+$, 522 [(L-CHO)Pd(PN)]$^+$, 291 [(L-CHO)Pd]$^+$. ^{1}H NMR: $\delta = 7.06$ (dd, H3, $^4J(H3H5) = 1.0$ Hz, $^4J(PH3) = 5.6$ Hz), 7.21 (d, H3′, $^4J(H3'H5) = 1.0$ Hz), 8.19 (d,Hi′, $^5J(Hi'H7) = 1.0$Hz), 8.22 (dd, Hi, $^5J(HiH7) = 1.0$ Hz, $^4J(PHi) = 7.3$ Hz), 9.43, 9.97 (s, Ha,Ha′). $^{31}P–\{^1H\}$ NMR: $\delta = 53.01$ (s).

3.2.8. [{Pd[5-(COH)C_6H_3C(H)=NCy-C2,N](Cl)}$_2$-{μ-$Ph_2P(CH_2)_2NH_2$}] (10)

Complex **10** was synthesized with a procedure similar to that described for complex **4**, but using acetone.

Yield: 25%. Anal. Calc. for $C_{42}H_{48}Cl_2N_3O_2PPd_2$: C, 53.6; H, 5.1; N, 4.5. Found: C, 53.4; H, 5.2; N, 4.4%. IR: *ν*(C=N): 1621m, *ν*(C=O): 1688s. FAB-Mass: 551 [LPd(PN)]$^+$, 522 [(L-CHO)Pd(PN)]$^+$, 291 [(L-CHO)Pd]$^+$. ^{1}H NMR: $\delta = 6.81$ (dd, H3, $^3J(H4H3) = 5.1$ Hz, $^4J(PH3) = 7.8$ Hz), 7.19 (dd, H4, $^4J(H6H4) = 1.0$ Hz), 7.99 (d,Hi′, $^5J(Hi'H7) = 1.0$Hz), 8.22 (d, Hi, $^4J(PHi) = 8.8$ Hz), 9.80, 9.88 (s,Ha, Ha′). $^{31}P–\{^1H\}$ NMR: $\delta = 53.01$ (s).

3.2.9. [Pd{4-(COH)C_6H_3C(H)=NCy-C2,N}{(o-Tol)$_2$-P(CH_2)$_2$P(o-Tol)$_2$-P,P}][PF_6] (11)

To a suspension of **1** (20.00 mg, 0.028 mmol) in acetone (*ca.* 15 mL), (*o*-Tol)$_2$P(CH_2)$_2$P(*o*-Tol)$_2$ (23.77 mg, 0.056 mmol) was added. The mixture was stirred for 2 h at room temperature, after which ammonium hexafluorophosphate in estequiometric amount was added, the resultant solution stirred for a further 1 h, water (*ca.* 40 mL) was added dropwise and the resulting mixture stirred for 2 h. A 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: 82%. Anal. Calc. for $C_{44}H_{48}F_6NOP_3Pd$: C, 57.4; H, 5.2; N, 1.5. Found: C, 57.2; H, 4.7; N, 1.4%. IR: *ν*(C=N): 1616 m, *ν*(C=O): 1695s. FAB-Mass: 773[M]$^+$, 291 [(L-CHO)Pd]$^+$. ^{1}H NMR: $\delta = 6.90$ (m, H3, $^3J(H3H5) = 2.1$ Hz, $^4J(P_\alpha H3) = 4.4$ Hz, $^4J(P_\beta H3) = 4.9$ Hz), 7.65 (dd, H5, $^3J(H5H6) = 7.5$ Hz), 8.50 (d, Hi, $^4J(P_\alpha Hi) = 7.8$ Hz), 9.26 (s, Ha). $^{31}P–\{^1H\}$ NMR: $\delta = 42.01$ (d, P_β, $^3J(PP) = 2.2$ Hz), 56.15 (d, P_α).

3.2.10. [Pd{5-(COH)C_6H_3C(H)=NCy-C2,N}-{(o-Tol)$_2$P(CH_2)$_2$P(o-Tol)$_2$-P,P}][PF_6] (12)

Compound **12** was synthesized following a procedure similar to that described for **11**, but using **2** as a starting material.

Yield: 76%. Anal. Calc. for $C_{44}H_{48}F_6NOP_3Pd$: C, 57.4; H, 5.2; N, 1.5. Found: C, 57.7; H, 5.2; N, 1.3%. R: *ν*(C=N): 1619m, *ν*(C=O): 1690m. FAB-Mass: 773 [M]$^+$, 690 [M−Cy]$^+$, 291 [(L-CHO)Pd]$^+$. ^{1}H NMR: $\delta = 3.73$ (dd, CH_2P), 6.70 (m, H3, $^3J(H4H3) = 8.3$ Hz), 7.18 (dd, H4, $^4J(H6H4) = 1.8$ Hz), 7.94 (b, H6), 8.49 (d, Hi, $^4J(P_\alpha Hi) = 8.3$ Hz), 9.83 (s, Ha). $^{31}P–\{^1H\}$ NMR: $\delta = 42.62$ (d, P_β, $^3J(PP) = 15.3$ Hz), 56.45 (d, P_α).

*3.2.11. [Pd{4-(COH)C$_6$H$_3$C(H)=NCy-C2,N}{Ph$_2$PC$_4$H$_2$(NH)CH$_2$PPh$_2$-P,P}][ClO$_4$] (**13**)*

To a suspension of **1** (20.00 mg, 0.028 mmol) in dichloromethane (*ca.* 15 mL), $Ph_2PC_4H_2(NH)CH_2PPh_2$ (25.40 mg, 0.056 mmol) was added. The mixture was stirred for 2 h at room temperature, after which estequiometric amount of sodium perchlorate was added, 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: 73%. Anal. Calc. for $C_{43}H_{41}ClN_2O_5P_2Pd$: C, 59.4; H, 4.7; N, 3.2. Found: C, 59.2; H, 4.8; N, 3.0%. IR: ν(C=N): 1618m, ν(C=O): 1691m. FAB-Mass: 769 $[M]^+$, 291 $[(L\text{-}CHO)Pd]^+$. ^{1}H NMR: $\delta = 6.70$ (dd, H3, $^4J(H3H5) = 1.2$ Hz, $^4J(P_\alpha H3) = 4.4$ Hz), 8.41 (d, Hi, $^4J(P_\alpha Hi) = 7.8$ Hz), 9.30 (s, Ha). ^{31}P–{^{1}H} NMR: $\delta = 7.71$ (d, P_β, $^5J(PP) = 114.4$ Hz), 36.93 (d, P_α).

*3.2.12. [Pd{5-(COH)C$_6$H$_3$C(H)=NCy-C2,N}{Ph$_2$PC$_4$H$_2$(NH)CH$_2$PPh$_2$-P, P}][ClO$_4$] (**14**)*

Compound **14** was synthesized following a procedure similar to that described for **13**, but using **2** as a starting material.

Yield: 65%. Anal. Calc. for $C_{43}H_{41}ClN_2O_5P_2Pd$: C, 59.4; H, 4.7; N, 3.2. Found: C, 59.2; H, 4.9; N, 3.1%. IR: ν(C=N): 1618m, ν(C=O): 1695m. FAB-Mass: 769 $[M]^+$, 687 $[M-Cy]^+$, 291 $[(L\text{-}CHO)Pd]^+$. ^{1}H NMR: $\delta = 6.55$ (m, H3, $^3J(H4H3) = 7.8$ Hz, $^4J(P_\alpha H3) = 4.4$ Hz, $^4J(P_\beta H3) = 4.9$ Hz), 7.12 (dd, H3, $^4J(H6H4) = 2.0$ Hz), 7.80 (d, H6), 8.42 (d, Hi, $^4J(P_\alpha Hi) = 4.9$ Hz), 9.81 (s, Ha). ^{31}P–{^{1}H} NMR: $\delta = 6.67$ (d, P_β, $^3J(PP) = 107.6$ Hz), 37.24 (d, P_α).

*3.2.13. [Pd{4-(COH)C$_6$H$_3$C(H)=NCy-C2,N}-{Ph$_2$As(CH$_2$)$_2$AsPh$_2$-As,As}][ClO$_4$] (**15**)*

Compound **15** was synthesized following a procedure similar to that described for **13**, but using $Ph_2As(CH_2)_2AsPh_2$ as a starting material.

Yield: 54%. Anal. Calc. for $C_{40}H_{40}As_2ClNO_5Pd$: C, 53.0; H, 4.5; N, 1.6. Found: C, 53.2; H, 4.4; N, 1.3%. IR: ν(C=N): 1615m, ν(C=O): 1692s. FAB-Mass: 807 $[M]^+$, 768 $[M-CHO]^+$. ^{1}H NMR: $\delta = 7.74$ (d, H5, $^3J(H5H6) = 7.8$ Hz), 8.54 (s, Hi), 9.44 (s, Ha).

*3.2.14. [Pd{5-(COH)C$_6$H$_3$C(H)=NCy-C2, N}-{Ph$_2$As(CH$_2$)$_2$AsPh$_2$-As,As}][ClO$_4$] (**16**)*

Compound **16** was synthesized following a procedure similar to that described for **13**, but using **2** and $Ph_2As(CH_2)_2AsPh_2$ as starting materials.

Yield: 53%. Anal. Calc. for $C_{40}H_{40}As_2ClNO_5Pd$: C, 53.0; H, 4.4; N, 1.6. Found: C, 53.1; H, 4.3; N, 1.6%. IR: ν(C=N): 1624m, ν(C=O): 1696m. FAB-Mass: 807 $[M]^+$. ^{1}H NMR: $\delta = 7.04$ (d, H3, $^3J(H4H3) = 8.3$ Hz), 8.00 (s, H6), 8.47 (s, Hi), 9.85 (s, Ha). ^{13}C NMR: $\delta = 24.8$ (s, C10), 25.0 (s, C9, C11), 29.7 (s, CH_2As), 33.7 (s, C8, C12), 63.5 (s, C7), 128.4 (s, C_i), 128.5 (s, C6), 129.6 (s, C4), 130.1 (s, C_m), 132.0 (s, C_p), 133.1 (s, C_o), 138.6 (s, C3), 155.7 (s, C1), 174.3 (s C2), 176.2 (s, C=N), 191.2 (s, COH).

*3.2.15. [Pd{5-(COH)C$_6$H$_3$C(H)=NCy-C2,N}-{Ph$_2$P(CH$_2$)$_3$N(=CMe$_2$)-P,N}][PF$_6$] (**17**)*

Compound **17** was synthesized following a procedure similar to that described for **11**, but using **2** and $Ph_2P(CH_2)_3NH_2$ as starting materials.

Yield: 29%. Anal. Calc. for $C_{32}H_{38}F_6N_2OP_2Pd$: C, 52.1; H, 5.5; N, 3.5. Found: C, 52.5; H, 5.4; N, 3.7FAB-Mass: 604 $[M]^+$, 291 $[(L\text{-}CHO)Pd]^+$. ^{1}H NMR: $\delta = 2.30$, 2.02 (s, Me), 6.44 (m, H3, $^3J(H4H3) = 7.8$ Hz), 7.11 (dd, H4, $^4J(H6H4) = 1.5$ Hz), 8.64 (d, Hi, $^4J(PHi) = 7.3$ Hz), 9.81 (s, Ha). ^{31}P–{^{1}H} NMR: $\delta = 28.61$ (s).

*3.2.16. [Pd{5-(COH)C$_6$H$_3$C(H)=NCy-C2,N}-{Ph$_2$P(CH$_2$)$_3$NH$_2$-P,N}][PF$_6$] (**18**)*

Compound **18** was synthesized following a procedure similar to that described for **11**, but using **2** and $Ph_2P(CH_2)_3NH_2$ as starting materials, and toluene as solvent.

Yield: 56%. Anal. Calc. for $C_{29}H_{34}F_6N_2OP_2Pd$: C, 49.2; H, 4.8; N, 4.0. Found: C, 49.0; H, 4.6; N, 4.1%. IR: ν(C=N): 1618m, ν(C=O): 1697m. FAB-Mass: 563 $[M]^+$, 562 $[M-CHO-Cy]^+$, 291 $[(L\text{-}CHO)Pd]^+$. ^{1}H NMR: $\delta = 6.57$ (dd, H3, $^3J(H4H3) = 7.9$ Hz, $^4J(PH3) = 5.8$ Hz), 8.31 (d, Hi, $^4J(PHi) = 7.6$ Hz), 9.80 (s, Ha). ^{31}P–{^{1}H} NMR: $\delta = 21.77$ (s).

*3.2.17. [Pd{4-(COH)C$_6$H$_3$C(H)=NCy-C2,N}-{Ph$_2$P(CH$_2$)$_2$NH$_2$-P,N}][PF$_6$] (**19**)*

Compound **19** was synthesized following a procedure similar to that described for **11**, but using $Ph_2P(CH_2)_2NH_2$ as starting material, and toluene as solvent.

Yield: 34%. Anal. Calc. for $C_{28}H_{32}F_6N_2OP_2Pd$: C, 48.4; H, 4.6; N, 4.0. Found: C, 48.5; H, 4.1; N, 4.0%. IR: ν(C=N): 1616m, ν(C=O): 1692f. FAB-Mass: 549 $[M]^+$, 520 $[M-CHO]^+$. ^{1}H NMR: $\delta = 6.76$ (d, H3, $^4J(H3H5) = 1.2$ Hz, $^4J(PH3) = 5.4$ Hz), 7.18 (dd, H5, $^3J(H5H6) = 5.1$ Hz,), 8.69 (dd, Hi, $^4J(PHi) = 7.8$ Hz, $^5J(HiH7) = 1.0$ Hz), 9.51 (s, Ha). ^{13}C NMR: $\delta = 25.1$ (s, C9, C11), 25.4 (s, C10), 33.5 (s, C8, C12), 67.3 (s, C7), 126.4 (s, C_i, $^1J(PC_i) = 51.3$ Hz), 128.7 (s, C6) 129.1 (s, C5), 129.6 (d, C_m, $^3J(PC_m) = 11.4$ Hz), 132.6 (d, C_p, $^4J(PC_p) = 2.8$ Hz), 134.1(d, C_o, $^2J(PC_o) = 12.1$ Hz), 136.6 (d, C4, $^4J(PC4) = 4.5$ Hz), 138.4 (d, C3, $^3J(PC3) = 11.1$ Hz), 153.8 (s, C1),156.8 (d, C2, $^2J(PC2) = 2.1$ Hz), 177.6 (d, C=N, $^3J(PC=N) = 6.4$ Hz), 191.5 (s, COH). ^{31}P–{^{1}H} NMR: $\delta = 54.20$ (s).

*3.2.18. [Pd{5-(COH)C$_6$H$_3$C(H)=NCy-C2,N}-{Ph$_2$P(CH$_2$)$_2$NH$_2$-P,N}][PF$_6$] (**20**)*

Compound **20** was synthesized following a procedure similar to that described for **11,** but using **2** and $Ph_2P(CH_2)_2NH_2$ as starting material, and toluene as solvent.

Yield: 19%. Anal. Calc. for $C_{28}H_{32}F_6N_2OP_2Pd$: C, 48.4; H, 4.6; N, 4.0. Found: C, 49.1; H, 4.3; N, 4.0%. IR: ν(C=N): 1621 m, ν(C=O): 1688m. FAB-Mass: 549 $[M]^+$, 520 $[M-CHO]^+$, 291 $[(L\text{-}CHO)Pd]^+$. ^1H NMR: $\delta = 6.79$ (dd, H3, $^3J(H4H3) = 7.8$ Hz, $^4J(PH3) = 5.4$ Hz), 7.20 (dd, H4, $^4J(H6H4) = 1.7$ Hz), 8.28 (d, Hi, $^4J(PHi) = 7.8$ Hz), 9.80 (s, Ha). $^{31}P-\{^1H\}$ NMR: $\delta = 21.77$ (s).

3.2.19. [Pd{4-(COH)C_6H_3C(H)=NCy-C2,N}{2-(Ph_2P)-C_6H_4CHO-P,O}][PF_6] (21)

Compound **21** was synthesized following a procedure similar to that described for **11,** but using $Ph_2P(C_6H_4)CHO$.

Yield: 57%. Anal. Calc. for $C_{33}H_{31}F_6NO_2P_2Pd \cdot (Me_2CO)$: C, 53.1; H, 4.6; N, 1.7. Found: C, 53.4; H, 4.4; N, 1.7%. IR: ν(C=N): 1624 m, ν(C=O): 1645m, 1695m. FAB-Mass: 611 $[M]^+$. ^1H NMR: $\delta = 6.68$ (d, H3, $^4J(PH3) = 5.9$ Hz), 8.27 (dd, Hi, $^4J(PHi) = 8.3$ Hz, $^5J(HiH7) = 1.0$ Hz), 9.32 (s, Ha), 10.15 (d, PCHO, $^4J(PCHO) = 1.5$ Hz). $^{31}P-\{^1H\}$ NMR: $\delta = 34.71$ (s).

3.2.20. [Pd{5-(COH)C_6H_3C(H)=NCy-C2,N}{2-(Ph_2P)C_6H_4CHO-P,O}][PF_6] (22)

Compound **22** was synthesized following a procedure similar to that described for **11,** but using **2** and $Ph_2P(C_6H_4)CHO$, as starting materials.

Yield: 39%. Anal. Calc. for $C_{33}H_{31}F_6NO_2P_2Pd$: C, 52.4; H, 4.1; N, 1.8. Found: C, 52.2; H, 4.3; N, 1.7%. IR: ν(C=N): 1626 m, ν(C=O): 1646m, 1694m. FAB-Mass: 611 $[M]^+$, 582 $[M-CHO]^+$, 291$[(L\text{-}CHO)Pd]^+$. ^1H NMR: $\delta = 6.65$ (m, H3), 7.10 (dd, H4, $^4J(H4H6) = 1.4$ Hz, $^4J(H4H3) = 8.0$ Hz), 7.80 (d, H6), 8.26 (d, Hi, $^4J(PHi) = 8.5$ Hz = 1.0 Hz), 9.82 (s, Ha), 10.20 (d,PCHO, $^4J(PCHO) = 1.5$ Hz). $^{31}P-\{^1H\}$ NMR: $\delta = 34.44$ (s).

3.2.21. X-ray crystallographic study

Three-dimensional, room temperature X-ray data were collected on a Siemens Smart CCD diffractometer by the ω scan method using graphite-monochromated Mo 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.

In compound **21** the PF_6^- ion was found to be disordered over two positions (74% and 26% occupancy). The refinement was carried out taking into account the minor components of the disorder.

Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final $R = 0.0662$, 0.0627, 0.0436 and 0.0386 (for complexes **7**,**11**,**15** and **21**, respectively, observed data, F) and $wR_2 = 0.1404$, 0.1849, 0.1209 and 0.0861 (for complexes **7**,**11**,**15** and **21**, respectively, unique data, F^2), with allowance for thermal anisotropy of all non-hydrogen atoms. The structure solution and refinement were carried out using the program package SHELX-97 [62].

4. Supplementary material

CCDC 634450, 634447, 634448 and 634449 contain the supplementary crystallographic data for **7**, **11**, **15** and **21**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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