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Functionalized cyclopalladated compounds with bidentate Group 15 donor atom ligands: the crystal and molecular structures of [{Pd[5-(COH)C_6H_3C(H)=NCy-*C*2,*N*](Cl)}$_2$(μ-Ph_2PRPPh_2)] (R = CH_2CH_2, Fe(C_5H_4)$_2$], [Pd{5-(COH)C_6H_3C(H)=NCy-*C*2,*N*}($Ph_2PCH_2PPh_2$-*P*,*P*)][PF_6] and [Pd{5-(COH)C_6H_3C(H)=N(Cy)-*C*2,*N*}($Ph_2PCH_2CH_2AsPh_2$-*P*,*As*)][PF_6]

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Abstract

The chloro-bridged dinuclear compound [{Pd[5-(COH)C_6H_3C(H)=N(Cy)-*C*2,*N*]}(μ-Cl)]$_2$ (**1**), reacts with tertiary diphosphines in 1:1 molar ratio to give [{Pd[5-(COH)C_6H_3C(H)=NCy-*C*2,*N*](Cl)}$_2$(μ-Ph_2PRPPh_2)] (R: CH_2, **2**; CH_2CH_2, **3**; $(CH_2)_4$, **4**; $(CH_2)_6$, **5**; Fe(C_5H_4)$_2$, **6**; *trans*-CH=CH, **7**; C≡C, **8**). Treatment of **1** with $Ph_2PCH_2CH_2AsPh_2$ (arphos) gives the dinuclear complex [{Pd[5-(COH)C_6H_3C(H)=N(Cy)-*C*2,*N*](Cl)}$_2$(μ-$Ph_2PCH_2CH_2AsPh_2$)] (**9**). The reaction of **1** with tertiary diphosphines or arphos in 1:2 molar ratio in the presence of NH_4PF_6 yields the mononuclear compounds [Pd{5-(COH)C_6H_3C(H)=NCy-*C*2,*N*}(Ph_2PRPPh_2-*P*,*P*)][PF_6] (R: $(CH_2)_4$, **10**; $(CH_2)_6$, **11**; Fe(C_5H_4)$_2$, **12**; 1,2-C_6H_4, **13**; *cis*-CH=CH, **14**; NH, **15**) and [Pd{5-(COH)C_6H_3C(H)=N(Cy)-*C*2,*N*}($Ph_2PCH_2CH_2AsPh_2$-*P*,*As*)][PF_6] (**16**). ^{1}H-, ^{31}P-{^{1}H}- and ^{13}C-{^{1}H}-NMR, IR and mass spectroscopic data are given. The crystal structures of compounds **3**, **6**, **9** and **16** have been determined by X-ray crystallography.

Keywords: Palladium; Metallation; Phosphines; As ligands; X-ray diffraction

1. Introduction

The synthesis of cyclometallated compounds [1,2] is an ever expanding area of chemical research and numerous articles and reviews have recorded their ongoing developments as well as their applications over the years, such as the use as active catalysts [3,4], as intermediates in the synthesis of new organometallic and organic compounds [5–7] in the resolution of racemic mixtures into the corresponding pure optically active components [8,9], in the design of complexes with promising photochemical and electrochemical properties [10,11] and specific antitumor activity toward various forms of cancer [12,13].

Our interest in cyclometallated systems has been related, in the majority of cases, with palladium(II) compounds which involved the coordination of one metal atom per organic ligand, i.e. derivatives of differently substituted [*C*,*N*] Schiff bases [14–16], ferrocenylimines [17] or substituted imidazoles [18], as well as derivatives of [*C*,*N*,*X*] (X = N, O, S) terdentate ligands [19–21]. Furthermore, we have also reported compounds with two metal atoms bonded to the same organic moiety derived from diamines [22] or dialdehydes [23,24].

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In the former case the reaction conditions influence the cyclometallation process, and we have found that potentially tetradentate Schiff bases derived from 1,4-$(COH)_2C_6H_4$ (terephthalaldehyde) and 1,3-$(COH)_2$-C_6H_4 (isophthaladehyde) give rise to different products. Thus, reaction of 1,4-$(CyN{=}CH)_2C_6H_4$ with palladium(II) acetate in glacial acetic acid afforded the monocyclometallated compound I (as depicted in Fig. 1) in which the acidic nature of the solvent caused hydrolysis of one of the C=N double bonds and palladium coordination stabilizes the second imine group [25]. The dicyclometallated compound II can only be achieved via oxidative addition reaction of $[Pd_2(dba)_3]$ with the dichloro derivative 1,4-$(CyN{=}CH)_2$-2,5-Cl_2-C_6H_2 in benzene [26]. Nevertheless treatment of 1,3-$(CyN{=}CH)_2C_6H_4$ with $Pd(OAc)_2$ in AcOH gives a mixture of the mono- and the dicyclometallated compounds III and IV, respectively, the formation of the former suggests that the *meta* disposition of the imine groups and ulterior coordination of the C=N group to the palladium atom impedes hydrolysis [27]. Mono- (V, VII) and dicyclomanganated (VI, VIII) compounds (see Fig. 1) derived from terephthalaldehyde and isophthaladehyde could also be achieved by the reaction of the Schiff base ligands with $[MeMn(CO)_5]$ in *n*-octane depending on the molar ratio [25,27]. The existence of a free formyl group in the monocyclometallated compounds represents a novel an interesting functionalization of these complexes.

A large number metal complexes containing one or more phosphorus donor atoms have been reported due to the versatility of their electronic and steric properties as well as their numerous applications [28–32]. Nevertheless, the corresponding derivatives of functionalized and/or heterobidentate ligands containing phosphorus atoms are scarce, probably due to their complicated synthetic procedures. The past years have seen a growing interest in reactions that include these type of ligands and complexes, which have proved to be active catalysts in numerous processes [33–36]. In the present paper we describe the synthesis and characterization of new cyclopalladated compounds derived from compound III with homo- *P*,*P*, and heterobidentate, *P*,*As*, ligands.

2. Results and discussion

For the convenience of the reader the compounds and reactions are shown in Scheme 1. The compounds described in this paper were characterized by elemental analysis (C, H, N), mass spectrometry, by IR, ^{1}H-, ^{31}P-$\{^1H\}$ and (in part) ^{13}C-$\{^1H\}$-NMR spectroscopy data in Section 4.

Reaction of $[Pd\{5\text{-}(COH)C_6H_3C(H){=}N(Cy)\text{-}C2,N\}\text{-}(\mu\text{-}Cl)]_2$ (**1**) [27] with bis(diphenylphosphine)methane (dppm), in a 1:1 molar ratio, in acetone at room temperature afforded the dinuclear complex $[\{Pd[5\text{-}(COH)C_6H_3C(H){=}NCy\text{-}C2,N](Cl)\}_2(\mu\text{-}Ph_2PCH_2PPh_2)]$ (**2**). The IR spectrum showed the shift of the C=N stretch towards lower wavenumbers, as compared with the free Schiff base ligand (1630 vs. 1623 cm^{-1}), indicating N-coordination of the C=N group [37]. A ν(C=O) band at 1693 cm^{-1} was assigned to the free

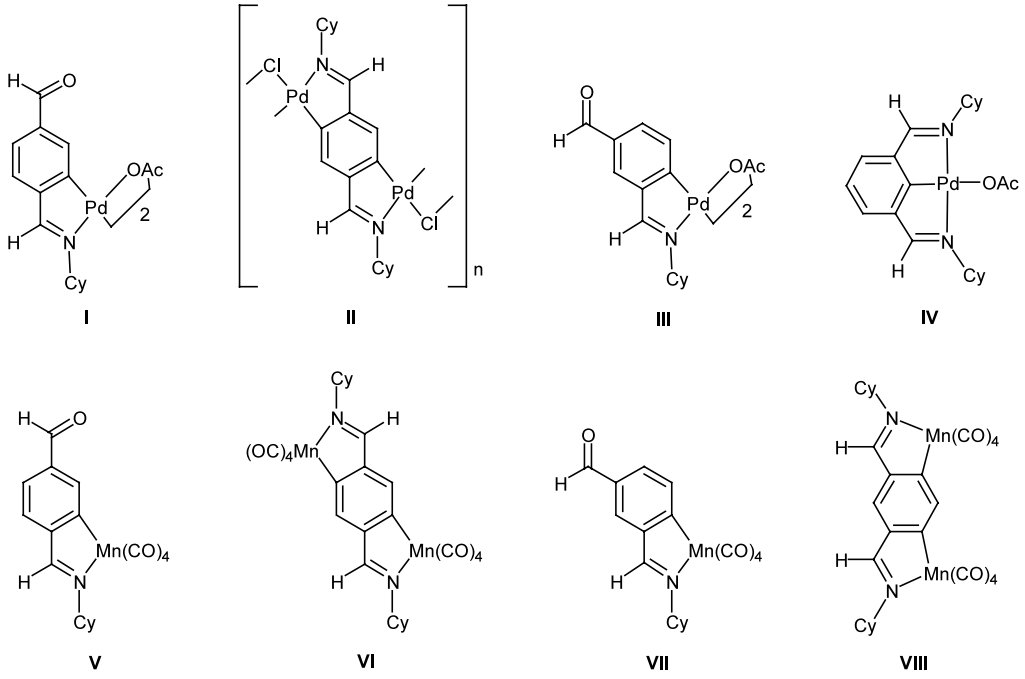
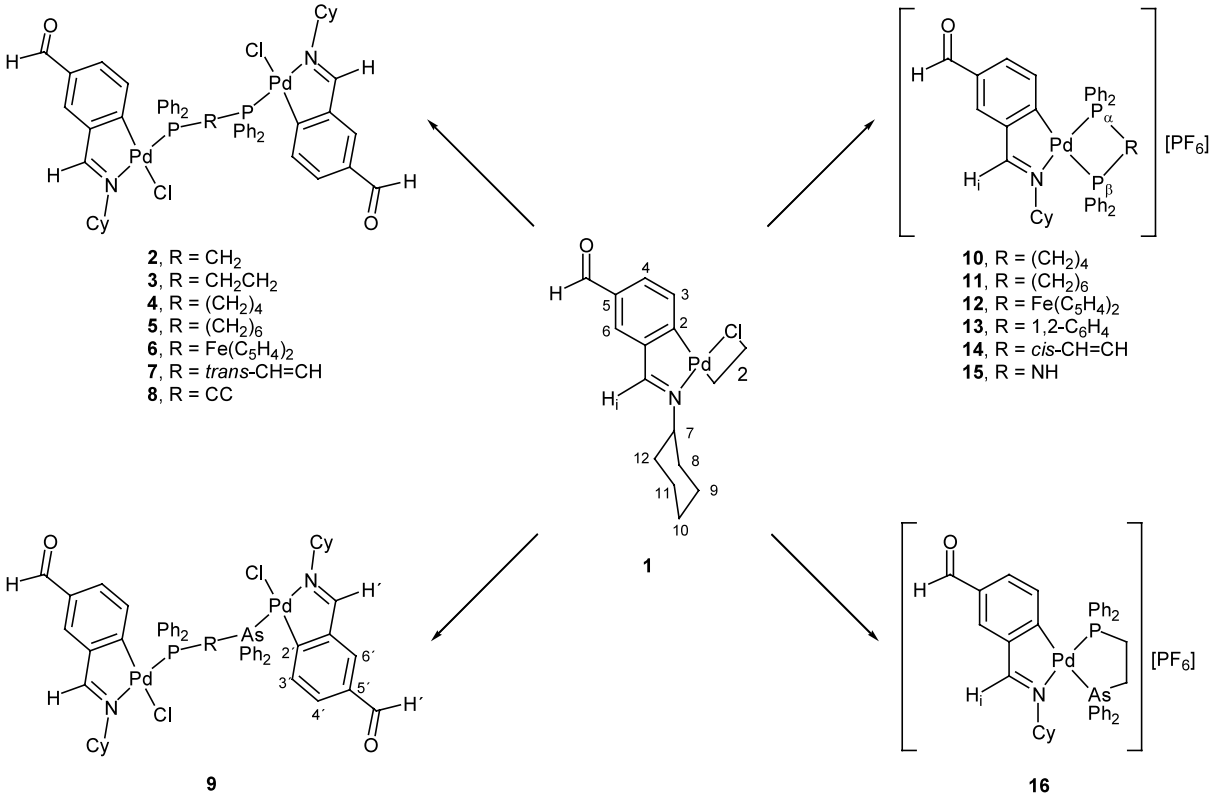


Fig. 1.



Scheme 1.

formyl group [38]. The MS-FAB spectrum showed peaks at m/z 1061, 704 and 676, assigned to $[M-Cl]^+$, $[LPd(PP)]^+$ and $[LPdCl]^+$, respectively, which were characteristic clusters of isotopic peaks covering ca. 10 m/z units, due to the presence of the numerous palladium isotopes [39,40], thereby confirming the dinuclear nature of this complex. The $^{31}P-\{^1H\}$-NMR spectrum showed a singlet at δ 30.45, shifted to higher frequency from the spectrum of the free phosphine, in agreement with phosphorus coordination to metal center [41] and indicated that the two phosphorus nuclei were equivalent, with the diphosphine acting as a bridging ligand.

In the ^{1}H-NMR spectrum a singlet at δ 9.73 was assigend to the HC=O resonance. The HCN resonance at δ 8.07 appeared as a doublet of doublets due to coupling with the ^{31}P nucleus [^4J(PHi) = 7.8 Hz] and with the α proton of the cyclohexyl ring [^5J(HiH7) = 1.0 Hz]. The signals corresponding to the metallated phenyl ring protons were clearly distinguished. Thus, a doublet at δ 7.64 and a doublet of doublets at δ 6.94 were assigned to H6 and H4, respectively [^4J(H4H6) = 1.5 Hz, ^3J(H3H4) = 8.1 Hz]. A doublet of doublets at δ 6.25 was assigned to H3, coupled to the phosphorus atom [^4J(PH3) = 5.8 Hz]. The former two resonances were shifted to lower field from the starting product ca. 0.5 and 1.3 ppm, respectively, due to the shielding effect of the phosphine phenyl rings. These data are in accordance with a P *trans* to N arrangement, typical of these reactions and within the terms of the 'transphobic effect' coined by Vicente et al. [42]. The reaction of **1** with the short-bite diphosphine bis(diphenyphosphino)amine, (dppa), under similar reaction conditions did not give the analogous dinuclear compound, and yielded a mixture of the starting complex and the chloride salt of compound **15** (vide infra), indicating a low tendency of this diphosphine to coordinate in a bridging mode. Other diphosphines such as *cis*-bis(diphenylphosphine) ethene (*cis*-dppe) and 1,2-bis(diphenylphosphino)benzene (1,2-dppb) failed to give dinuclear compounds, due to the *cis*-geometry of these ligands.

Treatment of **1** with 1,2-bis(diphenylphosphine)-ethane (dppe), 1,4-bis(diphenylphosphine)butane (dppb), 1,6-bis(diphenylphosphine)hexane (dpph) and 1,1′-bis(diphenylphosphine)ferrocene (dppf), long-bite diphosphines, gave the dinuclear complexes **3**–**5** and the trimetallic complex **6**, respectively, [{Pd[5-(COH)-C_6H_3C(H)=NCy-*C*2,*N*](Cl)}$_2$(μ-Ph_2PRPPh_2)] (R: CH_2, **2**; CH_2CH_2, **3**; $(CH_2)_4$, **4**; $(CH_2)_6$, **5**; $Fe(C_5H_4)_2$, **6**), which were fully characterized (see Section 4). The X-ray crystal structure determination of compounds **3** and **6** (see below) confirmed the spectroscopic data.

Reaction of **1** with *trans*-bis(diphenylphosphine)ethene (*trans*-dppe) and bis(diphenylphosphine)acetylene (dppac) afforded the dinuclear complexes [{Pd[5-(COH)C_6H_3C(H)=NCy-*C*2,*N*](Cl)}$_2$(μ-Ph_2PRPPh_2)]

(*trans*-CH=CH, **7**; C≡C, **8**), irrespective of the molar ratio used, probably due to the *trans*-geometry of these ligands. The compounds gave satisfactory elemental analysis, as well as IR, FAB-Mass and NMR spectra (see Section 4). The ^{13}C-{^{1}H}-NMR spectrum of compound **7** showed a broad signal at δ170.5 and a multiplet at δ149.8 assignable to HC=N and C2, respectively, downfield shifted from the spectrum of the free ligand (ca. 22 and 20 ppm, also respectively) [27], thereby confirming that cyclometallation was maintained [25,43]. The C3 and C4 resonances appeared as multiplet at δ138.0 and δ131.0, respectively, by coupling with the phosphorus nucleus. An apparent triplet at δ126.8 was assigned to the H*C*=*C*H carbon atoms. In the ^{1}H-NMR, the AA′XX′ spin sustem of the PC*H*=C*H*P group gave rise to an apparent triplet at δ6.80 [$N = 43.0$ Hz].

Reaction of [Pd{5-(COH)C$_6$H$_3$C(H)=N(Cy)-*C*2,*N*}-(μ-Cl)]$_2$ (**1**) with $Ph_2PCH_2CH_2AsPh_2$ (arphos) in 1:1 molar ratio, in acetone at room temperature afforded the dinuclear complex [{Pd[5-(COH)C$_6$H$_3$C(H)=N(Cy)-*C*2,*N*](Cl)}$_2$(μ-$Ph_2PCH_2CH_2AsPh_2$)] (**9**), which was fully characterized (see Section 4). A singlet at δ38.85 in the ^{31}P-{^{1}H}-NMR spectrum confirmed phosphorus coordination to metal center. In the ^{1}H-NMR spectrum the COH and COH′ groups gave rise to two singlets at δ9.74 and δ9.73 which could not be unambiguously assigned, as well as the H4/H4′ resonances, which appeared as two doublets of doublets ca. δ7.00. Nevertheless, the corresponding Hi/Hi′ and H3/H3′ resonances were clearly distinguished. Thus, two doublets of doublets at δ8.21 and δ6.60 were assigned to Hi and H3, respectively, and two doublets at δ8.16 and δ6.66 were assigned to Hi′and H3′, also respectively; the former two resonances were coupled to the phosphorus nucleus.

In the ^{13}C-{^{1}H}-NMR spectrum of compound **9** some resonances were well differentiated for each cyclometallated fragment and for the arphos phenyl rings (see Section 4). Thus, a singlet and a broad signal at δ170.5 and δ170.3 were assigned to C′=N and C=N carbons, respectively; two singlets at δ138.1 and δ135.4 to the C3′ and C4′, respectively; and two doublets at δ137.8 (^{3}J(PC) = 10.6 Hz) and δ135.2 (^{4}J(PC) = 3.6 Hz) to the C3 and C4 resonances, also respectively. The ethylene resonances appeared at δ30.5 [d, ^{1}J(PC) = 5.4 Hz, P*C*H$_2$] and δ24.7 [s, *C*H$_2$As]. These findings were confirmed by the X-ray crystal structure determination of compound **9** (see below).

Treatment of the chloride-bridged complex **1** with dppb, dpph, dppf, *cis*-dppe, 1,2-dppb, and dppa in 1:2 molar ratio in the presence of NH_4PF_6 yielded the cyclometallated compounds [Pd{5-(COH)C$_6$H$_3$C(H)=NCy-*C*2,*N*}(Ph_2PRPPh_2-*P*,*P*)][PF_6] (R: $(CH_2)_4$, **10**; $(CH_2)_6$, **11**; Fe(C_5H_4)$_2$, **12**; 1,2-C_6H_4, **13**; *cis*-CH=CH, **14**; NH, **15**). In the case of compound **14**, previous treatment of **1** with silver trifluorosulfonate was needed to obtain the desired product (see Section 4). The new compounds were air-stable and soluble in the more common solvents. 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 [44]. The IR spectrum showed a broad and strong band at 850 cm^{-1} arising from the PF_6^- counterion [38]. The MS-FAB spectra showed the corresponding peaks assigned to [M]$^+$, [M−COH]$^+$ and/or [M−Cy]$^+$, after consideration of the palladium isotopes. The ^{31}P-{^{1}H}-NMR spectra showed two doublets, suggesting the two phosphorus atoms to be non-equivalent (P_α, P_β), as well as an heptuplet ca. −146 ppm assignable to PF_6^- [^{1}J(PF) ca. 712 Hz]. 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 [41], and was confirmed by selective decoupling experiments. The ^{31}P chemical shifts were clearly influenced by ring size [45], and consequently were shifted downfield.

The HC=N resonance in the ^{1}H-NMR spectra ca. δ8.50 appeared as a doublet due to coupling with the ^{31}P nucleus *trans* to nitrogen. The H6 resonance was overlapped by the phosphine phenyl protons or appeared as a broad signal, but in compound **13** it could be clearly distinguished as a triplet at δ7.99 by coupling to H4 and long-range coupling to the phosphorus nucleus *trans* to the metallated carbon atom [^{4}J(H4H6) ≈ ^{5}J(PH6) ≈ 2.0 Hz]. A multiplet ca. δ7.00 was assigned to the H3 resonance, shifted to lower frequency by 0.4–0.9 ppm due to the shielding effect of the phosphine phenyl rings. This signal was split by coupling to both phosphorus atoms. In the case of compound **12**, selective decoupling experiments allowed the correct assignment of the corresponding coupling constants [*trans*-^{4}J(PH3) = 7.3, *cis*-^{4}J(PH3) = 4.9 Hz].

For complexes **12** and **14** the ^{13}C-{^{1}H} data were consistent with the proposed structure (see Section 4). Two doublets of doublets at δ185.5 (**12**) and δ178.4 (**14**) were assigned to the C=N carbon atom, coupled to both phosphorus atoms [$^{3}J(P_\alpha C) = 7.8$ Hz, $^{3}J(P_\beta C)$ ca. 4.0 Hz). The C2 resonance was downfield shifted from the spectrum of the free ligand by ca. 45 ppm, and showed strong coupling to the phosphorus atom *trans* to carbon ($^{3}J(P_\beta C)$ ca. 120 Hz). The diphosphine carbon atoms showed well defined resonances and most of them could be unambiguously assigned (see Section 4).

Treatment of complex **1** with $Ph_2PCH_2CH_2AsPh_2$ and NH_4PF_6 in a 1:2 molar ratio in acetone–water at room temperature yielded the mononuclear compound [Pd{5-(COH)C$_6$H$_3$C(H)=N(Cy)-*C2*,*N*}($Ph_2PCH_2CH_2$-$AsPh_2$-*P*,*As*)][PF_6] (**16**). The MS-FAB spectrum showed the corresponding peaks at *m*/*z* 762, 735 and 679 assigned to [M]$^+$, [M−COH]$^+$ and [M−Cy]$^+$, respectively. The NMR data were consistent with the pro-

posed structure. The $^{31}P-\{^{1}H\}$-NMR spectrum showed a singlet at δ 61.44, downfield shifted due to the ring size effect in five-membered chelates. In the ^{1}H-NMR spectra a doublet of doublets at δ 6.89 was assigned to the H3 resonance, split by coupling to the ^{31}P nucleus *trans* to nitrogen [$^{4}J(PH3) = 7.8$ Hz], as appeared in related systems with monophosphine ligands linked to a palladium atom, [46,47] and upfield shifted due to the shielding effect of the phenyl rings linked to the phosphorus atom. The crystal structure of **16** has been determined by X-ray diffraction analysis (see below) and confirms the spectroscopic data.

2.1. Molecular structures of complexes 3, 6, 9 and 16

Suitable crystals were grown by slowly evaporating chloroform–*n*-hexane (**3**, **16**) or dichloromethane–*n*-hexane (**6**, **9**) solutions of the complexes. The labeling schemes for the compounds are shown in Figs. 2–5. 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 compounds **3** and **9**, the crystal structure comprises a centrosymmetric dinuclear molecule (half molecule per asymmetric unit). In the case of complex **9**, even though the bridging ligand, 1-diphenylphosphino-2-diphenylarsinoethane, is asymmetric, the dinuclear molecule is crystallographically centrosymmetric; this is caused by the disordered distribution of the P and As atoms (population parameter 50%) and by the quasi centrosymmetric nature of the compound, which gives similar environments for both P and As. This behavior has been observed in other complexes derived from the arsinophosphine ligand [48,49]. The crystal structures of **6** and **16** comprise one molecule per asymmetric unit. In the case of complex **16**, the bridging ligand 1,1′-bis(diphenylphosphino)ferrocene is not totally symmetric, though both cyclometallated moieties have

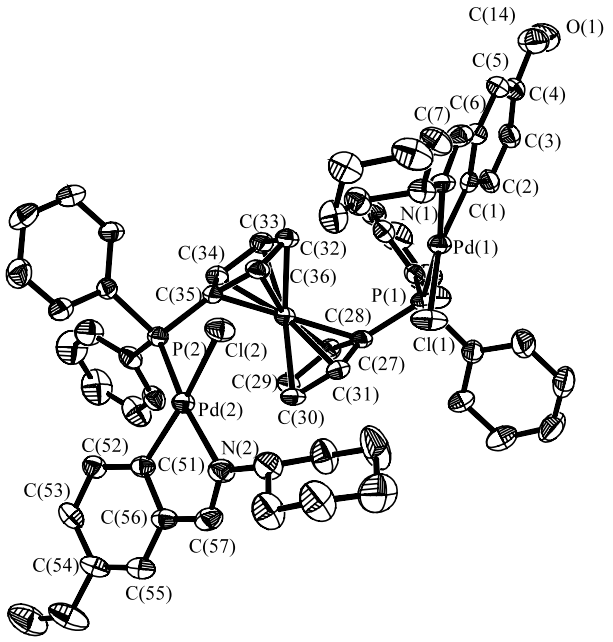


Fig. 3. Molecular structure of [{Pd[5-(COH)C_6H_3C(H)=NCy-*C*2,*N*](Cl)}$_2${μ-($Ph_2PC_5H_4$)$_2$Fe}] (**6**), with labelling scheme. Hydrogen atoms have been omitted for clarity.

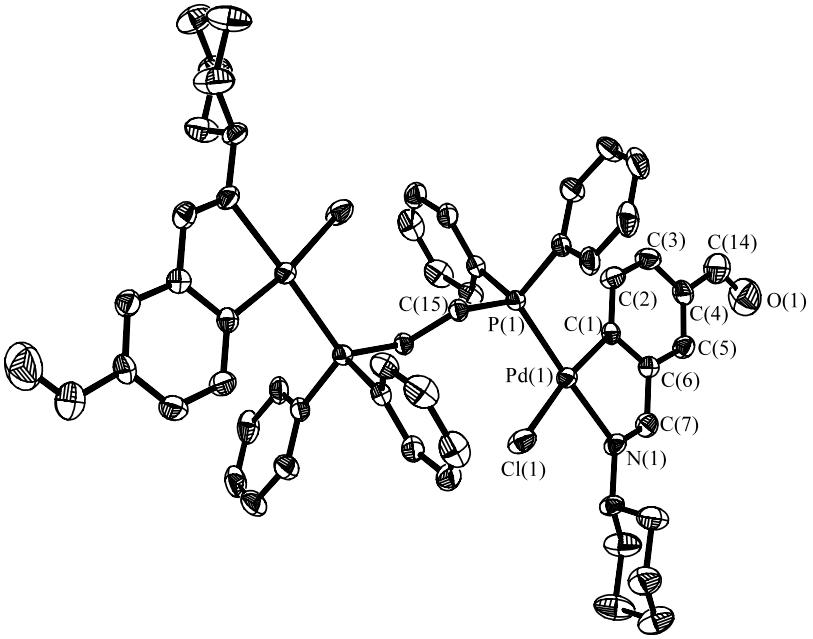


Fig. 2. Molecular structure of [{Pd[5-(COH)C_6H_3C(H)=NCy-*C*2,*N*](Cl)}$_2$(μ-$Ph_2PCH_2CH_2PPh_2$)] (**3**), with labelling scheme. Hydrogen atoms have been omitted for clarity.

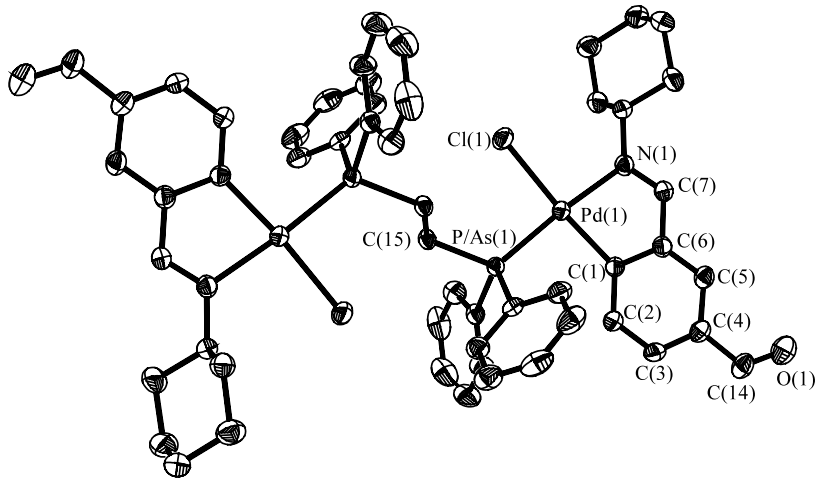


Fig. 4. Molecular structure of [{Pd[5-(COH)C_6H_3C(H)=NCy-*C*2,*N*](Cl)}$_2$(μ-$Ph_2PCH_2CH_2AsPh_2$)] (**9**), with labelling scheme. Hydrogen atoms have been omitted for clarity.

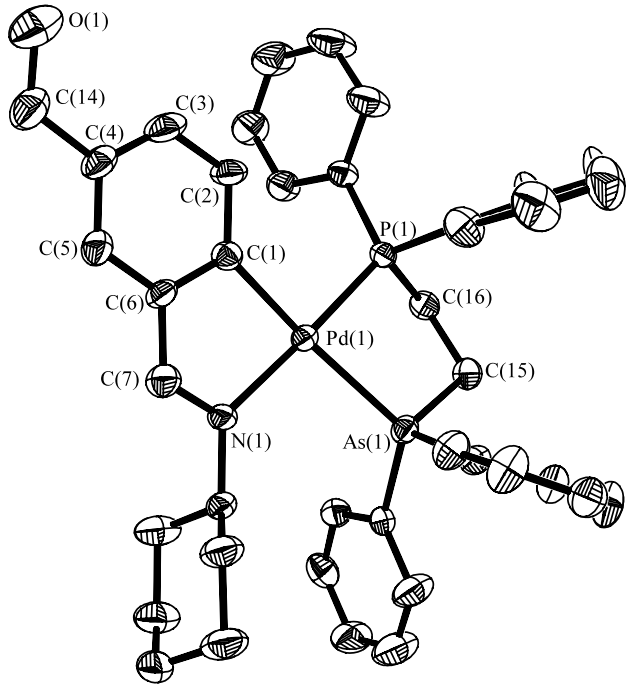


Fig. 5. Molecular structure of the cation for [Pd{5-(COH)C_6H_3C(H)=NCy-*C*2,*N*}($Ph_2PCH_2CH_2AsPh_2$-*P*,*As*)][PF_6] (**16**), with labelling scheme. Hydrogen atoms have been omitted for clarity.

very similar bond distances and angles; therefore, discussion will be limited to only one of them.

In compounds **3**, **6** and **9** each four-coordinated palladium(II) is bonded to an adjacent *ortho*-carbon atom and to the nitrogen atom of the imine group of the deprotonated Schiff base ligand and to a chlorine atom (*trans* to C2). The diphosphine (dppe, **3**; dppf, **6**) or the arsinophosphine ligand (**9**) which bridges the two metal centers, completes the metal coordination sphere. In compound **16** the palladium(II) atom is bonded to four different atoms: an *ortho* carbon of the phenyl ring and a nitrogen atom of the benzylidene ligand, and phosphorus and arsenic atoms of the chelating arsinophosphine ligand.

The sum of angles about palladium is 359.08° (**3**), 362.54° (**6**), 360.14° (**9**) and 360.50° (**16**); with the distortions most noticeable in the somewhat reduced 'bite' angles of the cyclometallated moiety consequent upon chelation. The requirements of the five-membered ring forces the bond angle N(1)–Pd(1)–C(1) to 81.1(2)° (**3**), 81.3(3)° (**6**), 80.6(2)° (**9**) and 81.3(2)° (**16**). In the case of compounds **3**, **9** and **16**, the geometry around the palladium atom is slightly distorted square-planar, the mean deviations from the least squares planes (plane 1: Pd1, C1, N1, P1, Cl1, **3**; Pd1, C1, N1, P1/As1, Cl1, **9**; Pd1, C1, N1, P1, As1, **16**) are 0.0330, 0.0381 and 0.1018 A, respectively. However, for compound **6**, coordination about palladium is slightly twisted toward tetrahedral (rms deviation of the mean plane 1:0.1920 Å), C1 and Cl1 are above the plane (deviations 0.2157 and 0.2644 Å, respectively), and N1 and P1 are below the plane (deviations 0.2463 and 0.1969 Å, also respectively).

The palladium–nitrogen bond length in the metallacycle (2.122(5) Å, **3**; 2.094(6) Å, **6**; 2.110(5) Å, **9**; 2.091(5) Å, **16**) is 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 [50,51], and reflects the *trans* influence of the phosphorus–arsenic atom [22,52,53]. The palladium–carbon bond length (2.020(6) Å, **3**; 2.021(8) Å, **6**; 2.015(6) Å, **9**; 2.060(6) Å, **16**) is within the expected value of 2.081 Å (based on the sum of covalent radii for carbon(sp^2) and palladium, 0.771 and 1.31 Å, respectively) [18,54,55].

The Pd–P and Pd–As bond distances (2.263(1) Å, **3**; 2.258(2) Å, **6**; 2.312(1) Å, **9**; 2.2598(16) and 2.4540(8) Å, **16**) are shorter than the sum of the single bond radii for palladium and the corresponding atom (2.41 Å for Pd–

Table 1
Crystal and structure refinement data for complexes **3**, **6**, **9** and **16**

	3	**6**·2CH_2Cl_2	**9**	**16**·H_2O
Formula	$C_{54}H_{56}Cl_2N_2O_2Pd_2P_2$	$C_{64}H_{62}Cl_8FeN_2O_2Pd_2P_2$	$C_{54}H_{56}AsCl_2N_2O_2Pd_2P$	$C_{40}H_{42}AsF_6NO_2PdP$
M_r	1110.65	1505.35	1154.60	926.01
Temperature (K)	293(2)	293(2)	293(2)	0(2)
Wavelenght (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Cell dimensions				
a (Å)	10.071(2)	12.4733(19)	10.130(5)	12.6211(13)
b (Å)	11.520(1)	16.020(2)	11.539(8)	14.0036(14)
c (Å)	11.532(1)	17.750(3)	11.568(1)	14.1417(14)
α (°)	89.128(10)	111.141(3)	88.857(10)	97.830(2)
β (°)	81.108(2)	105.159(3)	81.805(10)	116.288(2)
γ (°)	65.788(10)	92.585(3)	65.863(10)	105.001(2)
V (Å^3)	1203.90(14)	3190.1(8)	1220.26(15)	2071.7(4)
Z	1	2	1	2
$D_{calc.}$ (mg m^{-3})	1.532	1.567	1.571	1.484
μ (mm^{-1})	0.968	1.212	1.595	1.379
Crystal size (mm)	0.15 × 0.25 × 0.15	0.20 × 0.18 × 0.13	0.25 × 0.15 × 0.15	0.29 × 0.23 × 0.13
$2\theta_{max}$ (°)	56.62	52.82	56.64	56.60
Independent reflections	5853 (R_{int} = 0.0612)	13022 (R_{int} = 0.0000)	5546 (R_{int} = 0.0399)	10054 (R_{int} = 0.0484)
S	1.005	0.924	1.058	0.945
$R[F,I > 2\sigma(I)]$	0.0617	0.0593	0.0490	0.0545
wR [F^2, all data]	0.1766	0.1847	0.2049	0.1727
max ρ (e Å^{-3})	0.741	1.059	1.015	1.645

Table 2
Selected bond distances (Å) and angles (°) for complexes **3**, **6**, **9** and **16**

	3	**6**	**9**	**16**
Bond distances				
Pd(1)–C(1)	2.020(6)	2.021(8)	2.015(6)	2.060(6)
Pd(l)–N(1)	2.122(5)	2.094(6)	2.110(5)	2.091(5)
Pd(1)–P(1)	2.263(1)	2.258(2)	2.312(1)	2.2598(16)
Pd(1)–Cl(1)	2.367(1)	2.386(2)	2.375(2)	
Pd(1)–As(1)				2.4540(8)
C(1)–C(6)	1.401(9)	1.414(10)	1.418(9)	1.402(9)
C(6)–C(7)	1.432(10)	1.435(11)	1.454(9)	1.436(9)
N(1)–C(7)	1.268(8)	1.275(9)	1.255(8)	1.273(8)
O(1)–C(14)	1.267(11)	1.216(11)	1.210(10)	1.290(14)
P(1)–C(15)	1.853(6)		1.894(5)	
P(1)–C(27)		1.806(7)		
As(1)–C(15)				1.953(6)
P(1)–C(16)				1.826(6)
Bond angles				
C(1)–Pd(1)–N(1)	81.1(2)	81.3(3)	80.6(2)	81.3(2)
C(1)–Pd(1)–P(1)	94.86(19)	99.0(2)	95.32(17)	97.34(18)
P(1)–Pd(1)–Cl(1)	91.73(6)	89.50(8)	90.40(5)	
N(1)–Pd(1)–Cl(1)	92.39(15)	92.74(17)	93.82(15)	
N(1)–Pd(1)–As(1)				99.50(13)
P(1)–Pd(1)–As(1)				82.36(5)
C(7)–N(1)–Pd(1)	110.4(5)	112.7(5)	113.5(4)	111.6(4)
N(1)–C(7)–C(6)	121.2(6)	118.4(7)	118.5(6)	120.7(6)
C(1)–C(6)–C(7)	115.1(6)	116.7(7)	115.5(5)	116.0(5)
C(6)–C(1)–Pd(1)	111.9(5)	110.7(6)	112.0(4)	110.4(4)
C(15)–P(1)–Pd(1)	118.7(2)		120.20(18)	
C(27)–P(1)–Pd(1)		116.9(2)		
C(16)–P(1)–Pd(1)				107.7(2)
C(15)–As(1)–Pd(1)				106.36(19)

P, 2.55 Å for Pd–As), suggesting partial double bond character similar to others reported earlier [56,57]. In compounds **3**, **6** and **9**, the Pd–Cl bond lengths, ca. 2.37 Å, are consistent with Pd–Cl distances found in related species [57,58] but longer than the sum of the covalent radii (2.30 Å) 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 0.0169 and 0.0031 Å (**3**); 0.0114 and 0.0173 Å (**6**); 0.0082 and 0.0057 Å (**9**); 0.0032 and 0.0064 Å (**16**), respectively. The angles between these planes are as follows: 2.8, 4.8, 1.3 and 1.4°, also respectively. The angles between plane 1 and the previous planes are: plane 1/plane 2: 2.9° (**3**), 1.5° (**6**), 2.5° (**9**) and 5.9° (**16**); and plane 1/plane 3: 5.3° (**3**), 6.3° (**6**), 3.6° (**9**) and 7.2° (**16**).

3. Conclusion

New cyclopalladated compounds, functionalized through a free formyl group have been synthesized. The mono-, di- or trimetallic nature of these compounds depends on the chloro-bridged dimer–phosphine ligand molar ratio used, as well as on the characteristics of the phosphines. The reactions carried out with diohosphines in a 1:1 molar ratio give compounds with the diphosphine acting as a bridging ligand. In the case of the

arphos ligand, the resulting asymmetry in the final compound makes both metallated units non-equivalent. However, in the X-ray difraction analysis the P and As atoms are not distinguishable due to a disordered distribution of both atoms. The reactions performed in a 1:2 molar ratio gave compounds with the diphosphine acting as a chelating ligand. In the corresponding mononuclear compound with arphos, the X-ray difraction analysis discerns the P and As atoms, which are now in different chemical surroundings.

4. Experimental

4.1. General remarks

All solvents were distilled prior to use from appropriate drying agents [59]. All chemicals were used as supplied from commercial sources. Elemental analyzes (C, H, N) were carried out in a Carlo–Erba 1108 elemental analyzer. 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 (298K). The synthesis of [Pd{5-(COH)C_6H_3C(H)=NCy-*C2,N*}(μ-Cl)]$_2$ (**1**) was reported in a recent paper from this laboratory [27].

4.1.1. Preparation of [{Pd[5-(COH)C_6H_3C(H)=NCy-*C2,N*](Cl)}$_2$(μ-$Ph_2PCH_2PPh_2$)] (*2*)

To a solution of **1** (25.00 mg, 0.035 mmol) in acetone (ca. 10 ml), $Ph_2PCH_2PPh_2$ (dppm, 12.13 mg, 0.032 mmol) was added. The mixture was stirred for 12 h at r.t., after which the precipitate formed was filtered off, dried in vacuo, and recrystallized from chloroform–*n*-hexane to yield the desired product as pale yellow microcrystals.Yield: 36% (26.45 mg). Anal. Found: C, 58.2; H, 5.0; N, 2.4. $C_{53}H_{54}Cl_2N_2O_2P_2Pd_2$ requires: C, 58.0; H, 5.0; N, 2.5%. IR: ν(C=O): 1693s, ν(C=N): 1623m. FAB-Mass: 1061 $[M-Cl]^+$, 704 $[LPd(PP)]^+$, 676 $[LPdCl]^+$. ^{1}H-NMR: 9.73 (s, Ha), 8.07 (dd, Hi, ^4J(PHi) = 7.8 Hz, ^5J(HiH7) = 1.0 Hz), 7.64 (d, H6, ^4J(H4H6) = 1.5 Hz), 6.94 (dd, H4, ^3J(H3H4) = 8.1 Hz), 6.25 (dd, H3, ^4J(PH3) = 5.8 Hz). ^{31}P-{^{1}H}-NMR: 30.45 (s).

Compounds **3**–**6** were prepared similarly, but using dppe, dppb, dpph and dppf as appropriate, respectively.

4.1.2. [{Pd[5-(COH)C_6H_3C(H)=NCy-*C2,N*](Cl)}$_2$(μ-$Ph_2PCH_2CH_2PPh_2$)] (*3*)

Yield: 72%. Anal. Found: C, 58.2; H, 5.0; N, 2.3. $C_{54}H_{56}Cl_2N_2O_2P_2Pd_2$ requires: C, 58.4; H, 5.1; N, 2.5. IR: ν(C=O): 1689s, ν(C=N): 1621m. FAB-Mass: 826 $[M-2Cl-L]^+$, 718 $[LPd(PP)]^+$, 690 $[(L-COH)Pd(PP)]^+$. ^{1}H-NMR: 9.74 (s, Ha), 7.69 (d, H6, ^4J(H4H6) = 1.5 Hz), 6.99 (dd, H4, ^3J(H3H4) = 7.8 Hz), 4.51(t, CH_2P, ^2J(PH) = 10.5 Hz). ^{31}P-{^{1}H}-NMR: 38.00 (s).

4.1.3. [{Pd[5-(COH)C_6H_3C(H)=NCy-*C2,N*](Cl)}$_2${μ-$Ph_2P(CH_2)_4PPh_2$}] (*4*)

Yield: 58%. Anal. Found: C, 59.7; H, 5.5; N, 2.3. $C_{56}H_{60}Cl_2N_2O_2P_2Pd_2$ requires: C, 59.1; H, 5.3; N, 2.5%. IR: ν(C=O): 1692s, ν(C=N): 1624m. FAB-Mass: 1103 $[M-Cl]^+$, 853 $[M-2Cl-L]^+$, 746 $[LPd(PP)]^+$. ^{1}H-NMR: 9.71 (s, Ha), 8.17 (dd, Hi, ^4J(PHi) = 8.3 Hz, ^5J(HiH7) = 1.0 Hz), 7.68 (d, H6, ^4J(H4H6) = 1.9 Hz), 7.03 (dd, H4, ^3J(H3H4) = 8.0 Hz), 6.66 (dd, H3, ^4J(PH3) = 5.9 Hz). ^{31}P-{^{1}H}-NMR: 34.16 (s).

4.1.4. [{Pd[5-(COH)C_6H_3C(H)=NCy-*C2,N*](Cl)}$_2${μ-$Ph_2P(CH_2)_6PPh_2$}] (*5*)

Yield: 78%. Anal. Found: C, 59.6; H, 5.4; N, 2.3. $C_{58}H_{64}Cl_2N_2O_2P_2Pd_2$ requires: C, 59.7; H, 5.5; N, 2.4%. IR: ν(C=O): 1693s, ν(C=N): 1624m. FAB-Mass: 1131 $[M-Cl]^+$, 774 $[LPd(PP)]^+$.^{1}H-NMR: 9.76 (s, Ha), 8.18 (dd, Hi, ^4J(PHi) = 8.8 Hz, ^5J(HiH7) = 1.0 Hz), 7.70 (d, H6, ^4J(H4H6) = 1.7 Hz), 7.04 (dd, H4, ^3J(H3H4) = 8.1 Hz), 6.63 (dd, H3, ^4J(PH3) = 5.9 Hz). ^{31}P-{^{1}H}-NMR: 34.08 (s).

4.1.5. [{Pd[5-(COH)C_6H_3C(H)=NCy-*C2,N*](Cl)}$_2${μ-($Ph_2PC_5H_4$)$_2$Fe}] (*6*)

Yield: 57%. Anal. Found: C, 58.6; H, 4.4; N, 2.1. $C_{62}H_{58}Cl_2FeN_2O_2P_2Pd_2$ requires: C, 58.9; H, 4.6; N, 2.2%. IR: ν(C=O): 1695s, ν(C=N): 1623m. FAB-Mass: 1229 $[M-Cl]^+$, 982 $[M-2Cl-L]^+$, 874 $[LPd(PP)]^+$, 845 $[(L-COH)Pd(PP)]^+$.^{1}H-NMR: 9.97 (s, Ha), 8.19 (dd, Hi, ^4J(PHi) = 9.3 Hz, ^5J(HiH7) = 1.0 Hz), 7.73 (d, H6, ^4J(H4H6) = 1.9 Hz), 7.00 (dd, H4, ^3J(H3H4) = 7.8 Hz), 6.47 (dd, H3, ^4J(PH3) = 5.8 Hz), 5.00, 4.62, m, $H_{ferrocene}$). ^{31}P-{^{1}H}-NMR: 31.58 (s).

4.1.6. [{Pd[5-(COH)C_6H_3C(H)=NCy-*C2,N*](Cl)}$_2${μ-*trans*(Ph_2PCH=$CHPPh_2$)}] (*7*)

To a solution of **1** (50.00 mg, 0.070 mmol) in acetone (ca. 10 ml), *trans*-dppe (25.04 mg, 0.063 mmol) was added. The mixture was stirred for 12 h at r.t., after which solvent was removed under reduced pressure, and the residue triturated with diethylether to yield a brown solid, which was filtered off and dried in vacuo.

Yield: 54% (37.50 mg). Anal. Found: C, 58.5; H, 4.7; N, 2.6. $C_{54}H_{54}Cl_2N_2O_2P_2Pd_2$ requires: C, 58.5; H, 4.9; N, 2.5%. IR: ν(C=O): 1694s, ν(C=N): 1625m. FAB-

Mass: 1073 $[M-Cl]^+$, 1008 $[M-Cl-COH]^+$, 716 $[LPd(PP)]^+$. ^{1}H-NMR: 9.75 (s, Ha), 7.73 (d, H6, ^4J(H4H6) = 1.9 Hz), 7.00 (dd, H4, ^3J(H3H4) = 8.3 Hz), 6.80 (at, *HC*=C*H*, *N*(PH) = 43.0 Hz), 6.62 (m, H3). ^{31}P-{^{1}H}-NMR: 35.54 (s). ^{13}C-NMR: 191.3 (s, COH), 170.5 (b, C=N), 167.7 (s, C1), 149.8 (m, C2), 138.0 (m, C3), 135.5 (at, C_o), 132.7 (s, C5), 132.3 (s, C_p), 131.0 (m, C4), 128.7 (at, C_m), 126.8 (at, H*C*=*C*H), 126.7 (s, C6), 62.4 (s, C7), 33.5 (s, C8, C12), 25.7 (s, C9, C11), 25.4 (s, C10).

Compounds **8** and **9** were obtained in a similar fashion to **7**, but using dppac and arphos, respectively, as appropiate.

4.1.7. [{Pd[5-(COH)C$_6$H$_3$C(H)=NCy-C2,N](Cl)}$_2$(μ-Ph$_2$PCCPPh$_2$)] (**8**)

Yield: 28%. Anal. Found: C, 58.4; H, 4.6; N, 2.6 $C_{54}H_{52}Cl_2N_2O_2P_2Pd_2$ requires: C, 58.6; H, 4.7; N, 2.5%. IR: *v*(C=O): 1698s, *v*(C=N): 1626m. FAB-Mass: 1106 $[M]^+$, 714 $[LPd(PP)]^+$. ^{1}H-NMR: 9.71 (s, Ha), 8.17 (dd, Hi, ^4J(PHi) = 8.8 Hz, ^5J(HiH7) = 1.0 Hz)), 6.93 (dd, H4, ^3J(H3H4) = 8.0 Hz, ^4J(H4H6) = 1.7 Hz). ^{31}P-{^{1}H}-NMR: 15.59 (s).

4.1.8. [{Pd[5-(COH)C$_6$H$_3$C(H)=NCy-C2,N](Cl)}$_2$(μ-Ph$_2$PCH$_2$CH$_2$AsPh$_2$)] (**9**)

Yield: 43%. Anal. Found: C, 56.4; H, 4.8; N, 2.4. $C_{54}H_{56}AsCl_2N_2O_2PPd_2$ requires: C, 56.2; H, 4.9; N, 2.4%. IR: *v*(C=O): 1693s, *v*(C=N): 1625m. FAB-Mass: 762 $[LPd(PAs)]^+$. ^{1}H-NMR: 9.74, 9.73 (s, Ha/Ha′), 8.21 (dd, Hi, ^4J(PHi) = 8.8 Hz, ^5J(HiH7) = 1.0 Hz), 8.16 (d, Hi′, ^5J(HiH7) = 1.0 Hz), 7.70 (d, H6/H6′, ^4J(H4H6) = 1.9 Hz), 7.00, 6.97 (dd, H4/H4′, ^3J(H3H4) = 8.3 Hz), 6.66 (d, H3′), 6.60 (dd, H3, ^4J(PH3) = 7.0 Hz). ^{31}P-{^{1}H}-NMR: 38.85 (s). ^{13}C-NMR: 191.4, 191.3 (s, COH, COH′), 170.5 (s, C′=N), 170.3 (b, C=N), 149.7, 149.6 (s, C2, C2′), 138.1 (s, C3′), 137.8 (d, C3, ^3J(PC3) = 10.6 Hz), 135.4 (s, C4′), 135.2 (d, C4, ^4J(PC4) = 3.6 Hz), 134.4 (d, C_o, ^2J(PC_o) = 11.4 Hz), 134.0 (s, C_o'), 132.7 (s, C5, C5′), 131.2 (s, C_p'), 130.4 (d, C_p, ^4J(PC_p) = 1.4 Hz), 128.9 (s, C_m'), 128.6 (d, C_m, ^3J(PC_m) = 10.6 Hz), 126.8, 126.7 (s, C6, C6′), 62.7 (s, C7, C7′), 33.5 (s, C8, C8′, C12, C12′), 30.5 (d, P*C*H$_2$, ^1J(PC) = 5.4 Hz), 25.7 (s, C9, C9′, C11, C11′), 25.4 (s, C10, C10′), 24.7 (s, As*C*H$_2$).

4.1.9. Preparation of [Pd{5-(COH)C$_6$H$_3$C(H)=NCy-C2,N}{Ph$_2$P(CH$_2$)$_4$PPh$_2$-P,P}][PF$_6$] (**10**)

To a solution of **1** (20.00 mg, 0.028 mmol) in acetone (ca. 15 ml), dppb (23.95 mg, 0.056 mmol) was added. The mixture was stirred for 2 h at r.t., after which ammonium hexafluorophosphate (13.69 mg, 0.084 mmol) 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 over anhydrous $CaCl_2$. The desired complex was recrystallized from chloroform–*n*-hexane as pale yellow microcrystals.

Yield: 24% (12.20 mg). Anal. Found: C, 56.5; H, 4.7; N, 1.4. $C_{42}H_{44}F_6NOP_3Pd$ requires: C, 56.5; H, 5.0; N, 1.6%. IR: *v*(C=O): 1687s, *v*(C=N): 1616m. FAB-Mass: 664 $[M-Cy]^+$. ^{1}H-NMR: 9.78 (s, Ha), 6.74 (m, H3). ^{31}P-{^{1}H}-NMR: 32.43 (d, P_α, ^2J(PP) = 42.8 Hz), 20.62 (d, P_β).

Compounds **11**–**13** were prepared similarly, but using dpph, dppf, and 1,2-dppb, respectively, as appropriate.

4.1.10. [Pd{5-(COH)C$_6$H$_3$C(H)=NCy-C2,N}{Ph$_2$P(CH$_2$)$_6$PPh$_2$-P,P}][PF$_6$] (**11**)

Yield: 83%. Anal. Found: C, 53.2; H, 5.1; N, 1.7. $C_{44}H_{48}F_6NOP_3Pd$ requires: C, 53.4; H, 5.3; N, 1.5%. IR: *v*(C=O): 1690s, *v*(C=N): 1627m. FAB-Mass: 663 $[M-COH-Cy]^+$, 291 $[(L-COH)Pd]^+$. ^{1}H-NMR: 9.69 (s, Ha), 8.66 (b, Hi), 7.01 (dd, H4, ^3J(H3H4) = 7.7 Hz, ^4J(H4H6) = 1.9 Hz), 6.90 (m, H3). ^{31}P-{^{1}H}-NMR: 33.35 (d, P_α, ^2J(PP) = 43.7 Hz), 16.05 (d, P_β).

4.1.11. [Pd{5-(COH)C$_6$H$_3$C(H)=NCy-C2,N}{(Ph$_2$PC$_5$H$_4$)$_2$Fe-P,P}][PF$_6$] (**12**)

Yield: 77%. Anal. Found: C, 56.3; H, 4.0; N, 1.2. $C_{48}H_{42}F_6FeNOP_3Pd$ requires: C, 56.6; H, 4.2; N, 1.4%. IR: *v*(C=O): 1693s, *v*(C=N): 1618m. FAB-Mass: 790 $[M-Cy]^+$, 291 $[(L-COH)Pd]^+$. ^{1}H-NMR: 9.78 (s, Ha), 7.10 (dd, H4, ^3J(H3H4) = 7.8 Hz, ^4J(H4H6) = 2.0 Hz), 6.63 (m, H3, ^4J(P_βH3) = 7.3 Hz, ^4J(P_αH3) = 4.9 Hz), 4.80, 4.67, 4.32, 3.59 (d, $H_{ferrocene}$). ^{31}P-{^{1}H}-NMR: 40.09 (d, P_α, ^2J(PP) = 29.9 Hz), 23.69 (d, P_β). ^{13}C-NMR: 191.2 (s, COH), 185.5 (dd, C=N, ^3J(P_αC) = 7.8 Hz, ^3J(P_βC) = 4.3 Hz), 175.8 (dd, C2, ^3J(P_βC) = 124.2 Hz, ^3J(P_αC) = 2.1 Hz), 151.4 (s, C1), 139.0 (dd, C3, ^3J(P_αC) = 9.0 Hz, ^3J(P_βC) = 3.5 Hz), 135.3 (d, C_o, ^{2}J(PC) = 12.8 Hz), 133.8 (s, C5), 133.6 (d, C_o, ^2J(PC) = 12.8 Hz), 132.4 (d, C_p, ^4J(PC) = 2.8 Hz), 132.2 (d, C_p, ^4J(PC) = 2.2 Hz), 130.9 (dd, C4, ^4J(P_αC) = 9.2 Hz, ^4J(P_βC) = 4.3 Hz), 129.6 (d, C_m, ^3J(PC) = 9.9 Hz), 129.2 (d, C_m, ^3J(PC) = 11.4 Hz), 129.1 (s, C6), 75.7 (d, $C_{ferrocene}$, ^2J(PC) = 14.1 Hz), 75.5 (d, $C_{ferrocene}$, ^2J(PC) = 10.6 Hz), 75.3 (d, $C_{ferrocene}$, ^3J(PC) = 7.8 Hz), 73.3 (d, $C_{ferrocene}$, ^3J(PC) = 7.1 Hz), 69.5 (s, C7), 30.9 (s, C8, C12), 29.7 (s, C9, C11), 29.8 (s, C10).

4.1.12. [Pd{5-(COH)C$_6$H$_3$C(H)=NCy-C2,N}{1,2-(Ph$_2$P)$_2$C$_6$H$_4$-P,P}][PF$_6$] (**13**)

Yield: 70%. Anal. Found: C, 57.9; H, 4.2; N, 1.3. $C_{44}H_{40}F_6NOP_3Pd$ requires: C, 57.9; H, 4.4; N, 1.5%. IR: *v*(C=O): 1693m, *v*(C=N): 1618m. FAB-Mass: 766 $[M]^+$, 655 $[M-COH-Cy]^+$. ^{1}H-NMR: 9.87 (s, Ha), 8.70 (d, Hi, ^4J(PHi) = 5.0 Hz), 8.06 (b, H6), 7.10 (m, H3). ^{31}P-{^{1}H}-NMR: 55.76 (d, P_α, ^2J(PP) = 25.4 Hz), 43.39 (d, P_β).

4.1.13. Preparation of [Pd{5-(COH)C_6H_3C(H)=NCy-C2,N}(cis-Ph_2PCH=CHPPh_2-P,P)][PF_6] (**14**)

To a solution of **1** (40.00 mg, 0.056 mmol) in acetone (ca. 15 cm^3), silver trifluorosulfonate (14.42 mg, 0.056 mmol) was added. The mixture was stirred for 1 h and filtered through Celite to eliminate the silver chloride precipitate, cis-dppe (44–50 mg, 0.112 mmol) and NH_4PF_6 (27.38 mg, 0.168 mmol) were added to the resultant solution, stirred for 12 h, and the precipitate formed filtered off, yielding a pale yellow solid which was recrystallized in chloroform–*n*-hexane.

Yield: 57% (55.61 mg). Anal. Found: C, 56.1; H, 3.9; N, 1.6. $C_{40}H_{38}F_6NOP_3Pd$ requires: C, 55.7; H, 4.4; N, 1.6%. IR: ν(C=O): 1695s, ν(C=N): 1614m. FAB-Mass: 716 $[M]^+$, 688 $[M-COH]^+$, 291 $[(L-COH)Pd]^+$. ^{1}H-NMR: 9.84 (s, Ha), 8.54 (d, Hi, ^4J(PHi) = 8.3 Hz), 7.99 (t, H6, ^{4}J(H4H6) = 2.0 Hz, ^5J(PH6) = 2.0 Hz), 7.82 (dd, H4, ^{3}J(H3H4) = 8.0 Hz), 7.17 (m, H3). ^{31}P-{^{1}H}-NMR: 62.32 (d, P_α, ^2J(PP) = 11.0 Hz), 53.71 (d, P_β). ^{13}C-NMR: 191.4 (s, COH), 178.4 (dd, C=N, $^3J(P_\alpha C)$ = 7.8 Hz, $^3J(P_\beta C)$ = 4.0 Hz), 150.3 (s, C1), 174.5 (d, C2, $^3J(P_\beta C)$ = 119.2 Hz), 146.0 (dd, HC=CH, ^1J(PC) = 49.7 Hz, ^2J(PC) = 34.1 Hz), 142.8 (dd, HC=CH, ^1J(PC) = 41.2 Hz, ^2J(PC) = 22.0 Hz), 138.0 (dd, C3, $^3J(P_\alpha C)$ = 9.9 Hz, $^3J(P_\beta C)$ = 2.8 Hz), 134.5 (s, C5), 133.8 (d, C_o, ^2J(PC) = 12.8 Hz), 133.2 (d, C_o, ^2J(PC) = 12.8 Hz), 133.0, 132.8 (b, C_p), 131.8 (dd, C4, $^4J(P_\alpha C)$ = 12.8 Hz, $^4J(P_\beta C)$ = 5.0 Hz), 130.2 (d, C_m, ^3J(PC) = 9.9 Hz), 130.0 (d, C_m, ^3J(PC) = 10.6 Hz), 126.3 (d, C_i, ^1J(PC) = 41.2 Hz), 125.6 (d, C_i, ^1J(PC) = 55.4 Hz), 69.0 (s, C7), 33.8 (s, C8, C12), 25.1 (s, C9, C11), 24.6 (s, C10).

Compounds **15** and **16** were obtained in a similar fashion to **10**, but using dppa and arphos, respectively, as appropriate.

4.1.14. [Pd{5-(COH)C_6H_3C(H)=NCy-C2,N}(Ph_2PNHPPh_2-P,P)][PF_6] (**15**)

Yield: 71%. Anal. Found: C, 53.3; H, 4.4; N, 3.4. $C_{38}H_{37}F_6N_2OPdP_3$ requires: C, 53.6; H, 4.4; N, 3.3%. IR: ν(C=O): 1694s, ν(C=N): 1617m. FAB-Mass: 705 $[M]^+$, 677 $[M-COH]^+$. ^{1}H-NMR: 9.86 (s, Ha), 8.34 (d, Hi, ^4J(PHi) = 7.8 Hz), 7.90 (b, H6). ^{31}P-{^{1}H}-NMR: 43.77 (d, P_α, ^2J(PP) = 67.8 Hz), 32.59 (d, P_β).

4.1.15. [Pd{5-(COH)C_6H_3C(H)=NCy-C2,N}(Ph_2P$CH_2$$CH_2AsPh_2$-P,As)][$PF_6$] (**16**)

Yield: 86%. Anal. Found: C, 52.6; H, 4.5; N, 1.5. $C_{40}H_{40}AsF_6NOP_2Pd$ requires: C, 52.9; H, 4.4; N, 1.5%. IR: ν(C=O): 1693s, ν(C=N): 1620m. FAB-Mass: 762 $[M]^+$, 735 $[M-COH]^+$, 679 $[M-Cy]^+$, 647 $[M-COH-Cy]^+$, 291 $[(L-COH)Pd]^+$. ^{1}H-NMR: 9.84 (s, Ha), 7.29 (dd, H4, ^3J(H3H4) = 7.8 Hz, ^4J(H4H6) = 2.0 Hz), 6.89 (dd, ^4J(PH3) = 7.8 Hz). ^{31}P-{^{1}H}-NMR: 61.44 (s).

4.2. X-ray crystallographic study

Three-dimensional, r.t. X-ray data were collected on a Siemens Smart CCD diffractometer by the ω scan method using graphite-monochromated Mo–K_α radiation. All the measured reflections were corrected for Lorentz and polarization 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. The formyl oxygen atom in compound **16** was found to be disordered over two positions [O(1) and O(2)]. The occupancies of the pairs of positions were tied to give an overall value of 1.0 and then refined giving values of, ca. 0.5 for each component. Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final R = 0.0617, 0.0593, 0.0490 and 0.0545 (for complexes **3**, **6**, **9** and **16**, respectively, observed data, F) and wR_2 = 0.1766, 0.1847, 0.2049 and 0.1727 (for complexes **3**, **6**, **9** and **16**, 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 [60].

5. Supplementary material

Full details of data collection and structure refinement have been deposited with the Cambridge Crystallographic Data Center, CCDC reference numbers 185153, 185154, 185152 and 185155 for compounds **3**, **6**, **9** and **16**, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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