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Cyclometallated complexes of Pd(II) with heterobidentate P, As and P, N coordinating ligands

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Abstract

Treatment of the choride-bridged dimer [Pd{4-(COH)C_6H_3C(H)=N(Cy)−*C2*,*N*}(μ-Cl)]$_2$ (**1**), with $Ph_2PCH_2CH_2AsPh_2$ (arphos) in 1:1 molar ratio in acetone gave the dinuclear complex [{Pd[4-(COH)C_6H_3C(H)=N(Cy)−*C2*,*N*](Cl)}$_2$(μ-$Ph_2PCH_2CH_2AsPh_2$)] (**2**), with the arsinophosphine as a bridging ligand, and in 1:2 molar ratio in the presence of NH_4PF_6 gave the mononuclear compound [Pd{4-(COH)C_6H_3C(H)=N(Cy)−*C2*,*N*}($Ph_2PCH_2CH_2AsPh_2$−*P*,*As*)][PF_6], (**3**), with the arsinophosphine chelated to the metal center. Reaction of **1** with $Ph_2PCH_2CH_2CH_2NH_2$ in 1:2 molar ratio in acetone and NH_4PF_6 afforded [Pd{4-(COH)C_6H_3C(H)=N(Cy)−*C2*,*N*}{$Ph_2PCH_2CH_2CH_2N$(=CMe_2)−*P*,*N*}][PF_6] (**4**), after intermolecular condensation between the aminophosphine and the solvent. Condensation was precluded by treatment in toluene to give the mononuclear compound [Pd{4-(COH)C_6H_3C(H)=N(Cy)−*C2*,*N*}($Ph_2PCH_2CH_2CH_2NH_2$−*P*,*N*)][PF_6], (**5**). ^{1}H, ^{31}P{^{1}H} and ^{13}C{^{1}H}-NMR, IR and mass spectral data are given. The crystal structures of compounds **2**–**4** have been determined by X-Ray crystallography.

Keywords: Palladium; Metallation; Phosphines; As ligands; P,N ligands

1. Introduction

A large number of transition metal phosphine complexes have been used in catalysis due to the characteristic steric and electronic properties of the tertiary phosphine ligands [1]. The past decade has seen a growing interest in reactions that include these type of ligands and complexes, which have proved to be active catalysts in processes such as the hydrogenation of aldehydes [2] and aromatic ketones [3] or the carbonylation of metal–methyl bonds [4], as therapeutic agents in anticancer drugs [5] or as structural fragments on polystyrene-immobilized catalysts [6]. The pronounced difference in electronic as well as in steric properties between the coordinating atoms (i.e. N/P/As, in terms or the soft and hard base concept) has been shown to be the key to these reactions. Unfortunately, the metallic species involved have not been fully characterized in most of the published work in this field.

The cyclometallation reaction, i.e. the intramolecular activation of aromatic C–H bonds of coordinated ligands by transition metals, has been widely investigated in view of their growing chemistry [7] and of the novel and outstanding applications they present. To name but a few, the synthesis of new organometallic and organic compounds, many of which are obtained via insertion reactions of unsaturated species to the metal–carbon bond [8]; the design of complexes with interesting photochemical and electrochemical properties [9], the remarkable and specific antitumor activity toward some forms of cancer [10] or promising properties as liquid crystals [11]; and their use in the isolation of enantiomerically pure chiral compounds [12] or as efficient catalytic materials [13].

We have been interested in cyclopalladation reactions in which the metallated carbon atom, bearing sp^2 hybridization, is part of an aromatic ring belonging to

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differently substituted [C, N] Schiff bases derived from mono- or diamines [14], and dialdehydes [15], as well as [C, N, X] (X = N, [16] O, [17] S [18]) terdentate ligands. We have also reported five-membered metallacycles derived from substituted imidazoles [19] and ferrocenylimines [20]. The corresponding derivatives of these complexes with nucleophiles such as acetylacetonate, cyclopentadienyl or mono-, di- and triphospines have been described. Also, compounds derived from [C, N, N] terdentate ligands with Pt(II) [21] and [C, P] bidentate ligands with Pd(II) [22] have been reported. In the present paper we describe the synthesis and characterization of new cyclopalladated compounds derived from heterobidentate P, N and P, As ligands.

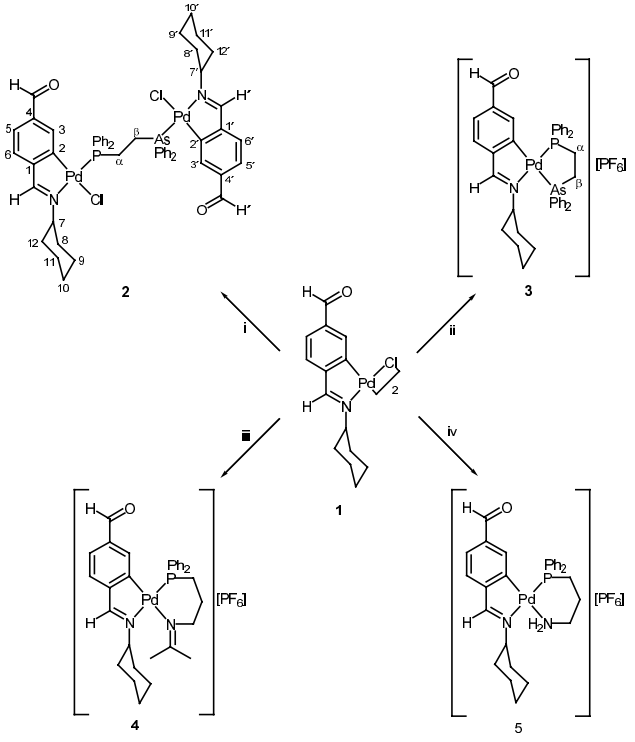
2. Results and discussion

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), 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).

Reaction of $[Pd\{4\text{-}(COH)C_6H_3C(H)=N(Cy)\text{–}C2,N\}(\mu\text{-}Cl)]_2$ (**1**) [23] with $Ph_2PCH_2CH_2AsPh_2$ (arphos) in 1:1 molar ratio, in acetone at room temperature afforded the dinuclear complex $[\{Pd[4\text{-}(COH)C_6H_3C(H)=N(Cy)\text{–}C2,N](Cl)\}_2(\mu\text{-}Ph_2PCH_2CH_2AsPh_2)]$ (**2**). The FAB mass spectrum only showed a maximum peak at *m/z* 762 assigned to the $[LPd(arphos)]^+$ ion; nevertheless, the new compound gave a satisfactory elemental analysis. The $^{31}P\{^{1}H\}$-NMR spectrum showed a singlet at δ 37.78, shifted to higher frequency from the free phosphine, in agreement with phosphorus coordination to metal center [24]. The IR spectrum showed the shift of the C=N stretch towards lower wavenumbers, as compared with the free Schiff base ligand (1638 vs. 1621 cm^{-1}), indicating N-coordination of the C=N group [25]. Å ν(C=O) band at 1687 cm^{-1} was assigned to the free formyl group [26].

In the ^{1}H-NMR spectrum the COH and COH′ groups gave rise to two singlets ca. δ 9.15 which could not be unambiguously assigned. The signals were shifted to lower field from the starting product ca. 0.8 ppm due to the shielding effect of the arphos phenyl rings, in agreement with a P, As *cis* to carbon disposition. The resonances of the H5/H5′ and H6/H6′ protons were overlapped and could not be adequately assigned. Nevertheless, the corresponding Hi/Hi′ and H3/H3′ resonances were clearly distinguished (see Section 3). Thus, two doublets of doublets at δ 8.15 and δ 6.80 were assigned Hi and H3, and two doublets at δ 8.11 and δ 6.86 were assigned to Hi′and H3′; the former two resonances coupled to the phosphorus nucleus [^{4}J(PHi) = 8.3 Hz, ^{4}J(PH3) = 5.9 Hz]. Similar chloro-bridge splitting reactions of dinuclear compounds derived from tris–*t*-butylphosphine with arphos yielded, irrespective of the molar ratio used, complexes in which the arsinophosphine was acting as a monodentate ligand via P-coordination, whilst the arsenic atom remained uncoordinated [22]. The $^{13}C\{^{1}H\}$-NMR spectrum of compound **2** also showed that some resonances were well diferentiated for each cyclometallated fragment and for the arphos phenyl rings (see Section 3). The signals at δ 170.3 and δ 170.2 [d, ^{4}J(PC) = 5.7 Hz] were asigned to C′=N and C=N carbons, respectively, and the signals at δ 154.4 and δ 154.3 to the C2/C2′carbons. These values were shifted downfield compared with the spectrum of the free ligand (ca. 12, C=N, and 26, C2, ppm) thereby confirming cyclometallation [23,27]. The ethylene resonances appeared at δ 30.7 [d, ^{1}J(PC) = 5.7 Hz] and δ 24.4, and were assigned to the PCH_2 and CH_2As carbon atoms, respectively. These findings were confirmed by the X-ray crystal structure determination of compound **2** (see below).

Treatment of the chloro-bridged complex **1** with $Ph_2PCH_2CH_2AsPh_2$ and NH_4PF_6 in 1:2 molar ratio in acetone–water at room temperature yielded the mononuclear compound $[Pd\{4\text{-}(COH)C_6H_3C(H)=N(Cy)\text{–}C2,N\}(Ph_2PCH_2CH_2AsPh_2\text{–}P,As)][PF_6]$ (**3**). The IR spectrum showed, as the main difference from the starting material, a broad and strong band at 850 cm^{-1} arising from the PF_6^- counterion [26]. The



Scheme 1. (i) $Ph_2PCH_2CH_2AsPh_2$ (1:1), acetone; (ii) $Ph_2PCH_2CH_2AsPh_2$, NH_4PF_6 (1:2), acetone–water; (iii) $Ph_2PCH_2CH_2CH_2NH_2$, NH_4PF_6 (1:2), acetone–water; (iv) $Ph_2PCH_2CH_2CH_2NH_2$, NH_4PF_6 (1:2), toluene.

MSFAB spectrum showed the corresponding peaks at *m/z* 762 and 735 assigned to $[M]^+$ and $[M-COH]^+$, respectively, after consideration of the palladium isotopes [28]. The $^{31}P\{^1H\}$-NMR spectrum showed a singlet at δ 60.27, downfield shifted due to the ring size effect in five-membered chelates [29]. The HC=N and H3 resonances in the ^{1}H-NMR spectrum at δ 8.48 and δ 6.98 were split by coupling to the ^{31}P nucleus *trans* to nitrogen [^4J(PHi) = 7.8 Hz, ^4J(PH3) = 5.6 Hz], as we found in related systems with monophosphine ligands linked to a palladium atom [23,30]. The $^{13}C\{^1H\}$ data were consistent with the proposed structure. A broad signal at δ 176.8 and two doublets at δ 161.0 [^2J(PC) = 5.7 Hz] and δ 137.2 [^3J(PC) = 10.6 Hz] were assigned to the HC=N, C2 and C3 carbon atoms, respectively. The crystal structure of **3** has been determined by X-ray diffraction analysis (see below) and confirms the spectroscopic data.

The reaction of **1** with $Ph_2PCH_2CH_2CH_2NH_2$, under a similar experimental procedure as above, afforded [Pd{4-(COH)C_6H_3C(H)=N(Cy)–*C2*,N}{$Ph_2PCH_2CH_2$-CH_2N(=CMe_2)–*P,N*}][PF_6] (**4**), after intermolecular condensation between the aminophosphine and the solvent. The elemental analysis was in agreement with the proposed structure (see Section 3). The mass spectrum showed very well defined peaks at *m/z* 603, 576, 522 and 497 assigned to $[M]^+$, $[M-COH]^+$, $[M-Cy]^+$ and $[M-COH-Cy]^+$, respectively. The IR stretches for compound **4** at 1644 and 1620 cm^{-1} were consistent with the presence of two different imino groups, Me_2C=N– and HC=N–, respectively. The chemical shift in the $^{31}P\{^1H\}$-NMR spectrum at δ 27.97 was indicative of P-coordination to the palladium atom. The displacement of the HC=N, HC=O and H3 resonances in the ^{1}H-NMR spectrum with respect to the corresponding ones in the spectrum of the starting compound, as well as the observed splittings (see Section 3) were in accordance with a P *trans* to N arrangement in the palladium environment. The ^{1}H-NMR spectrum also showed two singlets at δ 2.30 and δ 2.02 assignable to the NMe_2 methyl groups, which were non-equivalent. X-ray diffraction analysis of compound **4** confirmed these findings (see below).

Following a similar procedure to that for **4**, reaction of **1** with $Ph_2PCH_2CH_2CH_2NH_2$ in toluene, where condensation of the solvent to the NH_2 group is precluded, gave the expected mononuclear compound [Pd{4-(COH)C_6H_3C(H)=N(Cy)–*C2*,*N*}(Ph_2-PCH_2CH_2–CH_2NH_2–*P*,*N*)][PF_6] (**5**). The elemental analysis and the mass spectrum ($[M]^+$ at *m/z* 563) gave satisfactory results. The conductivity data (164.6 Ω^{-1} cm^2 mol^{-1} in 10^{-3} mol dm^3 solution in dry acetonitrile) showed it to be a 1:1 electrolyte [31], confirming the presence of the aminophosphine ligand in its neutral form. The spectroscopic data was similar to that observed for compound **4**, with absence of the $NCMe_2$ resonances in the ^{1}H-NMR spectrum (see Section 3).

2.1. Molecular structures of complexes 2, 3 and 4

Suitable crystals were grown by slowly evaporating chloroform–*n*-hexane (**2**), dichloromethane–*n*-hexane (**3**) or acetonitrile–ethyl ether (**4**) solutions of the complexes. The labeling schemes for the compounds are shown in Figs. 1–3. 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.

In compound **2**, the dinuclear molecule comprises two palladium centers each of which 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 ligand 1-diphenylphosphino-2-diphenylarsinoethane which bridges the two metal centers, completes the metal coordination sphere. Although the bridging ligand, $Ph_2PCH_2CH_2AsPh_2$, 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. However, in compound **3** (vide supra) where the P and As atoms are in different chemical surroundings, the technique clearly distinguishes both atoms. This behavior has been observed in other complexes derived from the arsinophosphine ligand [32,33].

For mononuclear complexes **3** and **4** the palladium(II) atom is bonded to four atoms: an *ortho* carbon of the phenyl ring and a nitrogen atom of the benzylidene ligand, and a phosphorus atom and an arsenic (**3**) or a nitrogen (**4**) atom of the chelating arsinophosphine or phosphinoamine ligands, respectively.

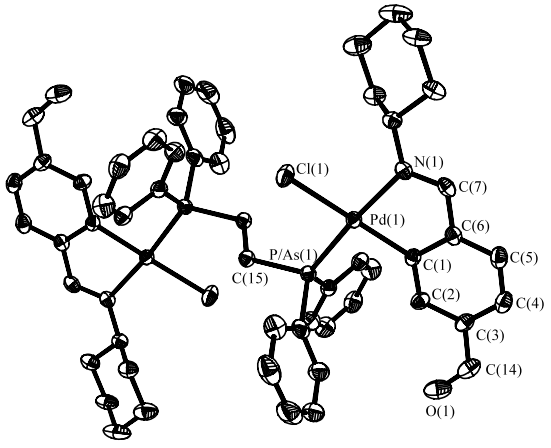


Fig. 1. Molecular structure of [{Pd[4-(COH)C_6H_3C(H)=N(Cy)–*C2*,*N*](Cl)}$_2$(μ-$Ph_2PCH_2CH_2AsPh_2$)] (**2**), with labeling scheme. Hydrogen atoms have been omitted for clarity.

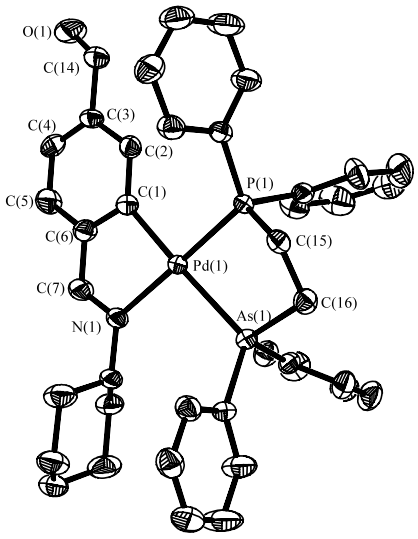


Fig. 2. Molecular structure of the cation for [Pd{4-(COH)C_6H_3C(H)=N(Cy)–*C2,N*}($Ph_2PCH_2CH_2AsPh_2$–*P,As*)][PF_6] (**3**), with labeling scheme. Hydrogen atoms have been omitted for clarity.

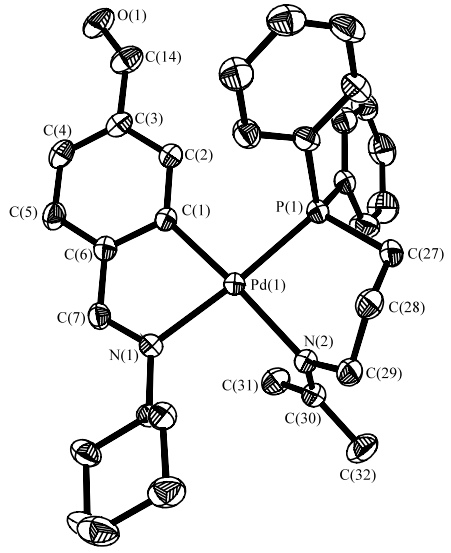


Fig. 3. Molecular structure of the cation for [Pd{4-(COH)C_6H_3C(H)=N(Cy)–*C2,N*}{$Ph_2PCH_2CH_2CH_2N(=CMe_2)$–*P,N*}][$PF_6$] (**4**), with labeling scheme. Hydrogen atoms have been omitted for clarity.

The sum of angles about palladium is 360.56 (**2**), 360.23 (**3**) and 361.27° (**4**); 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 80.57(19) (**2**), 81.37(19) (**3**) and 81.00(12)° (**4**). 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–As1, Cl1, **2**; Pd1, C1, N1, P1, As1, **3**; Pd1, C1, N1, P1, N2, **4**) are 0.1084, 0.0796 and 0.1296 Å, respectively.

The palladium–nitrogen bond length in the metallacycle (2.104(4) Å, **2**; 2.107(4) Å, **3**; 2.114(3), **4**) 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 [34], and reflects the *trans* influence of the phosphorus–arsenic atom [5,35].

The palladium–carbon bond length (2.003(5) Å, **2**; 2.066(5) Å, **3**; 2.010(3) Å, **4**) 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), but longer than those found in related complexes where partial multiple-bond character of the Pd–C bond was proposed [19,30].

The Pd–P and Pd–As bond distances (2.311(1) Å, **2**; 2.263(1) Å and 2.452(1) Å, **3**; 2.250(1) Å, **4**) are shorter than the sum of the single bond radii for palladium and the corresponding atom (2.41 Å for Pd–P, 2.55 Å for Pd–As), suggesting partial double bond character similar to others reported earlier [36]. In compound **2**, the Pd–Cl bond length, 2.384(5) Å, is consistent with Pd–Cl distances found in related species [37] but longer than the sum of the covalent radii (2.30 Å) as a consecuence of the *trans* influence of the C(phenyl) carbon.

3. Experimental

3.1. General remarks

All solvents were distilled prior to use from appropriate drying agents [38]. All chemicals were used as supplied from commercial sources. Elemental analyses (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. NMR spectra were obtained as $CDCl_3$ solutions and referenced to $SiMe_4$ (^1H, $^{13}C\{^1H\}$) or 85% H_3PO_4 ($^{31}P\{^1H\}$); and were recorded on a Bruker AC-200F spectrometer (200.0 MHz for ^1H, 50.3 MHz for $^{13}C\{^1H\}$, 81.0 MHz for $^{31}P\{^1H\}$). Mass spectra were obtained in a QUATRO mass spectrometer with Cs ion-gun and 3-NBA matrix. Conductivity measurements were made on a Crison GLP 32 conductivimeter using 10^{-3} M solutions in dry acetonitrile at room temperature (r.t.) (298 K). The synthesis of [Pd{4-(COH)C_6H_3C(H)=N(Cy)–*C2,N*}(μ-Cl)]$_2$ (**1**) was reported in a recent paper from this laboratory [23].

3.2. Synthesis of [{Pd[4-(COH)C_6H_3C(H)=N(Cy)–C2,N](Cl)}$_2$(μ-$Ph_2PCH_2CH_2AsPh_2$)] (2)

To a solution of **1** (50 mg, 0.070 mmol) in acetone (ca. 10 ml), $Ph_2PCH_2CH_2AsPh_2$ (28 mg, 0.064 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

Table 1
Crystal and structure refinement data for complexes **2**–**4**

	2	**3**	**4**
Formula	$C_{54}H_{56}AsCl_2N_2O_2PPd_2$	$C_{40}H_{40}AsF_6NOP_2Pd$	$C_{32}H_{38}F_6N_2OP_2Pd$
M_r	1154.60	907.99	748.98
Temperature (K)	293(2)	293(2)	293(2)
Wavelenght (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Cell dimensions			
a (Å)	9.838(1)	12.613(1)	10.642(1)
b (Å)	11.311(1)	13.767(1)	11.639(1)
c (Å)	13.132(1)	14.049(2)	13.810(2)
α (°)	76.65(1)	99.45(1)	79.59(1)
β (°)	73.00(1)	116.43(1)	81.62(1)
γ (°)	88.626(2)	101.25(1)	80.04(1)
V (Å^3)	1358.2(2)	2052.9(2)	1645.4(1)
Z	1	2	2
$D_{calc.}$ (Mg m^{-3})	1.412	1.469	1.512
μ (mm^{-1})	1.433	1.388	0.724
Crystal size (mm)	$0.20 \times 0.15 \times 0.15$	$0.35 \times 0.25 \times 0.20$	$0.30 \times 0.20 \times 0.20$
$2\theta_{max}$ (°)	56.58	56.62	56.58
Reflections collected	9771	14 644	11 795
Reflections independent	6595 ($R_{int} = 0.0560$)	9961 ($R_{int} = 0.0475$)	7971 ($R_{int} = 0.0396$)
R [F, $I > 2\sigma(I)$]	0.0525	0.0528	0.0480
wR [F^2, all data]	0.1937	0.2230	0.1235
max ρ (e Å^{-3})	0.665	0.916	0.623

yield the desired product as pale yellow microcrystals. Yield: 68% (49.9 mg). Anal. Found: C, 56.6; H, 4.9; N, 2.2%. $C_{54}H_{56}AsCl_2N_2O_2PPd_2$ requires: C, 56.2; H, 4.9; N, 2.4. IR: ν(C=N): 1621m, ν(C=O): 1687s. FAB-Mass: 762 [LPd(arphos)]$^+$. ^{1}H-NMR: 9.20, 9.13 (s, Ha, Ha′), 8.15 (dd, Hi, ^4J(PHi) = 8.3 Hz, ^5J(HiH7) = 1.0 Hz), 8.11 (d, Hi′, ^5J(Hi′H7′) = 1.0 Hz), 6.86 (d, H3′, ^3J(H3′H5′) = 1.0 Hz), 6.80 (dd, H3, ^4J(PH3) = 5.9 Hz,

Table 2
Selected bond distances (Å) and angles (°) for complexes **2**–**4**

2		**3**		**4**	
Bond lengths					
Pd(1)–C(1)	2.003(5)	Pd(1)–C(1)	2.066(5)	Pd(1)–C(1)	2.010(3)
Pd(1)–N(1)	2.104(4)	Pd(1)–N(1)	2.107(4)	Pd(1)–N(1)	2.114(3)
Pd(1)–Cl(1)	2.384(5)	Pd(1)–P(1)	2.263(1)	Pd(1)–P(1)	2.250(1)
Pd(1)–As(1)	2.311(1)	Pd(1)–As(1)	2.452(1)	Pd(1)–N(2)	2.144(3)
C(1)–C(6)	1.403(7)	C(1)–C(6)	1.396(8)	C(1)–C(6)	1.413(5)
C(6)–C(7)	1.465(8)	C(6)–C(7)	1.446(9)	C(6)–C(7)	1.448(5)
N(1)–C(7)	1.276(7)	N(1)–C(7)	1.284(8)	N(1)–C(7)	1.283(4)
O(1)–C(14)	1.181(9)	O(1)–C(14)	1.205(8)	O(1A)–C(14)	1.113(7)
Pd(2)–P(1)	2.311(1)	P(1)–C(15)	1.847(7)	O(1B)–C(14)	1.127(10)
		As(1)–C(16)		N(2)–C(30)	
Bond angles					
C(1)–Pd(1)–N(1)	80.57(19)		1.956(6)		1.285(5)
C(1)–Pd(1)–As(1)	94.05(15)	C(1)–Pd(1)–N(1)	81.37(19)	C(1)–Pd(1)–N(1)	81.00(12)
As(1)–Pd(1)–Cl(1)	91.12(4)	C(1)–Pd(1)–P(1)	98.38(15)	C(1)–Pd(1)–P(1)	96.31(10)
N(1)–Pd(1)–Cl(1)	94.82(13)	P(1)–Pd(1)–As(1)	82.27(4)	N(2)–Pd(1)–P(1)	88.21(8)
C(7)–N(1)–Pd(1)	113.7(4)	N(1)–Pd(1)–As(1)	98.21(13)	N(1)–Pd(1)–N(2)	95.75(11)
N(1)–C(7)–C(6)	116.6(5)	C(7)–N(1)–Pd(1)	111.1(4)	C(7)–N(1)–Pd(1)	112.7(2)
C(1)–C(6)–C(7)	116.1(5)	N(1)–C(7)–C(6)	120.6(5)	N(1)–C(7)–C(6)	117.8(3)
C(6)–C(1)–Pd(1)	112.4(4)	C(1)–C(6)–C(7)	116.2(5)	C(1)–C(6)–C(7)	116.5(3)
		C(6)–C(1)–Pd(1)	110.6(4)	C(6)–C(1)–Pd(1)	111.7(2)
		C(15)–Pd(1)–P(1)	107.45(18)	C(27)–P(1)–Pd(1)	107.75(12)
		C(16)–Pd(1)–As(1)	106.69(18)	C(29)–N(2)–Pd(1)	120.6(2)

^3J(H3H5) = 1.9 Hz), 4.5 (m, H_α). $^{31}P\{^1H\}$-NMR: 37.78 (s). ^{13}C-NMR: 192.2 (s, COH), 192.1 (s, C′OH), 170.3 (s, C′=N), 170.2 (d, C=N, ^4J(PC) = 5.7 Hz), 155.7 (s, C1, C1′), 154.4, 154.3 (C2, C2′), 139.4 (d, C3, ^3J(PC3) = 10.6 Hz), 139.8 (s, C3′), 135.6 (d, C4, ^4J(PC4) = 4.3 Hz), 135.5 (s, C4′), 127.4 (C5, C5′), 134.2 (d, C_o, $^2J(PC_o)$ = 11.4 Hz), 134.0 (s, C_o'), 131.1 (d, C_p, $^4J(PC_p)$ = 2.1 Hz) 130.5 (s, C_p'), 129.0 (s, C_m'), 128.6 (d, C_m, $^3J(PC_m)$ = 10.6 Hz), 124.3, 124.0 (C6, C6′), 63.0 (s, C7, C7′), 33.4 (s, C8, C8′, C12, C12′), 30.7 (d, C_α, $^1J(PC_\alpha)$ = 5.7Hz), 25, 8 (C10, C10′), 25.4 (s, C9, C9′, C11, C11′), 24.4 (s, C_β).

3.3. Synthesis of [Pd{4-(COH)C$_6$H$_3$C(H)=N(Cy)–C2,N}(Ph$_2$PCH$_2$CH$_2$AsPh$_2$–P,As)][PF$_6$] (3)

To a solution of **1** (20 mg, 0.028 mmol) in acetone (ca. 15 ml), $Ph_2PCH_2CH_2AsPh_2$ (24.84 mg, 0.056 mmol) was added. The mixture was stirred for 2 h at r.t., after which ammonium hexafluorophosphate (4.6 mg, 0.028 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 anhidrous $CaCl_2$. The desired complex was recrystallized from dichloromethane–*n*-hexane as pale yellow microcrystals. Yield: 88% (22.4 mg). Anal. Found: C, 53.1; 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=N): 1619m, ν(C=O): 1691s. FAB-Mass: 762 $[M]^+$, 735 $[M-COH]^+$. ^{1}H-NMR: 9.37 (s, Ha), 8.48 (d, Hi, ^4J(PHi) = 7.8 Hz), 6.98 (dd, H3, ^4J(PH3) = 5.6 Hz, ^4J(H3H5) = 1.2 Hz). $^{31}P\{^1H\}$-NMR: 60.27 (s). ^{13}C-NMR: 191.6 (s, COH), 176.8 (b, C=N), 161.0 (d, C2, ^2J(PC2) = 5.7 Hz), 154.8 (s, C1), 137.2 (d, C3, ^3J(PC3) = 10.6 Hz), 137.0 (d, C4, ^3J(PC4) = 4.2 Hz), 134.0 (d, C_o, $^2J(PC_o)$ = 11.1 Hz), 132.9 (s, C_o'), 130.1 (d, C_m, $^3J(PC_m)$ = 14.8 Hz, 129.7 (s, C_m'), 127.8 (s, C6), 126.9 (d, C_i, $^1J(PC_i)$ = 87.2 Hz), 125.0 (s, C_i'), 131.8 (s, C_p, C_p'), 70.5 (s, C7), 33.6 (s, C8, C12), 31.4 (d, C_α, $^1J(PC_\alpha)$ = 36.7 Hz), 24.6 (s, C9, C11), 24.9 (s, C10), 24.3 (d, C_β, $^1J(PC_\beta)$ = 7.1 Hz)

3.4. Synthesis of [Pd{4-(COH)C$_6$H$_3$C(H)=N(Cy)–C2,N}{Ph$_2$PCH$_2$CH$_2$CH$_2$N(=CMe$_2$)–P,N}][PF$_6$] (4)

The desired compound was prepared similarly and isolated as a pale yellow solid, but using $Ph_2PCH_2CH_2CH_2NH_2$ as appropiate. Yield: 62% (26 mg). Anal. Found: C, 51.1; H, 5.0; N, 3.6%. $C_{32}H_{38}F_6N_2OP_2Pd$ requires: C, 51.3; H, 5.1; N, 3.7. IR: ν(C=N): 1644m, 1620m, ν(C=O): 1697s. FAB-Mass: 603 $[M]^+$, 576 $[M-COH]^+$, 522 $[M-Cy]^+$, 497 $[M-COH-Cy]^+$. ^{1}H-NMR: 9.21 (s, Ha), 8.33 (d, Hi, ^4J(PHi) = 7.8 Hz), 6.58 (d, H3, ^4J(PH3) = 5.9 Hz, ^4J(H3H5) = 1.2 Hz), 2.30 (s, Me), 2.02 (s, Me). $^{31}P\{^1H\}$-NMR: 27.97 (s)

3.5. Synthesis of [Pd{4-(COH)C$_6$H$_3$C(H)=N(Cy)–C2,N}(Ph$_2$PCH$_2$CH$_2$CH$_2$NH$_2$–P,N)][PF$_6$] (5)

To a solution of **1** (20 mg, 0.028 mmol) in toluene (ca. 15 ml), $Ph_2PCH_2CH_2CH_2NH_2$ (13.67 mg, 0.056 mmol) was added. The mixture was stirred for 2 h at r.t., after which ammonium hexafluorophosphate (4.6 mg, 0.028 mmol) was added and the resultant solution stirred for a further 1 h. A precipitate formed was filtered off, dried in vacuo over anhidrous $CaCl_2$, and the desired complex recrystallized from chloroform–*n*-hexane as yellow crystals. Yield: 50% (20.2 mg). Anal. Found: C, 49.0; H, 4.4; N, 4.1%. $C_{29}H_{34}F_6N_2OP_2Pd$ requires: C, 49.2; H, 4.7; N, 4.0. IR: ν(C=N): 1622sh, m, ν(C=O): 1698s. FAB-Mass: 563 $[M]^+$, 534 $[M-COH]^+$, 480 $[M-Cy]^+$, 291 $[(L-COH)Pd]^+$. ^{1}H-NMR: 9.25 (s, Ha), 8.30 (dd, Hi, ^4J(PHi) = 7.3 Hz, ^5J(HiH7) = 1.0 Hz), 6.74 (d, H3, ^4J(PH3) = 5.9 Hz, ^4J(H3H5) = 1.2 Hz). $^{31}P\{^1H\}$-NMR: 28.29 (s).

4. X-ray crystallographic study

Three-dimensional, room temperature X-ray data were collected on a Siemens Smart CCD diffractometer by the ω scan method using graphite-monochromated Mo–K_α radiation. All the measured reflections were corrected for Lorentz and 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. As the molecule of **2**, which is not centrosymmetric, lies on a symmetry center, it was necessary to postulate a disordered distribution of As and P assuming an occupancy factor which turned out to be 0.5 for both atoms, from the refinement. For complex **4** the O(1) oxygen atom was found to be disordered over two positions. The occupancies of these were tied to give an overall value of 1.0 and then refined taking into account the minor components (final occupancies: 0.5). Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final $R = 0.0525$, 0.0528 and 0.0480 (for complexes **2**, **3** and **4**, respectively, observed data, F) and $wR_2 = 0.1937$, 0.2230 and 0.1235 (for complexes **2**, **3** and **4**, 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 [39].

5. Supporting information available

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 190994, 190995 and 190996 for compounds **4**, **3** and **2**, respectively. Copies of the 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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