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Directed regioselectivity in cyclometallated palladium(II) compounds of N-benzylidenebenzylamines. Crystal and molecular structure of [Pd{3,4-(OCH₂O)C₆H₂C(H)=NCH₂-[3,4-(OCH₂O)C₆H₃]-C2,N}(µ-O₂CMe)]₂

Samuel Castro-Juiz^a, Margarita López-Torres^a, Alberto Fernández^a, Roberto Mosteiro^a, Antonio Suárez^a, José M. Vila^{b,*}, Jesús J. Fernández^{a,*}

^a Departamento de Química Fundamental, Universidad de La Coruña, E-15071 La Coruña, Spain ^b Departamento de Química Inorgánica, Universidad de Santiago de Compostela, E-15782 Santiago de Compostela, Spain

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Abstract

The reaction of the Schiff base ligand $3,4-(OCH_2O)C_6H_3C(H)=NCH_2[3,4-(OCH_2O)C_6H_3]$ (a) with Pd(OAc)₂ yields two endocyclic cyclometallated compounds: [Pd{3,4-(OCH_2O)C_6H_2C(H)=NCH_2[3,4-(OCH_2O)C_6H_3]-C2,N}(\mu-O_2CMe)]_2 (C2,N-bonded) (1a), and [Pd{3,4-(OCH_2O)C_6H_2C(H)=NCH_2[3,4-(OCH_2O)C_6H_3]-C6,N}(\mu-O_2CMe)]_2 (C6,N-bonded) (1b), which may be separated by fractional crystallization. The corresponding cyclopalladated dimers with bridging chloride ligands, 2a, 2b, have been prepared by a metathesis reaction with aqueous sodium chloride. Treatment of the latter compounds with tertiary phosphines in the appropriate molar ratio gave the mono and dinuclear compounds, 3a-8a and 3b-5b, respectively. The structure of compound 1a has been determined by X-ray diffraction analysis. The molecular configuration is a dimeric form of the *anti* isomer with the cyclopalladated moieties in an 'open-book' arrangement linked by two acetate bridging ligands. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: C-H activation; Phosphorus ligands; Palladium; Schiff base

1. Introduction

The last two decades have seen a growing interest in reactions that produce cyclometallated palladium(II) complexes [1] in view of their novel and outstanding applications, for instance the use as intermediates in organic and organometallic synthesis [2], and the design of liquid crystals [3] or antitumor drugs [4]. Therefore, the characterization of new cyclopalladated compounds has been of great interest in a wide variety of areas, and many of them have been described as efficient catalytic materials [5], chiral discriminators in asymmetric synthesis [6] or interesting photochemical reagents [7].

Cyclometallated compounds are usually classified ac-

cording to the metal, the donor atom, or the chelate ring size; by far the most well studied examples are five-membered palladacycles containing nitrogen donor organic substrates [8]. We have been interested in cyclopalladation reactions of differently substituted Schiff base ligands derived from amines [9], diamines [10] and dialdehydes [11] and we have also reported five-membered metallacycles derived from substituted imidazoles [12]. When cyclometallation involves polyfunctional ligands the question of regioselectivity immediately arises. Thus, N-benzylidenebenzylamines may yield either endocyclic or exocyclic compounds, depending on whether or not the C=N group is included in the metallated ring. Endocyclic compounds are obtained when the ortho positions are occupied by hydrogen atoms, whereas exocyclic derivatives are obtained when the *ortho* positions of the benzylidene ring are occupied by halogens, methyl or methoxy groups [13] or when

^{*} Corresponding authors. José M. Vila. Tel.: +34-981-563100 x. 14255; fax: +34-981-595012.

E-mail address: qideport@usc.es (J.M. Vila).

the reaction is carried out via oxidative addition with ligands derived from 2-bromobenzylamine [14].

We have studied the influence of different substituents adjacent to the potential metallation sites [15,16], showing that MeO or OCH_2CH_2O groups hinder direct metallation by palladium(II), in contrast to the less sterically demanding Me or OCH_2O groups which allow attack of the palladium atom at the *ortho* position of the ring substituent.

In the present paper, we report the synthesis and characterization of new examples of mono- and polynuclear cyclometallated compounds of palladium(II) derived from a polyfunctional Schiff base ligand, N-benzylidenebenzylamine (**a**), which may undergo metallation on different carbon atoms.

2. Experimental

2.1. Materials and instrumentation

Solvents were dried according to the standard methods [17]. The following compounds were used as supplied from commercial sources: palladium(II) acetate from Johnson Matthey, PPh₃, P(p-C₆H₄OMe)₃, Ph₂P(p- $C_6H_4NMe_2$), $Ph_2P(CH_2)_4PPh_2$ (dppb), $Ph_2PC_5H_4FeC_5$ -H₄PPh₂ (dppf) and *cis*-Ph₂PCH=CHPPh₂ (*cis*-dppe) from Aldrich-Chemie. Elemental analyses were carried out by the Servicios Generales de la Universidad de La Coruña using a Carlo-Erba elemental analyzer, model 1108. IR spectra were recorded as Nujol mulls or polythene discs on a Perkin-Elmer 1330 spectrophotometer. NMR spectra were obtained as CDCl₃ solutions and referenced to SiMe4 [(1H) and ${}^{13}C{1H}$] or 85% H_3PO_4 (³¹P{¹H}) and were recorded on a Bruker AC 200F spectrometer (200 MHz for ¹H, 81 MHz for ${}^{31}P{}^{1}H$). Mass spectra were obtained in a VG QUAT-TRO mass spectrometer with Cs ion-gun and 3-NBA matrix. Conductivity measurements were made on a CRISON GLP 32 conductivimeter using 10⁻³ mol dm⁻³ solutions in dry acetonitrile.

2.2. Synthesis of 3,4-(OCH_2O) $C_6H_3C(H)=NCH_2-$ [3,4-(OCH_2O) C_6H_3] (a)

The preparation of ligand **a** was performed by heating a chloroform solution of piperonal (2 g, 13.321 mmol) and piperonylamine (2.014 g, 13.323 mmol) in a Dean–Stark apparatus under reflux. Yield: 85.0%. *Anal.* Found: C, 68.0; H, 4.5; N, 5.0. Calc.: C, 67.8; H, 4.6; N, 4.9%. IR: v(C=N) 1635s cm⁻¹. ¹³C{¹H} NMR: δ 160.8 (C=N); 149.9, 148.3 (C3, C4); 147.7, 146.5 (C9, C10); 133.4 (C7); 131.0 (C1); 124.5 (C5); 121.0 (C11); 108.6, 108.2 (C8, C12); 108.0, 106.7 (C2, C6); 104.4, 100.9 (OCH₂O); 64.5 (NCH₂). m/z (FAB): 282 [M⁺].

2.3. Synthesis of the complexes

2.3.1. Synthesis of $[Pd{3,4-(OCH_2O)C_6H_2C(H)=NCH_2-[3,4-(OCH_2O)C_6H_3]-C2,N}(\mu-O_2CMe)]_2$ (**1a**) and $[Pd{3,4-(OCH_2O)C_6H_2C(H)=NCH_2[3,4-(OCH_2O)-C_6H_3]-C6,N}(\mu-O_2CMe)]_2$ (**1b**)

 $3,4-(OCH_2O)C_6H_3C(H)=NCH_2[3,4-(OCH_2O)C_6H_3]$ (0.640 g, 2.249 mmol) and palladium(II) acetate (0.500 g, 2.227 mmol) were added to 25 cm³ of dry toluene to give a yellow solution which was heated at 80°C for 3 h under argon. After cooling to room temperature (r.t.) the solution was filtered to eliminate the small amount of black palladium formed. The solvent was removed under vacuum and the product recrystallized from chloroform-*n*-hexane to give a mixture of 1a-1b in 20:1 molar ratio. Both compounds could be obtained in pure form from the mixture by fractional crystallization. The mixture was dissolved in 50 cm³ of warm dichloromethane, filtered, n-hexane carefully added and the resultant solution slowly evaporated. The yellow crystals formed were filtered to give compound 1a. The mother liquor was evaporated to dryness to give a mixture of **1a**-**1b** in 2:1 molar ratio and the residue was added to a mixture of dichloromethane-n-hexane, kept at -15° C for 48 h and filtered, yielding a further batch of compound 1a as a crystalline precipitate and a solution from which compound 1b was obtained after solvent elimination. Overall yield: 80%. Anal. Found: C, 48.3; H, 3.5; N, 3.2. Calc.: C, 48.2; H, 3.4; N, 3.1%. IR (1a): v(C=N) 1607s, $v_{as}(COO)$ 1580m; $v_{s}(COO)$ 1425m,sh cm⁻¹. IR (1b): v(C=N) 1610s, $v_{as}(COO)$ 1580m; v_s (COO) 1430m,sh cm⁻¹. ¹³C{¹H} NMR (1a): δ 182.2 (O₂CMe); 171.4 (C=N); 151.5 (C2); 148.5 (C3); 147.9 (C4); 147.4 (C9); 141.7 (C10); 128.5 (C7); 128.0 (C1); 123.4, 123.2 (C5, C11); 109.9, 108.4 (C8, C12); 104.3 (C6); 101.1, 100.3 (OCH₂O); 60.4 (NCH₂); 23.4 (O_2CMe) . ¹³C{¹H} NMR (1b): δ 181.8 (O_2CMe); 170.2 (C=N); 151.3 (C6); 147.2 (C3); 147.5(C4); 144.7 (C9); 142.1 (C10); 137.8 (C1); 128.7 (C7); 123.1 (C11); 112.3 (C5); 106.8 (C2); 100.7 (OCH₂O); 60.5 (NCH₂); 23.3 (O_2CMe) . m/z (FAB) (1a): 837 [M⁺ – OAc], 388 [(L– H)Pd⁺]. m/z (FAB) (1b): 837 [M⁺ – OAc], 388 [(L– H)Pd⁺].

2.3.2. Synthesis of $[Pd\{3,4-(OCH_2O)C_6H_2C(H)=NCH_2-[3,4-(OCH_2O)C_6H_3]-C2,N\}(\mu-Cl)]_2$ (2a)

Aqueous sodium chloride (ca. 10^{-2} M) was added dropwise to **1a** (0.400 g, 0.446 mmol) in acetone (ca. 20 cm³). The mixture was stirred for 24 h after which a yellow solid precipitated which was filtered off, washed with water and cold acetone and dried in vacuo. Yield: >95%. *Anal.* Found: C, 45.2; H, 3.0; N, 3.2. Calc.: C, 45.3; H, 2.9; N, 3.3%. IR: ν (C=N) 1605s, ν (Pd-Cl_{trans-N}) 325m, ν (Pd-Cl_{trans-C}) 290m cm⁻¹.

Compound **2b** was prepared similarly and isolated as a solid. [Pd{3,4-(OCH₂O)C₆H₂C(H)=NCH₂[3,4-(OCH₂-

O)C₆H₃]-C6,N}(μ -Cl)]₂ (**2b**). Yield: 89.4%. Anal. Found: C, 45.1; H, 3.0; N, 3.4. Calc.: C, 45.3; H, 2.9; N, 3.3%. IR: ν (C=N) 1607s, ν (Pd-Cl_{trans-N}) 320m, ν (Pd-Cl_{trans-C}) 290m cm⁻¹.

2.3.3. Synthesis of $[Pd{3,4-(OCH_2O)C_6H_2C(H)=NCH_2-[3,4-(OCH_2O)C_6H_3]-C2,N}(PPh_3)(Cl)]$ (3a)

To a solution of **2a** (50 mg, 0.059 mmol) in acetone (ca. 15 cm³), PPh₃ (31 mg, 0.118 mmol) was added. The mixture was stirred for 3 h at r.t., after which the precipitate formed was filtered off, washed with cold acetone and dried in vacuo. Yield: 81.1%. *Anal.* Found: C, 59.2; H, 3.9; N, 2.1. Calc.: C, 59.5; H, 4.0; N, 2.0%. IR: v(C=N) 1610s, v(Pd-Cl) 280m cm⁻¹. m/z (FAB): 650 [M⁺ - Cl].

Compounds 4a, 5a, 3b and 4b were prepared similarly and isolated as solids.

[Pd{3,4-(OCH₂O)C₆H₂C(H)=NCH₂[3,4-(OCH₂O)-C₆H₃]-*C*2,*N*}{P(p-OMeC₆H₄)₃}(Cl)] (**4a**). Yield: 78.0%. *Anal.* Found: C, 57.4; H, 4.2; N, 1.9. Calc.: C, 57.2; H, 4.3; N, 1.8%. IR: ν (C=N) 1602s, ν (Pd–Cl) 285m cm⁻¹.

[Pd{3,4-(OCH₂O)C₆H₂C(H)=NCH₂[3,4-(OCH₂O)-C₆H₃]-*C*2,*N*}{P(*p*-NMe₂C₆H₄)Ph₂}(Cl)] (**5a**). Yield: 75.9%. *Anal.* Found: C, 59.5; H, 4.5; N, 4.0. Calc.: C, 59.3; H, 4.4; N, 3.8%. IR: v(C=N) 1605s, v(Pd-Cl) 275m cm⁻¹.

[Pd{3,4-(OCH₂O)C₆H₂C(H)=NCH₂[3,4-(OCH₂O)-C₆H₃]-*C*6,*N*}{P(p-OMeC₆H₄)₃}(Cl)] (**3b**). Yield: 80.2%. *Anal.* Found: C, 56.9; H, 4.4; N, 1.9. Calc.: C, 57.2; H, 4.3; N, 1.8%. IR: v(C=N) 1610s, v(Pd–Cl) 280m cm⁻¹.

[Pd{3,4-(OCH₂O)C₆H₂C(H)=NCH₂[3,4-(OCH₂O)-C₆H₃]-*C*6,*N*}{P(*p*-NMe₂C₆H₄)Ph₂}(Cl)] (**4b**). Yield: 79.0%. *Anal.* Found: C, 59.1; H, 4.6; N, 3.9. Calc.: C, 59.3; H, 4.4; N, 3.8%. IR: v(C=N) 1610s, v(Pd-Cl) 275m cm⁻¹.

2.3.4. Synthesis of [$Pd{3,4-(OCH_2O)-C_6H_2C(H)=NCH_2[3,4-(OCH_2O)C_6H_3]-C2,N}(Cl)$ }_- { μ -Ph_2P(CH_2)_4PPh_2] (6a)

To a solution of **2a** (50 mg, 0.059 mmol) in acetone (ca. 15 cm³), dppb (25 mg, 0.059 mmol) was added. The mixture was stirred for 8 h at r.t., after which the precipitate formed was filtered off, washed with cold acetone, dried in vacuo, and recrystallized from dichloromethane–*n*-hexane. Yield: 84.9%. *Anal.* Found: C, 56.7; H, 3.9; N, 2.3. Calc.: C, 56.5; H, 4.1; N, 2.2%. IR: v(C=N) 1600s, v(Pd-Cl) 280m cm⁻¹. m/z (FAB): 1239 [M⁺ – Cl], 957 [M⁺ – (L–H)–Cl], 815 [(L–H)Pd(PP)⁺], 532 [Pd(PP)⁺].

Compound 7a was prepared similarly and isolated as a solid.

[{Pd{3,4-(OCH₂O)C₆H₂C(H)=NCH₂[3,4-(OCH₂O)-C₆H₃]-*C*2,*N*}(Cl)}₂(μ -Ph₂PC₅H₄FeC₅H₄-PPh₂)] (7**a**). Yield: 79.3%. *Anal.* Found: C, 56.8; H, 3.9; N, 1.9. Calc.: C, 56.5; H, 3.7; N, 2.0%. IR: ν (C=N) 1605s, ν (Pd-Cl) 275m cm⁻¹. 2.3.5. Synthesis of $[Pd{3,4-(OCH_2O)C_6H_2C(H)=NCH_2-[3,4-(OCH_2O)C_6H_3]-C2,N}{cis-Ph_2PCH=CHPPh_2-P,P'}](ClO_4)$ (8a)

To a solution of **2a** (35 mg, 0.041 mmol) in acetone (ca. 15 cm³), *cis*-dppe (33 mg, 0.083 mmol) was added. The mixture was stirred for 1 h at r.t., and sodium perchlorate (22 mg, 0.084 mmol) was added. The resulting mixture was stirred for 1 h, and water added dropwise until a precipitate formed, which was filtered off, washed with water, cold acetone and ethanol, dried in vacuo, and recrystallized from chloroform–*n*-hexane. Yield: 92.4%. *Anal.* Found: C, 56.8; H, 4.0; N, 1.7. Calc.: C, 57.0; H, 3.9; N, 1.6%. IR: v(C=N) 1610s cm⁻¹. m/z (FAB): 785 [M⁺], 502 [Pd(PP)⁺].

Compound **5b** was prepared similarly and isolated as a solid.

[Pd{3,4-(OCH₂O)C₆H₂C(H)=NCH₂[3,4-(OCH₂O)-C₆H₃]-*C*6,*N*}{*cis*-Ph₂PCH=CHPPh₂-*P*,*P'*}](ClO₄) (**5b**). Yield: 83.7%. *Anal.* Found: C, 56.9; H, 4.0; N, 1.8. Calc.: C, 57.0; H, 3.9; N, 1.6%. IR: v(C=N) 1610s cm⁻¹. *m*/*z* (FAB): 785 [M⁺], 502 [Pd(PP)⁺].

2.4. Single-crystal X-ray diffraction analysis

Crystal data for **1a**: $C_{36}H_{30}N_2O_{12}Pd_2 \cdot CH_2Cl_2$, $M_r =$ 980.35, crystal dimensions $0.40 \times 0.20 \times 0.20$ mm, a =b = 12.994(1),12.590(1), c = 13.733(1)А, $\alpha = 68.769(1)^{\circ}, \quad \beta = 73.559(1)^{\circ}, \quad \gamma = 65.011(1)^{\circ}, \quad V =$ 1875.65(2) Å³, μ (Mo K α) = 1.168 mm⁻¹, λ = 0.71073 Å, Z = 2, T = 293(2) K, triclinic, space group $P\overline{1}$. Crystal structure determination: three-dimensional, room temperature X-ray data were collected in the range $1.61 < \theta < 28.31^{\circ}$ on a Siemens Smart CCD diffractometer by the ω scan method using graphitemonochromated Mo Ka radiation. Of the 13042 reflections measured, all of which were corrected for Lorentz and polarization effects and for absorption by semi-empirical methods based on symmetry-equivalent and repeated reflections [minimum and maximum transmission coefficients 0.800, 0.652], 6908 independent reflections exceeded the significance level |F|/ $\sigma(|F|) > 4.0$. The structure was solved by direct methods and refined by full matrix least squares on F^2 . Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final R = 0.0500 (observed data, F) and $wR_2 = 0.1281$ (8980 unique data, F^2), with allowance for thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density were -1.271 and 1.184e $Å^{-3}$. The structure solution and refinement were carried out using the program package SHELX-97 [18].

3. Results and discussion

For the convenience of the reader the compounds and reactions are shown in Schemes 1-3. The com-

pounds described in this paper were characterized by elemental analysis (C, H, N) and by IR (data in Section 2) and by ¹H and ³¹P{¹H} NMR spectroscopy (Table 1) and (in part) by ¹³C{¹H} NMR spectroscopy and mass spectrometry (Section 2).

Reaction of the Schiff base ligand 3,4-(OCH₂O)- $C_6H_3C(H)=NCH_2[3,4-(OCH_2O)C_6H_3]$ (a) with palladium(II) acetate in toluene at 80°C for 3 h gave a yellow solid as a mixture of two products, both of which are five-membered endo-palladacycles: [Pd{3,4-(OCH₂O)- $C_6H_2C(H) = NCH_2[3, 4-(OCH_2O)C_6H_3] - C2, N \{(\mu - O_2 - O_2) - O_2(H_2O_2) - O_2$ CMe_{2} (1a), and $[Pd_{3,4-}(OCH_{2}O)C_{6}H_{2}C(H)=NCH_{2} [3,4-(OCH_2O)C_6H_3]-C6,N\{(\mu-O_2CMe)\}_2$ (1b), in 20:1 (1a-1b) molar ratio, showing C(2)-H and C(6)-H activation, respectively (see Scheme 1). These results, together with our previous findings [15,16], allow us to confirm unambiguously that the OCH₂O moiety is not only a weak sterically demanding group, as opposed to the bulkier OCH₂CH₂O substituent which imposes metallation at the C6 atom exclusively, but also that it seems to direct metallation preferably at the C2 carbon atom. Furthermore, in the present case we have successfully achieved total separation of both isomers in pure form by fractional crystallization from dichloromethane–*n*-hexane.

The shift of the C=N stretch towards lower wavenumbers, as compared to **a** (ca. 1610 vs. 1635 cm⁻¹), indicates *N*-coordination of the C=N group [19]. The HC=N proton resonance in the ¹H NMR spectra is upfield shifted by ca. 1.2 ppm from its position in the free ligand, in accordance with Pd–N bonding. Previous studies [20] have shown that for cyclometallated complexes derived from Schiff bases, the position of the imine proton is also indicative of the conformation of the ligand in the complexes. In the present paper the δ (HC=N)_{complexes} < δ (HC=N)_{free ligand}, which suggests that the ligand adopts the *anti*-form in the palladacycles. The C(2)–H (**2a**) and C(6)–H (**2b**) proton resonances are absent showing metallation of the C(2) and C(6) atoms, respectively.

Complexes **1a** and **1b** react with aqueous sodium chloride to give $[Pd{3,4-(OCH_2O)C_6H_2C(H)=NCH_2-}$

[3,4-(OCH₂O)C₆H₃]-*C*2,*N*}(μ -Cl)]₂ (**2a**) and [Pd{3,4-(OCH₂O)C₆H₂C(H)=NCH₂[3,4-(OCH₂O)C₆H₃]-*C*6,*N*}-(μ -Cl)]₂ (**2b**), respectively, with exchange of the acetatebridging groups by chloride-bridging ligands. The IR spectra showed the absence of the acetate bands and the appearance of two *v*(Pd-Cl) bands, consistent with an asymmetric Pd₂Cl₂ bridging unit [21].

Treatment of **2a** or **2b** with tertiary monophosphines in 1:2 molar ratio gave the mononuclear derivatives [Pd{3,4-(OCH₂O)C₆H₂C(H)=NCH₂[3,4-(OCH₂O)C₆- H_3 (PR₃)(Cl)] (3a-5a and 3b-4b, respectively) after cleavage of the Pd₂Cl₂ moiety, which were fully characterized (see Section 2). The IR spectra show a band at ca. 280 cm⁻¹ assigned to the v(Pd–Cl) stretching vibration consistent with a trans-Cl-Pd-C geometry [22]. The ¹H NMR spectra showed the HC=N proton resonance coupled to the phosphorus atom $[{}^{4}J(PH5)$ ca. 8.0 Hz]. For complexes 3a-5a, the OCH₂O resonance was strongly shifted to lower frequency, ca. 1.00 ppm, due to the shielding effect of the phosphine phenyl rings. This is in accordance with a P trans to N arrangement and within the terms of the 'transphobic effect' as coined by Vicente et al. [23]. For complexes 3b and 4b the H5 resonance was coupled to the phosphorus atom $[{}^{4}J(\text{PH5}) = 7.8 \text{ Hz}]$, thus confirming the *cis* geometry of the phosphine and of the metallated phenyl group. The ³¹P{¹H} NMR spectra showed a singlet resonance in all cases, shifted to higher frequency from the free phosphine, in agreement with phosphorus coordination to metal center [24].

The reaction of **2a** with dppb and dppf in 1:1 molar ratio afforded the dinuclear complexes [{Pd[3,4-(OCH₂O)C₆H₂C(H)=NCH₂[3,4-(OCH₂O)C₆H₃]-*C*2,*N*]-(Cl)₂(μ -Ph₂PR-PPh₂)] (**6a** [R = (CH₂)₄] and **7a** [R = C₃H₄FeC₅H₄]), respectively, which were fully characterized (see Section 2). The phosphorus resonance in the ³¹P{¹H} NMR spectra was a singlet showing the equivalence of the two phosphorus nuclei. The MS-FAB spectrum of complex **6a** shows, among others, a peak assigned to [M⁺ - Cl] ions, thereby confirming the dinuclear nature of these complexes [25].



Scheme 1.

Table 1 ¹H^a and ³¹P{¹H}^b NMR data^c

	$\delta(\mathrm{Hi})$	$\delta(\text{H2})$	$\delta({ m H5})$	$\delta({ m H6})$	$\delta(\text{NC}H_2)$	$\delta(\text{OC}H_2\text{O})$	$\delta(\mathbf{P})$
a ^d	8.24t, ${}^{4}J(\text{HiNCH}_{2}) = 1.5$	7.41d, ${}^{4}J(\text{H2H6}) = 1.9$	6.83d, ${}^{3}J(\text{H5H6}) = 8.3$	7.13dd	4.69d	5.99s, 5.94s	
1a °	7.05t, ${}^{4}J(\text{HiNCH}_{2}) = 1.5$		6.54d, ${}^{3}J(\text{H5H6}) = 8.3$	6.71d	4.53d, 3.99d, $J_{row} = 15.6$	5.95s, 5.89d, 5.79d, $J_{\text{corr}} = 1.5$	
$1b^{\rm f}$	7.02t, ${}^{4}J(\text{HiNCH}_{2}) = 1.5$	6.64s	6.62s		0	5.96s, 5.92d, 5.89d, $J_{acm} = 1.5$	
2a ^g	7.51b		6.51d, ${}^{3}J(\text{H5H6}) = 7.8$	6.80d	4.68b	5.97s, 5.94s	
3a h	7.87dt, ${}^{4}J(PHi) = 7.8$, ${}^{4}J(HiNCH_{2}) = 1.5$		6.42d, ${}^{3}J(\text{H5H6}) = 7.8$	6.88d	5.09b	5.97s, 4.61s	37.9s
4a ⁱ	7.83dt, ${}^{4}J(PHi) = 8.3$, ${}^{4}J(HiNCH_{2}) = 1.5$		6.42d, ${}^{3}J(\text{H5H6}) = 7.8$	6.88d	5.05b	5.96s, 4.70s	30.0s
5a ^j	7.83dt, ${}^{4}J(PHi) = 7.8$, ${}^{4}J(HiNCH_{2}) = 1.5$		6.40d, ${}^{3}J(\text{H5H6}) = 7.8$	6.87d	5.09b	5.96s, 4.65s	35.7s
6a ^k	0		6.38d, ${}^{3}J(\text{H5H6}) = 7.8$	6.85d	5.05b	5.93s, 4.70s	30.0s
7a ¹	7.88d, ${}^{4}J(\text{PHi}) = 7.8$		6.39d, ${}^{3}J(\text{H5H6}) = 7.8$	6.89d	4.95b	5.90s, 4.62s	27.5s
8a m	8.00dt, ${}^{4}J(PHi) = 7.8, 1.5,$ ${}^{4}J(HiNCH_{2}) = 1.5$		6.55d, ${}^{3}J(\text{H5H6}) = 7.8$	7.09d, ${}^{5}J(PH6) = 2.3$	4.49b	5.94s, 5.06s	62.4d ^p , 54.5d, ${}^{3}J(PP) = 11.0$
2b ⁿ	7.53d, ${}^{4}J(PHi) = 7.7$	6.69s	6.68s		4.69b	5.96s, 5.92s	
3b ⁿ	7.76dt, ${}^{4}J(\text{PHi}) = 7.8$, ${}^{4}J(\text{HiNCH}_{2}) = 1.5$	6.72s	6.39d, ${}^{4}J(\text{PH5}) = 7.8$		4.90b	5.94s, 5.71s	39.20s
4b ⁿ	7.75dt, ${}^{4}J(\text{PHi}) = 7.8$, ${}^{4}J(\text{HiNCH}_{2}) = 1.5$	6.71s	6.38d, ${}^{4}J(\text{PH5}) = 7.8$		4.91b	5.97s, 5.70s	40.94s
5b ⁿ	7.60d, ${}^{4}J(PHi) = 7.6$	6.90d, ${}^{5}J(PH2) = 2.3$	6.28dd, ${}^{4}J(PH5) = 5.5, 2.3 \text{ q}$		4.46b	5.83s, 4.99s	$63.9d^{\text{p}}$, $53.1d$, ${}^{3}J(\text{PP}) = 11.1$

^a In CDCl₃. Measured at 200 MHz (ca. 20 °C), chemical shifts (δ) in ppm (± 0.01) to high frequency of SiMe₄.

^b In CDCl₃. Measured at 81 MHz (ca. 20 °C), chemical shifts (δ) in ppm (\pm 0.01) to high frequency of 85% H₃PO₄.

^c Coupling contants in Hz; s, singlet; d, doublet, dd, doublet of doublets, t, triplet; dt, doublet of triplets; b, broad; m, multiplet, ^d δ (H8, H11, H12) = 6.80m.

 $^{\circ}\delta(\text{H8}) = 6.31d, {}^{4}J(\text{H8H12}) = 1.5; \delta(\text{H11}) = 6.73d, {}^{3}J(\text{H11H12}) = 7.8; \delta(\text{H12}) = 6.44dd; \delta(MeCO_2) = 2.09s.$

 $^{f}\delta(H8) = 6.26d, {}^{4}J(H8H12) = 1.5; \delta(H11) = 6.73d, {}^{3}J(H11H12) = 7.8; \delta(H12) = 6.37dd; \delta(MeCO_2)$ occluded.

 ${}^{g}\delta$ (H8, H11, H12) = 6.81m.

^h $\delta(\text{H8}) = 6.86\text{d}, \ ^4J(\text{H8H12}) = 1.5; \ \delta(\text{H11}) = 6.80\text{d}, \ ^3J(\text{H11H12}) = 7.8; \ \delta(\text{H12}) = 6.92\text{dd}.$

 ${}^{i}\delta(H8) = 6.99d, {}^{4}J(H8H12) = 1.5; \delta(H11) = 6.78d, {}^{3}J(H11H12) = 7.8; \delta(H12) = 6.95dd; \delta(OMe) = 3.80s.$

 ${}^{j}\delta(H8) = 6.94d$, ${}^{4}J(H8H12) = 1.5$; $\delta(H11) = 6.83d$, ${}^{3}J(H11H12) = 7.8$; $\delta(H12) = 6.65dd$; $\delta(NMe_{2}) = 2.99s$.

^k $\delta(H8) = 7.00d$, ⁴J(H8H12) = 1.5; $\delta(H11) = 6.79d$, ³J(H11H12) = 7.8; $\delta(H12) = 6.89dd$.

 $^{1}\delta(\text{H8}) = 6.94d, ^{4}J(\text{H8}\text{H12}) = 1.5; \delta(\text{H11}) = 6.77d, ^{3}J(\text{H11}\text{H12}) = 7.8; \delta(\text{H12}) = 6.86dd; \delta(\text{C}_{\varsigma}H_{4}) = 5.05d, 4.41d, ^{3}J(\text{H}_{\alpha}\text{H}_{\beta}) = 2.9 \text{ Hz}.$

 ${}^{m}\delta(H8) = 6.25d, {}^{4}J(H8H12) = 1.5; \delta(H11) = 6.68d, {}^{3}J(H11H12) = 7.8; \delta(H12) = 6.40dd; \delta(HC = CH)$ occluded.

ⁿ δ (H8), δ (H11), δ (H12) occluded; δ (OMe) = 3.82s (**3b**); δ (NMe₂) = 3.01s (**4b**); δ (HC=CH) occluded (**5b**).

° Occluded.

$${}^{\mathrm{p}} \delta(\mathbf{P}_{trans-\mathbf{N}}) > \delta(\mathbf{P}_{trans-\mathbf{C}}).$$

 $^{q} {}^{4}J(P_{trans}H) > {}^{4}J(P_{cis}H).$

S



Scheme 2. (i) NaCl, Me_2CO-H_2O . (ii) PPh₃ (**3a**), $P(p-C_6H_4OMe)_3$ (**4a**), $PPh_2(p-C_6H_4NMe_2)$ (**5a**) (1:2 molar ratio), Me_2CO . (iii) dppb (1:1 molar ratio), Me_2CO . (iv) dppf (1:1 molar ratio), Me_2CO . (v) *cis*-dppe (1:2 molar ratio), $NaClO_4$, Me_2CO-H_2O .

Treatment of the chlorine-bridged complexes **2a** and **2b** with *cis*-dppe in 1:2 molar ratio and sodium perchlorate yielded the mononuclear cyclometallated compounds $[Pd{3,4-(OCH_2O)C_6H_2C(H)=NCH_2[3,4-(OCH_2O)C_6H_3]}{cis-Ph_2PCH=CHPPh_2-P,P'}](ClO_4)$ (**8a** (*C2,N*-bonded) and **5b** (*C6,N*-bonded)), respectively. The MS-FAB spectra showed similar fragmentation patterns, containing peaks assigned to $[M^+]$ and $[M^+ - diphosphine]$ ions. The conductivity data (125– 150 Ω^{-1} cm² mol⁻¹ in 10⁻³ mol dm⁻³ solutions in dry acetonitrile) showed them to be 1:1 electrolytes [26]. The HC=N resonance in the ¹H NMR spectra at ca. 7.60 ppm appeared as a doublet due to coupling with the ³¹P nucleus [⁴*J*(PHi) = 7.6 Hz] *trans* to nitrogen. For complex **8a**, long-range coupling was observed for the H6 resonance, which appeared as a doublet by coupling to the phosphorus atom *trans* to the metallated carbon atom [${}^{5}J(PH6) = 2.3$ Hz]. For complex **5b**, the H5 resonance in the ${}^{1}H$ NMR spectrum of **5b** appeared as a doublet of doublets by coupling to both phosphorus atoms. Selective decoupling experiments allowed the correct assignment of the corresponding coupling constants [*trans*- ${}^{4}J(PH5) = 5.5$, *cis*- ${}^{4}J(PH5) =$ 2.3 Hz]. The ${}^{31}P{}^{1}H{}$ NMR spectra showed two doublets, indicating the two phosphorus atoms to be non-equivalent in each case. Selective irradiation allowed the assignment of the doublets, in accordance with the assumption that a ligand of greater *trans* influence shifts the resonance of the phosphorus atoms *trans* to it to lower frequency [24].

4. Molecular structure of complex 1a

Suitable crystals of the title compound were grown by slow evaporation of a cooled dichloromethane-nhexane solution of the complex. The numbering scheme is shown in Fig. 1. Crystallographic data and selected bond lengths and angles are listed in Table 2. The crystal structure consists of discrete dinuclear molecules separated by normal van der Waals distances. The molecular configuration is a dimeric form of the *anti* isomer with the cyclopalladated moieties in an 'open book' arrangement linked by two acetate bridging ligands between the palladium atoms, as observed in the related dimers [27]. The species possesses approximate (non-crystallographic) C_2 symmetry with the two-fold axis perpendicular to the Pd–Pd vector. In accordance with the spectroscopic results, the molecular structure of **1a** corresponds to the *endo* isomer in which the palladium atom is bonded to the carbon atom adjacent to the OCH₂O and C=N groups of the benzylidene ring.

The palladium palladium distance is 2.9330(5) Å, which may be regarded as non-bonding (the covalent radius of square-planar Pd(II) has been estimated as approximately 1.31 Å) [28]. Each palladium atom is in a slightly distorted square-planar coordination environment. The coordination sphere around each palladium atom consists of an *ortho* carbon of the phenyl ring, the C=N nitrogen atom, and two oxygen atoms, one from each of the bridging acetate ligands. The angles between adjacent atoms in the coordination sphere are close to the expected value of 90°, in the range 81.2– 94.3°, with the more noticeable distortions in the 'bite' angles C(6)-Pd(1)-N(1) and C(26)-Pd(2)-N(2), 81.2(2)° consequent upon chelation.

The palladium-nitrogen bond lengths [Pd(1)-N(1) = 2.009(4) and Pd(2)-N(2) = 2.005(4) Å] are in



Scheme 3. (i) NaCl, Me_2CO-H_2O . (ii) $P(p-C_6H_4OMe)_3$ (**3b**), $PPh_2(p-C_6H_4NMe_2)$ (**4b**) (1:2 molar ratio), Me_2CO . (iii) *cis*-dppe (1:2 molar ratio), NaClO₄, Me_2CO-H_2O .



Fig. 1. Labeling of atoms in $[Pd-{3,4-(OCH_2O)C_6H_2C(H)=NCH_2(3,4-{OCH_2O}C_6H_3)-C2,N}(\mu-O_2CMe)]_2$ (1a).

good agreement with the predicted value of 2.01 Å, based on the sum of covalent radii for nitrogen(sp²) and palladium, 0.701 and 1.31 Å, respectively [29]. However, the palladium–carbon bond lengths, [Pd(1)–C(6) = 1.967(5) and Pd(2)–C(26) = 1.964(5) Å], are rather shorter than the predicted value of 2.081 Å, based on the sum of covalent radii for carbon(sp²) and palladium, 0.771 and 1.31 Å, respectively, suggesting some degree of multiple-bond character in the Pd–C(aryl) linkage, as has been observed before [30].

The *trans* influence of σ -bonded carbon is put forward by the lengthening of the palladium-oxygen distances *trans* to carbon [Pd(1)-O(7) = 2.125(3), Pd(2)-O(6) = 2.120(4) Å] as opposed to the shorter Pd-O bond lengths *trans* to nitrogen [Pd(1)-O(5) = 2.033(3), Pd(2)-O(8) = 2.041(3) Å].

As a result of the Pd(1) and Pd(2) atoms being bridged by two mutually *cis* μ -acetate ligands, the chelating *C*,*N* bonded Schiff bases are forced to lie above one another in the dimeric molecule. This leads to interligand repulsions on the 'open' side of the molecule and results in the coordination planes of the palladium atoms being tilted at an angle of 34.6° to one another. The two acetate bridges are separated by dihedral angles of 85.1°.

The cyclometallated moiety is almost planar. The mean deviations from the least squares planes determined by the coordination spheres of palladium (plane 1: Pd1, N1, C6, O5, O7; plane 4: Pd2, N2, C26, O8, O6), the metallacycles (plane 2: Pd1, N1, C7, C1, C6; plane 5: Pd2, N2, C27, C21, C26) and the metallated phenyl rings (plane 3: C1, C2, C3, C4, C5, C6; plane 6: C21, C22, C23, C24, C25, C26) are 0.0295, 0.0380;

0.0071, 0.0061 and 0.0065, 0.0037 Å, respectively. The angles between planes are as follows: plane 1/plane 2 3.9°, plane 1/plane 3 6.4°, plane 2/plane 3 3.8° and plane 4/plane 5 3.8°, plane 4/plane 6 5.2°, plane 5/plane 6 1.4°.

Table 2									
Selected	bond	lengths	(Å)	and	angles	(°)	for	1a	

1.967(5)	Pd(2)–C(26)	1.964(5)				
2.009(4)	Pd(2)-N(2)	2.005(4)				
2.033(3)	Pd(2)-O(8)	2.041(3)				
2.125(3)	Pd(2)–O(6)	2.120(4)				
2.9330(5)						
1.290(6)	N(2)–C(27)	1.276(6)				
1.473(6)	N(2)–C(28)	1.477(6)				
1.383(7)	O(9)–C(24)	1.373(7)				
1.425(10)	O(9)–C(35)	1.400(10)				
1.363(6)	O(10)-C(25)	1.368(7)				
1.420(8)	O(10)-C(35)	1.440(8)				
1.373(7)	O(11)–C(31)	1.366(6)				
1.406(10)	O(11)–C(36)	1.426(8)				
1.378(7)	O(12)–C(32)	1.374(6)				
1.423(11)	O(12)-C(36)	1.422(8)				
1.441(6)	C(21)–C(27)	1.442(7)				
Bond angles						
81.18(17)	C(26)-Pd(2)-N(2)	81.20(18)				
93.98(17)	C(26)-Pd(2)-O(8)	94.32(18)				
174.12(15)	N(2)-Pd(2)-O(8)	175.01(15)				
172.59(16)	C(26)-Pd(2)-O(6)	172.48(16)				
94.07(14)	N(2)-Pd(2)-O(6)	94.25(15)				
90.39(15)	O(8)–Pd(2)–O(6)	89.97(15)				
126.0(6)	C(23)-C(24)-O(9)	125.0(6)				
129.3(5)	O(10)-C(25)-C(26)	128.9(5)				
128.1(5)	O(3)-C(11)-C(10)	127.9(6)				
128.8(5)	C(13)-C(12)-O(4)	127.3(6)				
	$\begin{array}{c} 1.967(5)\\ 2.009(4)\\ 2.033(3)\\ 2.125(3)\\ 2.9330(5)\\ 1.290(6)\\ 1.473(6)\\ 1.383(7)\\ 1.425(10)\\ 1.363(6)\\ 1.420(8)\\ 1.373(7)\\ 1.406(10)\\ 1.378(7)\\ 1.423(11)\\ 1.441(6)\\ \end{array}$	$\begin{array}{llllllllllllllllllllllllllllllllllll$				

5. Supplementary data

Full details of data collection and structure refinement have been deposited with the Cambridge Crystallographic Data Centre, CCDC no.160355 for compound **1a**. 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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