APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. **14**, 634–639 (2000)

Cyclopalladation of Schiff base ligands: crystal and molecular structures of [Pd-{2,4-$(OCH_3)_2C_6H_2C(H)=N(C_6H_{11})$-$C^6$,$N$} ($\mu$-$O_2CCH_3$)]$_2$ and [Pd-{3,4-$(OCH_3)_2C_6H_2C(H)=N(C_6H_{11})$-$C^6$,$N$}($\mu$-$O_2CCH_3$]$_2$†

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X-ray diffraction studies show that the title cyclometallated compounds show each palladium atom *C,N*-bonded to a deprotonated Schiff base ligand. The molecular configuration is a dimeric form of the *anti* isomer with the cyclopalladated moieites in an 'open-book' arrangement linked by two acetate bridging ligands. Copyright © 2000 John Wiley & Sons, Ltd.

Keywords: cyclometallation; Schiff bases; palladium(II); crystal structure

INTRODUCTION

The cyclometallation reaction[1] (together with the associated activation of C–H bonds) has been the subject of a number of review articles,[2] not only because of the importance of these compounds in themselves but also because it has been thoroughly studied by numerous research groups in view of the enormous potential use of the compounds, for example in organic synthesis[3] and catalytic processes,[4] design of new metallomesogens,[5] and characterization of enantiomerically chiral compounds.[6] Recently, new cyclopalladated complexes have been described that exhibit some interesting photochemical and electrochemical properties[7] or which show promising cytotoxic activity by interaction with DNA forming covalent bonds with nucleobases of DNA or acting as intercalation agents.[8] The variety of cyclometallated compounds is such that they may be classified according to the metal, to the donor atom, or to chelate ring size. By far the best-studied examples are five-membered palladacycles with nitrogen as the donor atom.

We have studied the influence of different substituents adjacent to the carbon atom where metallation is possible, as depicted in Fig. 1.[9–11] In the simplest case only one *ortho* C–H bond is present (i), but when there is more than one possible metallation site on the ligand the question of regioselectivity arises. Methoxy groups at the C3 and C5 atoms hinder metallation by palladium(II) at

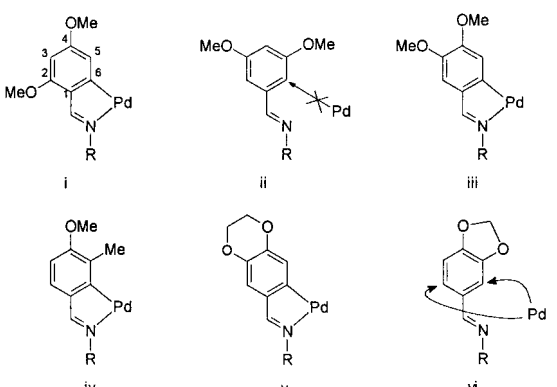

Figure 1 Regioselectivity of cyclometallation reactions.

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† Presented at the XIIIth FECHEM Conference on Organometallic Chemistry, held 29 August–3 September 1999, Lisbon, Portugal

the C2 and at the C6 atoms (ii); with only one methoxy group, in the C3 position, the C6 carbon is selectively metallated (iii), whereas the less sterecally demanding methyl group at the 3 position allows attack of the palladium atom at the C2 atom (iv). The directing effect of different cyclic substituents depends on substituent ring size; benzodioxane derivatives gave only the *ortho* metallation reaction at the C6 atom (v), whereas piperonal derivatives afforded a mixture of the two possible isomers (vi).

EXPERIMENTAL

Solvents were purified and dried according to the standard methods.[12] Palladium(II) acetate was used as supplied from Johnson Matthey. Elemental analyses were carried out by the Servicios Generales de la Universidad de La Coruña using a Carlo-Erba elemental analyser, Model 1108. IR spectra were recorded on a Perkin-Elmer 1330 spectrophotometer. NMR spectra were obtained as $CDCl_3$ solutions and referenced to $SiMe_4$ (^1H and $^{13}C\{^1H\}$) and were recorded on a Bruker AC 200F spectrometer.

Synthetic procedures

Ligands

The preparation of ligand **a** was carried out as described in an earlier paper;[9] ligand **b** was synthesized in a similar fashion.

2,4-$(OCH_3)_2C_6H_3C(H)=N(C_6H_{11})$ (**a**)
IR: ν(C=N) (cm^{-1}) = 1640s. ^1H NMR: δ = 8.64 [s, H1], 7.90 [d, ^3J(H5–H6) = 8.3 Hz, H6], 6.49 [dd, ^4J(H3–H5) = 1.9 Hz, H5], 6.40 [d, H3], 3.82, 3.81 [s, 2-OCH_3, 4-OCH_3]. $^{13}C\{^1H\}$ NMR: δ = 162.6, 159.8 (C2, C4), 154.0 (C=N), 128.4 (C6), 118.3 (C1), 105.1, 97.9 (C3, C5), 55.4, 55.3 (2-OCH_3, 4-OCH_3); C_6H_{11} group δ = 70.2 (C7), 34.5 (C8, C12), 25.6 (C10), 24.9 (C9, C11).

3,4-$(OCH_3)_2C_6H_3C(H)=N(C_6H_{11})$ (**b**)
IR: ν(C=N) (cm^{-1}) = 1635s. ^1H NMR: δ = 8.21 [s, Hi]; 7.41 [d, ^3J(H5–H6) = 8.2 Hz, H2]; 7.13 [dd, ^4J(H2–H6) = 1.9 Hz, H6]; 6.85 [d, H5]; 3.94, 3.90 [s, 3-OCH_3, 4-OCH_3]. $^{13}C\{^1H\}$ NMR: δ = 158.0 (C=N), 150.9, 149.2 (C3, C4), 129.8 (C1), 122.7 (C6), 110.3, 108.8 (C2, C5), 55.9, 55.8 (3-OCH_3, 4-OCH_3); C_6H_{11} group: δ = 69.8 (C7), 36.6 (C8, C12), 26.0 (C10), 25.6 (C9, C11).

Complexes

[Pd{2,4-$(OCH_3)_2C_6H_2C(H)=N(C_6H_{11})$-$C^6N$}($\mu$-$O_2CCH_3$)]$_2$, **1a**
2,4-$(OCH_3)_2C_6H_3C(H)=N(C_6H_{11})$ (0.483 g; 1.952 mmol) and palladium(II) acetate (0.400 g; 1.781 mmol) were added to 25 cm^3 of dry toluene to give a yellow solution, which was heated at 80 °C for 3 h under argon. After being cooled at room temperature 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, washed with cold ethanol and filtered to give the desired complex as yellow microcrystals.

Yield: 92.0%. Analysis: Found: C, 50.5; H, 3.5; N, 5.5. Calod: C, 50.3; H, 3.4; N, 5.6%. IR (cm^{-1}): ν C=N = 1610m, ν_{as}(COO) = 1590m, sh; ν_s(COO) = 1430m, sh. ^1H NMR: δ = 7.57 [s, Hi], 6.20 [d, ^4J(H3–H5) = 1.9 Hz, H3], 6.00 [d, H5], 3.78, 3.73 [s, 2-OCH_3, 4-OCH_3], 2.11 [s, O_2CCH_3]. $^{13}C\{^1H\}$ NMR: δ = 180.4 (O_2CCH_3), 163.7 (C=N), 160.8, 159.0, 157.8 (C2, C4, C6); 127.9 (C1), 108.9, 93.4 (C3, C5), 55.2, 55.1 (2-OCH_3, 4-OCH_3), 24.3 (O_2CCH_3); C_6H_{11} group: δ = 64.1 (C7), 34.6, 30.4, 26.0, 25.7, 25.3 (C8, C9, C10, C11, C12).

Complex **1b**
This was prepared similarly and isolated as yellow crystals.

Yield: 90.5%. Analysis: Found: C, 50.6; H, 3.4; N, 5.4. Calcd: C, 50.3; H, 3.4; N, 5.6%. IR (cm^{-1}): ν(C=N) = 1605s, ν_{as}(COO) = 1580m; ν_s(COO) = 1420m, sh. ^1H NMR: δ = 7.71 [s, Hi], 6.94 [s, H2], 6.77 [s, H5], 3.89, 3.79 [s, 3-OCH_3, 4-OCH_3], 2.16 [s, O_2CCH_3]. $^{13}C\{^1H\}$ NMR: δ = 190.8 (O_2CCH_3), 165.2 (C=N), 150.3, 148.7, 145.6 (C3, C4, C6), 140.7 (C1), 114.0, 109.8 (C2, C5), 56.7, 56.5 (3-OCH_3, 4-OCH_3), 24.4 (O_2CCH_3), C_6H_{11} group: δ = 64.5 (C7), 34.5, 30.3, 26.0, 25.6, 25.4 (C8, C9, C10, C11, C12).

Single-crystal X-ray diffraction analysis

Three-dimensional, room-temperature X-ray data were collected in the θ range 1.51–28.30 ° for **1a** and 1.22–28.33 ° for **1b** on a Siemens Smart CCD diffractometer by the omega scan method. Reflections were measured from a hemisphere of data collected in frames each covering 0.3 ° in omega. Of the 55 087 **1a** and 17 813 **1b** reflections measured, all of which were corrected from Lorentz and polarization effects and for absorption by semi-empirical methods based on symmetry-equivalent

and repeated reflections, 6440 of the **1a** and 8927 of the **1b** 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 of 0.0548 for **1a** and 0.0381 for **1b** (wR_2 = 0.1193, **1a**; 0.1040, **1b** for all 9199 **1a** data and 11477 **1b** data, with 421 **1a** and 523 **1b** parameters; mean and maximum $\delta\sigma$ = 0.000, 0.001) with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density (e A^{-3}), −0.623 for **1a** and −0.673 for **1b**; 0.584 for **1a** and 0.783 for **1b**. The structure solution and refinement were carried out using the *SHELX-97* program package.[13]

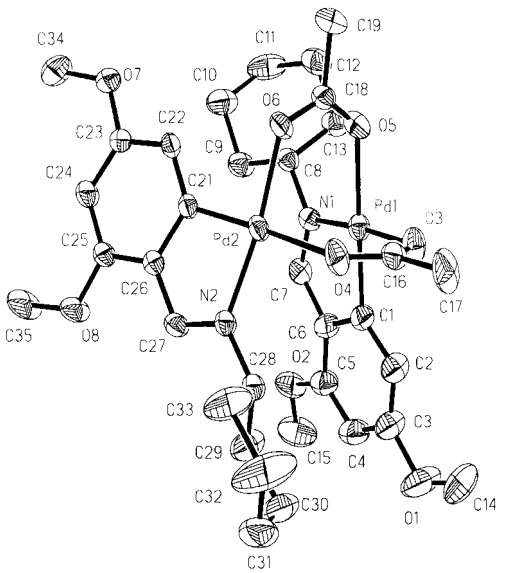


Figure 2 ORTEP projection of [Pd-{2,4-$(OCH_3)_2C_6H_2C(H)$ $=N(C_6H_{11})$-C^6, N}(μ-O_2CCH_3)]$_2$, **1a**.

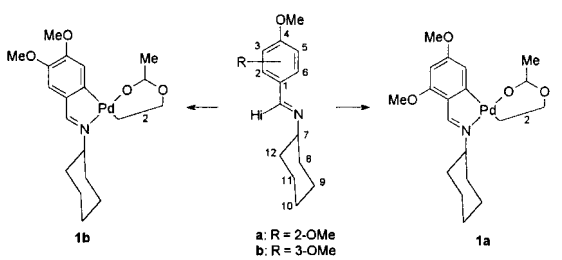
RESULTS AND DISCUSSION

Cyclopalladation reaction

A schematic representation of the synthesis of complexes is given in Scheme 1. The compounds described in this paper were characterized by elemental analysis (C, H, N) and by IR and by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy (data in Experimental section).

Treatment of *N*-(2,4-dimethoxybenzylidene) cyclohexylamine (**a**) and $Pd(OAc)_2$ in toluene at 80 °C for 2 h gave a yellow crystalline solid identified as the cyclometallated product derived from C–H activation at the 6 position (**1a**). The ^{1}H NMR spectrum for **1a** showed two doublets assigned to the H3 and H5 protons [^4J(H3–H5) = 1.9 Hz]. The signal for the H6 nucleus was absent upon metallation at C6, as expected.

In the case of ligand **b**, there are two possible metallation sites, the C2 and C6 atoms, the electrophilic attack[14] of the palladium atom on



Scheme 1 Reaction conditions: $Pd(OAc)_2$, 80 °C, toluene.

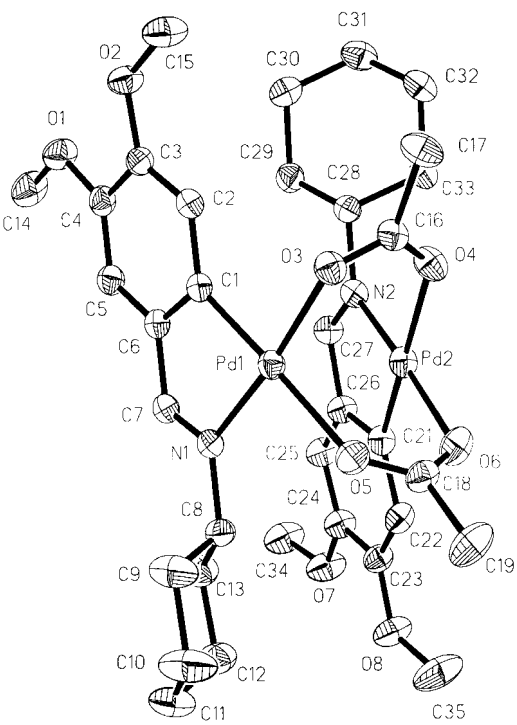


Figure 3 ORTEP projection of [Pd-{3,4-$(OCH_3)_2C_6H_2C(H)$ $=N(C_6H_{11})$-C^6,N}(μ-O_2CCH_3)]$_2$, **1b**.

Table 1 Crystal data and structure refinement

	1a	**1b**·($3HCCl_3$)
Formula	$C_{34}H_{46}N_2O_8Pd_2$	$C_{37}H_{49}N_2O_8Cl_9Pd_2$
M_r	823.53	1181.63
Temperature (°K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Tetragonal	Triclinic
Space group	$P4_12_12$	P-1
Cell dimensions		
a (Å)	14.723(1)	9.163(1)
b (Å)	14.723(1)	16.298(1)
c (Å)	34.144(1)	17.027(1)
α (°)	90	94.435(1)
β (°)	90	99.469(1)
γ (°)	90	103.006(1)
V (Å^3)	7401.7(1)	2426.4(1)
Z	8	2
μ(mm^{-1})	1.020	1.284
Crystal size (mm^3)	0.50 × 0.35 × 0.30	0.55 × 0.45 × 0.20
$2\theta_{max}$ (°)	56.6	56.6
Reflections		
Collected	55087	17813
Unique	9199 (R_{int} = 0.081)	11477 (R_{int} = 0.019)
Transmissions	1.00, 0.59	1.00, 0.70
No. of parameters	421	523
S[a]	1.097	1.030
R [F, $I > 2\sigma(I)$]	0.0548	0.0381
wR [F^2, all data]	0.1193	0.1040
max Δ/σ	0.001	0.001
max ρ (e Å^3)	0.584	0.738

[a] GOF, goodness-of-fit.

either one being influenced by both electronic and steric effects. Palladation may occur at any one of the C2 and C6 atoms, and a mixture of isomers is also possible. The reaction between **b** and $Pd(OAc)_2$ in toluene only gave one product, that derived from C–H activation exclusively at the 6 position (**2b**), and no isomer with the metal bonded to the C2 atom was found. Two singlets were assigned to the H2 and H5 protons in the ^{1}H NMR spectrum for **2b**, and no resonance signal for H6 was observed. We rationalized this behaviour by assuming that the high sterically demanding group 3-OCH_3, in ligand **b**, impedes attack of the palladium atom at the C2 carbon atom; metallation is only produced at the C6 atom.

In the IR spectra of the complexes the ν(C=N) stretching band appeared at lower frequency than the corresponding one in the free imines, in accordance with nitrogen coordination to the metal centre.[15] This was supported by the upfield shift of the NMR signal for the imine proton, by *ca* 1 ppm.[16] The ν_{as}(COO) and ν_s(COO) values were consistent with bridging acetato groups,[17] and the singlet resonance at *ca* 2.00 (6H) in the ^{1}H NMR spectra was assigned to the equivalent methyl acetate protons, consistent with a *trans* geometry of the cyclometallated moieties.[18]

In the $^{13}C\{^1H\}$ spectra of the cyclometallated compounds the resonances for the C=N and for the metallated carbon were shifted towards higher frequency by *ca* 10 ppm compared with the free donors, confirming that metallation had occurred. The singlet resonances at *ca* 24 ppm were assigned to the methyl acetate carbon atoms, consistently with a *trans* geometry of the cyclometallated moieties (*vide supra*).[19]

Molecular structure of complexes 1a and 1b

Suitable crystals were grown by recrystallization from chloroform/n-hexane solution of complexes

Table 2 Selected bond distances (Å) and angles (°) for complexes **1a** and **1b**

	1a	**1b**
Pd(1)–Pd(2)	2.8922(6)	2.8989(3)
Pd(1)–C(1)	1.965(6)	1.957(3)
Pd(1)–N(1)	2.017(5)	2.020(3)
Pd(1)–O(3)	2.034(4)	2.046(2)
Pd(1)–O(5)	2.130(4)	2.139(2)
O(3)–C(16)	1.237(8)	1.254(4)
O(4)–C(16)	1.249(7)	1.247(4)
C(16)–C(17)	1.518(8)	1.509(4)
N(1)–C(7)	1.288(7)	1.457(7)
C(1)–C(6)	1.427(9)	1.400(4)
C(6)–C(7)	1.462(9)	1.442(4)
C(1)-Pd(1)-N(1)	82.0(2)	8.42(11)
C(1)-Pd(1)-O(3)	93.1(2)	91.19(11)
O(3)-Pd(1)-O(5)	88.30(19)	90.69(9)
N(1)-Pd(1)-O(5)	96.61(19)	96.70(10)
Pd(1)-O(3)-C(16)	122.2(4)	120.8(2)
O(3)-C(16)-O(4)	127.5(6)	126.5(3)
C(6)-C(1)-Pd(1)	112.0(5)	112.8(2)
C(7)-N(1)-Pd(1)	113.3(4)	114.0(2)
N(1)-C(7)-C(6)	117.6(6)	116.6(3)
C(1)-C(6)-C(7)	114.7(6)	114.2(3)

1a and **1b**. The schemes used for labelling atoms in the Schiff base complexes are shown in Figs 2 and 3. Crystallographic data and selected bond lengths and angles are listed in Tables 1 and 2. The crystals consist of discrete dinuclear molecules separated by normal van der Waals distances. The species possess approximate (non-crystallographic) C_2 symmetry with the two-fold axis perpendicular to the Pd–Pd vector. The molecular configuration of these species 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 (see Fig. 4).[20]

As a result of Pd(1) and Pd(2) 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 molecules. 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 29.3 ° and 26.1 ° to one another in complexes **1a** and **1b**, respectively. These deviations are clearly illustrated in Fig. 4. The two acetate bridges are separated by dihedral angles of 87.0 ° in **1a** and 79.6 ° in **1b**.

The palladium–palladium distances are 2.8922(6) Å in complex **1a** and 2.8989(3) Å in complex **1b**, which may be regarded as non-bonding; the covalent radius of square-planar palladium(II) has been estimated as aproximately 1.31 Å.[21] Each palladium atom is in a slightly distorted square-planar environment. The coordination sphere around each palladium atom consists of a nitrogen atom of the imine group, an *ortho* carbon of the phenyl ring, and two oxygen atoms (one from each of the bridging acetate ligands). Both Schiff base ligands are bonded through the C6 carbon atom in the complexes, in accordance with the spectroscopic results. The angles between adjacent atoms in the coordination sphere are close to the expected value of 90 °, in the range 81.1–96.5 °, with the distortions more noticeable in the 'bite' angles, which are C1-Pd1-N1 82.0(2) ° in **1a**, and 81.42(11) ° in **1b**.

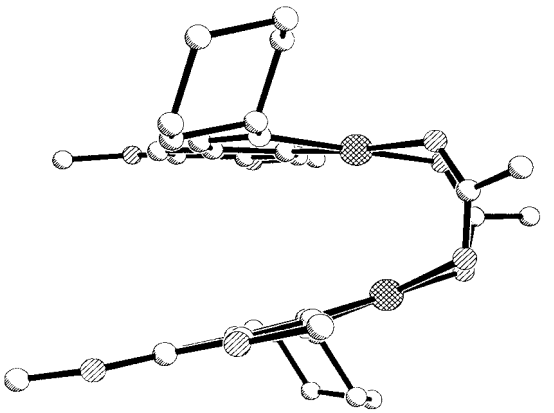


Figure 4 View of complex **1b**, showing the non-parallel nature of the cyclometallated moieties. Complex **1a** is closely similar.

The palladium–carbon bond lengths, Pd1–C1, are 1.965(6) (**1a**) and 1.957(3) Å (**1b**), which are substantially shorter than the predicted 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). This suggests some degree of multiple-bond character in the Pd–C(aryl) linkage. The palladium–nitrogen bond lengths, Pd1–N1, are 2.017(5) Å for **1a** and 2.020(3) Å for **1b**. This is in agreement with the predicted 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.[22]

The *trans* lengthening influence of σ-bonded carbon is clearly illustrated by the lengthening of the palladium–oxygen distance *trans* to carbon, relative to that *trans* to oxygen. Thus, we have Pd1–O5 = 2.130(4) Å vs Pd1–O3 = 2.034(4) Å in com-

plex **1a** and Pd1–O5 = 2.139(2) Å vs Pd1–O3 = 2.046(2) Å in complex **1b**.

Except for the cyclohexyl and methoxy groups, the Schiff base ligand is nearly planar. The mean deviations from the least-squares plane at the phenyl ring [plane 1: C1, C2, C3, C4, C5, C6], the metallacycle [plane 2: Pd1, C1, C6, C7, N1] and the coordination sphere of palladium [plane 3: Pd1, C1, N1, O5, O3] are 0.038, 0.0322 and 0.0189 Å for **1a** and 0.0116, 0.0470 and 0.0204 Å for **1b**, respectively. The angles between planes are as follows: plane 1/plane 2,3.5 °; plane 1/plane 3,5.2 °; plane 2/plane 3,2.4 ° (**1a**), and plane 1/plane 2,5.5 °; plane 1/plane 3,9.4 °; plane 2/plane 3,4.7 ° (**1b**).

SUPPLEMENTARY INFORMATION

Tables of atomic positional and isotropic displacement parameters, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters for the crystal structures of complexes **1a** and **1b** are available on request from the authors.

Acknowledgements We thank the Universidad de la Coruña and the Xunta de Galicia (Spain) (Proyecto XUGA20913B96) for financial support.

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