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Influence of phenyl ring substituents in the cyclometallation of Schiff base ligands: crystal and molecular structures of [Pd-{3,4-(OCH_2O)C_6H_2C(H)=N(Cy)-*C*2,*N*}(μ-O_2CMe)]$_2$ and [Pd-{3,4-(OCH_2CH_2O)C_6H_2C(H)=N(Cy)-*C*6,*N*}(μ-O_2CMe)]$_2$

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Abstract

Reaction of $Pd(OAc)_2$ with the Schiff base ligands 3,4-{$O(CH_2)_nO$}C_6H_3C(H)=NR ($n = 1, 2$; R = Cy, 3,4-(OCH_2O)$C_6H_3CH_2$-) leads to dinuclear cyclometallated products in which each palladium atom is *C*,*N* bonded to a deprotonated organic ligand, and to two acetate groups which bridge both metal centers. Treatment of 3,4-{$O(CH_2)_2O$}C_6H_3C(H)=$NCH_2CH_2NMe_2$ with [$PtMe_2$(COD)] gives mononuclear compounds with the ligand as terdentate through the [C, N, N] atoms. The regioselectivity of the cyclometallation processes is discussed by ^{1}H-NMR spectroscopy and X-ray diffraction studies. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Palladium(II); Platinum(II); Schiff bases; Cyclometallation; Crystal structure

1. Introduction

The reaction that gives cyclometallated palladium(II) complexes — albeit described for the first time more than 25 years ago [1] — has been studied thoroughly since then by numerous research groups in view of the enormous potential use of the compounds in organic synthesis [2], design of new metallomesogens [3] or characterization of enatiomerically chiral compounds [4], among others. Recently, new cyclopalladated complexes have been described that catalyze the Heck olefination [5], that exhibit some interesting photochemical and electrochemical properties [6] or which show promising cytotoxic activity [7]. Cyclometallated compounds are usually classified according to the metal, to the donor atom, or to chelate ring size [8]. By far the most well-studied examples are five-membered palladacycles with nitrogen donor atoms.

When there are more than one possible metallation sites on the ligand the question of regioselectivity arises as we have been reported previously [9,10]. We have studied the influence of different substituents adjacent to the carbon atom where metallation is possible as is depicted in Fig. 1. Methoxy groups at the C3 and C5 atoms hinder direct metallation by palladium(II) at the C2 or at the C6 atoms (i); with only one methoxy group, in the C3 position, the C6 carbon is selectively metallated (ii); whereas the less sterically demanding methyl group allows attack of the palladium atom at the C2 atom in all cases (iii, iv).

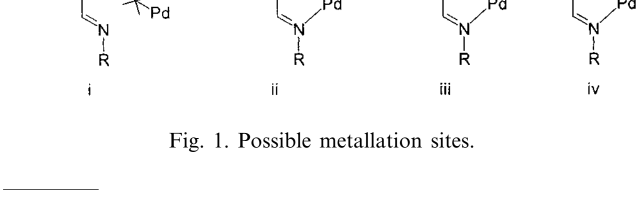

Fig. 1. Possible metallation sites.

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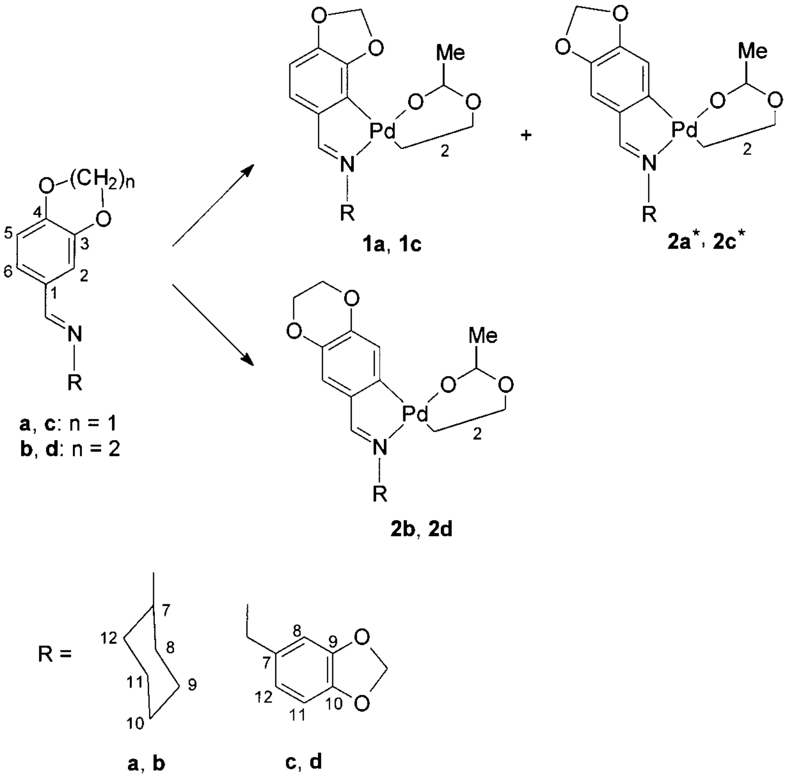


Scheme 1. Condition reactions: $Pd(OAc)_2$, 80°C, AcOH or toluene. *, impurified with **1a** and **1c**, respectively.

Recently, metallation of a methoxy group has been achieved to give cyclometallated complexes with a six-membered metallacycle [11].

Therefore, in view of the influence that methoxy and methyl substituents bear on the metallated ring, we sought out to study the influence that change in the size of the ring attached to the phenyl ring would exert.

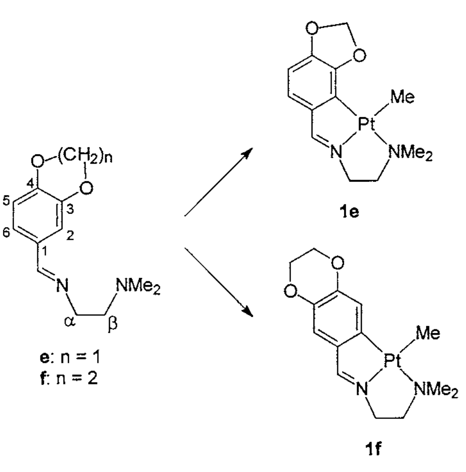
We have shown that in related systems the OCH_2O group does not impede metallation of the phenyl ring by palladium(II) at the *ortho* position of the methylenedioxo group, i.e. C(2), for reasons given earlier [10]. For example, the bidentate Schiff base ligand, in 1,4-{3,4-$(OCH_2O)C_6H_3C(H){=}N{-}\}_2C_6H_4$, double palladation occurred at the carbon atom *ortho* to the OCH_2O group [12]. Platinum(II) seems to show a similar behavior towards the metallation of related systems, as is the case with potentially terdentate ligand 3,4-$(OCH_2O)C_6H_3C(H){=}NCH_2CH_2NMe_2$ where the C2 carbon atom is exclusively platinated [13].

Here we present our results on the synthesis of new cyclometallated compounds derived from Schiff base ligands with two potential metallation sites, in an attempt to study the influence of the cyclic substituent ring size on the potential metallation position of the phenyl ring.

2. Results and discussion

2.1. Cyclometallation reaction

For the convenience of the reader, the compounds and reactions are shown in Schemes 1 and 2. The compounds described in this paper were characterized by elemental analysis (C, H, N) and by IR (data in Section 4) and by ^1H-, and ^{13}C-{^1H}-NMR spectroscopy (Table 1).



Scheme 2. Condition reactions: $PtMe_2(COD)$, 90°C, toluene.

Table 1
^{1}H-NMR [a] data [b,c]

Compound	δ(Hi)	δ(H2)	δ(H5)	δ(H6)	δ(O(CH$_2$)$_n$O)	Others
a	8.18s	7.35d ^{4}J(H2H6) = 1.5	6.80d ^{3}J(H5H6) = 8.0	7.10dd	5.98s	
1a	7.26s		6.47d ^{3}J(H5H6) = 7.7	6.72d	5.93d 5.88d	J(CH$_2$) = 1.1 δ(MeCO$_2$) = 2.03s
2a	7.23s	6.48s	6.52s		5.90d 5.83d	J(CH$_2$) = 1.1 δ(MeCO$_2$) = 2.05s
b	8.18s	7.27d ^{4}J(H2H6) = 1.9	6.87d ^{3}J(H5H6) = 8.3	7.21dd	4.27m	
1b	7.19s	6.48s	6.64s		4.20m	δ(MeCO$_2$) = 2.11s
c [d]	8.24t ^{4}J(HiNCH$_2$) = 1.4	7.41d ^{4}J(H2H6) = 1.9	6.83d ^{3}J(H5H6) = 8.3	7.13dd	5.99s 5.94s	
1c [e]	7.05s		6.54d ^{3}J(H5H6) = 7.8	6.71d	5.94s 5.88d 5.78d	J(CH$_2$) = 1.3 δ(MeCO$_2$) = 2.09s
2c [f]	7.02s	6.61s	6.64s		[g]	[g]
d [h,i]	8.23t ^{4}J(HiNCH$_2$) = 1.4	7.33d ^{4}J(H2H6) = 1.9	6.89d ^{3}J(H5H6) = 8.3	7.26dd	5.94s 4.28m	
1d [h,j]	6.97t ^{4}J(HiNCH$_2$) = 1.5	6.55s	6.66s		5.95m 4.20m	δ(MeCO$_2$) = 2.16s
f [k]	8.17t ^{4}J(Hiα-CH$_2$) = 1.4	7.26d ^{4}J(H2H6) = 1.9	6.86d ^{3}J(H5H6) = 8.3	7.21dd	4.27m	δ(NMe$_2$) = 2.30s
1f [l]	8.39t ^{4}J(Hiα-CH$_2$) = 1.4 N(PtHi) = 59.1	6.99s	6.86d J(PtH5) = 11.2		4.21m	δ(NMe$_2$) = 2.81s J(PtNMe$_2$) = 20.5 δ(PtMe) = 0.86s J(PtMe) = 78.6

[a] In CDCl$_3$. Measured at 200 MHz (ca. 20°C), chemical shifts (δ) in ppm ($\pm$0.01) to high frequency of SiMe$_4$.

[b] Coupling constants in Hz.

[c] s, singlet; d, doublet, dd, doublet of doublets, t, triplet; b, broad; m, multiplet.

[d] δ(NCH$_2$) = 4.69d, δ(H8,H9,H12) = 6.84b, 6.79b.

[e] δ(NCH$_2$) = 4.53d, 3.99d, J(CH$_2$) = 15.6, δ(H8) = 6.31d, ^{4}J(H8H12) = 1.5, δ(H11) = 6.73d, ^{3}J(H11H12) = 7.8, δ(H12) = 6.44dd.

[f] δ(NCH$_2$) = 4.44d, 3.95d, J(CH$_2$) = 15.0, δ(H8) = 6.25d, ^{4}J(H8H12) = 1.5, δ(H11), δ(H12) occluded.

[g] δ(OCH$_2$O), δ(MeCO$_2$) occluded.

[h] δ(OCH$_2$O) > δ(OCH$_2$CH$_2$O).

[i] δ(NCH$_2$) = 4.69d, δ(H8,H9,H12) = 6.83b, 6.78b.

[j] δ(NCH$_2$) = 4.47dd, 4.12dd, J(NCH$_2$) = 16.6, δ(H8) = 6.19d, ^{4}J(H8H12) = 1.4, δ(H11) = 6.76d, ^{3}J(H11H12) = 7.8, δ(H12) = 6.32dd.

[k] δ(α-CH$_2$) = 3.96td, δ(β-CH$_2$) = 2.62t, J(α,β-CH$_2$) = 12.7.

[l] δ(α-CH$_2$) = 3.97td, δ(β-CH$_2$) = 3.11t, J(α,β-CH$_2$) = 11.6.

Reaction of the Schiff base ligands **a** or **c** with palladium(II) acetate in toluene at 80°C for 2 h gave yellow solids identified as mixtures of two products each: one derived from C–H activation at the 2-position (*ortho* to the OCH$_2$O group), **1a**, **1c**, and the other one derived from C–H activation at the 6-position (*meta* to the OCH$_2$O group) **2a**, **2c**. The mixtures are in 2:1 (**1a**/**2a**) and 20:1 (**1c**/**2c**) ratios, as calculated from the integrals in the ^{1}H-NMR spectra. No modification of these ratios was found for shorter reaction times or even when the mixtures were heated for 24 h. The metallation process was repeated for ligand **a** in glacial acetic acid to give an analogous mixture, but in a **1a**/**2a** 9:1 ratio. Attempts to separate the reaction products by chromatographic methods failed, and we only obtained in pure form (as shown by ^{1}H-NMR) isomers **1a** and **1c**, whereas **2a** and **2c** were always contaminated with **1a** and **1c**, respectively. The ^{1}H-NMR spectra for **1a** and **1c** showed two doublets assigned to the H(5) and H(6) protons. The signal for the H(2) nucleus was absent upon metallation at C(2), as expected.

On the other hand, the reaction between ligands **b** or **d** and palladium(II) acetate in toluene or in glacial acetic acid afforded a single product, i.e. the one derived from C–H activation exclusively at the 6-position, **2b** and **2d**, and no isomer with the metal boned to the C(2) atom was found. Two singlets assigned to the H(2) and H(5) protons were observed in the ^{1}H-NMR spectrum for **2b** and **2d**; the resonance for the H(6) proton being absent.

In the IR spectra of the complexes the ν(C=N) stretching band (see Section 4) appeared at lower frequency than the corresponding one in the free imines in accordance with nitrogen coordination to metal center [14]. This was supported by the upfield shift of the HC=N resonance in the ^{1}H-NMR spectra, ca. 1 ppm

[15]. The ν_{as}(COO) and ν_s(COO) values were consistent with bridging acetato groups [16]; the singlet resonance at ca. 2.00 ppm (6H) in the ^{1}H-NMR spectra was assigned to the equivalent methyl acetate protons, consistent with a *trans* geometry of the cyclometallated moieties [17]. The ^{13}C-{^{1}H}-NMR spectra revealed the election of the metallated carbon atom, by the strong downfield shift of the corresponding C2 or C6 carbon resonance to values greater than 140 ppm (see Section 4).

The next step in the comparison of OCH_2O versus OCH_2CH_2O was to change the denticity of the ligand and also the nature of the metal. For potentially terdentate ligands such as 3,4-$(OCH_2O)C_6H_3C(H) = NCH_2CH_2NMe_2$ the reaction with [$PtMe_2$(COD)] gave the complex with platinum(II) bonded to the carbon next to the OCH_2O moiety, as we have reported previously [13]. However, when the related ligand 3,4-$\{O(CH_2)_2O\}C_6H_3C(H)$=$NCH_2CH_2NMe_2$ (**f**), was tested towards metallation by platinum(II), the metal atom only binds to the C(6) carbon atom. Thus, treatment of ligand **f** with [$PtMe_2$(COD)] in toluene gave the mononuclear compound [Pt(3,4-$\{O(CH_2)_2O\}C_6H_3$-C(H)=$NCH_2CH_2NMe_2$,)] (**1f**), as an air-stable orange solid which as fully characterized (see Section 4 and Table 1). The ^{1}H-NMR spectrum contains only one set of signals in accordance with the presence of only one isomer in solution, i.e. the one with the platinated C6 carbon atom. The ^{13}C-{^{1}H}-NMR spectrum showed the strong downfield shift of the C6, C=N and C1 resonances, confirming metallation of the ligand at the C6 carbon atom. Two singlet resonances were assigned to the H2 and H5 protons, at δ 6.99 and 6.86 ppm, respectively, with the latter showing coupling to platinum, ^3J(PtH) = 11.2 Hz. The HC=N and NMe_2 signals also showed coupling to platinum with ^3J(PtH) = 59.1 and 78.6 Hz, respectively. The remaining signals were unequivocally assigned (see Section 4 and Table 1).

2.2. Molecular structure of complexes 1a and 2b

Suitable crystals were grown by recrystallization from chloroform–*n*-hexane solution of complexes **1a** and **2b**. The schemes used for labeling atoms in the Schiff base complex are shown in Figs. 2 and 3. Crystallographic data and selected bond lengths and angles are listed in Tables 2 and 3. The crystals consist of discrete dinuclear molecules separated by normal van der Waals distances. The species possess C_2 symmetry with the twofold 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) [18,19].

The palladium···palladium distances are 2.8653(3) Å in the piperonal derivative (**1a**) and 2.8485(10) Å in the benzodioxan derivative (**2b**), which may be regarded as nonbonding; the covalent radius of square-planar Pd(II) has been estimated as approximately 1.31 Å [20]. Each palladium atom is in a slightly distorted square-planar coordination environment. The coordination sphere around each palladium atom consists of a nitrogen atom of the imine group, a *ortho* carbon of the phenyl ring, and two oxygen atoms (one from each of the bridging acetate ligands). The Schiff base ligands are bonded through the C2 (**1a**) and C6 (**2b**) carbon atoms in the complexes, in accordance with the spectroscopic results. Furthermore, the C(2)–C(3)–O(1) angle of 118.2(7) in **2b** is smaller than the C(2)–C(3)–O(1) angle of 128.2(3) in **1a**, which confirms the steric effect of the OCH_2CH_2O group which impedes the metal to come close to the aromatic C2–H bond of ligand **b**.

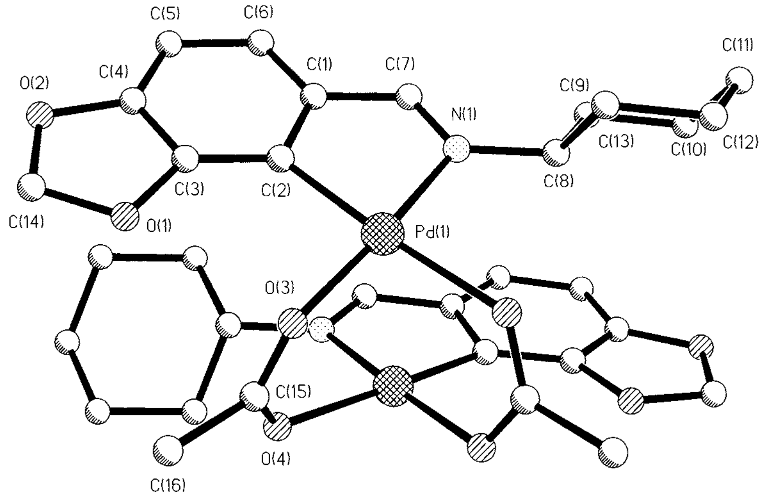


Fig. 2. Labeling of atoms in [Pd-{3,4-$(OCH_2O)C_6H_2C(H)$=N(Cy)-*C*2,*N*}(μ-O_2CMe)]$_2$ (**1a**).

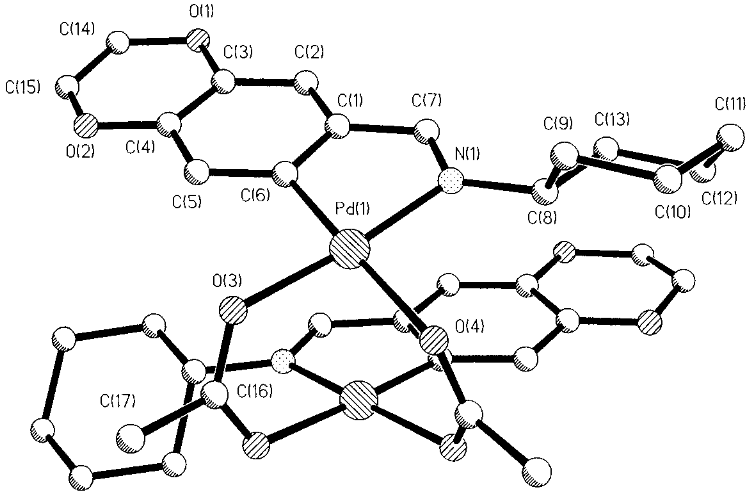


Fig. 3. Labeling of atoms in [Pd-{3,4-$(OCH_2CH_2O)C_6H_2C(H){=}N(Cy)$-*C*6,*N*}($\mu$-$O_2CMe$)]$_2$ (**2b**).

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 C(2)–Pd(1)–N(1), 81.51(9)°, in the piperonal complex and C(6)–Pd(1)–N(1), 81.1(2)°, in the benzodioxan complex.

The palladium–nitrogen bond lengths are Pd(1)–N(1) = 2.018(2) Å for **1a** and Pd(1)–N(1) = 2.015(5) Å for **2b**. This is in agreement with the predicted value of 2.01 Å, based on the sum of covalent radii for nitrogen (sp^2) and palladium, 0.701 and 1.31 Å, respectively [21].

In contrast with this, the palladium–carbon bond lengths are Pd(1)–C(2) = 1.974(2) (**1a**) and Pd(1)–C(6) = 1.949(6) Å (**2b**), 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, as has been observed before [12,22].

The *trans*-lengthening influence of σ-bonded carbon is illustrated clearly by the lengthening of the palladium–oxygen distance *trans* to carbon, relative to that *trans* to nitrogen. Thus, we have Pd(1)–O(4A) = 2.139(2) versus Pd(1)–O(3) = 2.037(2) in complex **1a** and Pd(1)–O(4) = 2.153(5) versus Pd(1)–O(3) = 2.050(4) Å in complex **2b**.

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 26.0 and 25.6° to one another in complexes **1a** and **2b**, respectively. These deviations are clearly illustrated in Fig. 4. The two acetate bridges are separated by dihedral angles of 89.3° in the piperonal complex and 83.5° in the benzodioxan complex.

Table 2
Crystal data and structure refinement

	1a	**2b·2CHCl$_3$**
Formula	$C_{32}H_{38}N_2O_8Pd_2$	$C_{36}H_{44}Cl_6N_2O_8Pd_2$
M_r	791.44	1058.23
Temperature (°C)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Tetragonal	Tetragonal
Space group	*P*-4	*I*4$_1$/*a*
Cell dimensions		
a (Å)	13.02633(3)	17.5686(1)
b (Å)	13.02633(3)	17.5686(1)
c (Å)	9.6612(2)	29.4984(2)
V (Å^3)	1639.36(6)	9104.85(10)
Z	2	8
$D_{calc.}$ (Mg m^{-3})	1.603	1.544
μ (mm^{-1})	1.148	1.189
F(000)	800	4256
Crystal size (mm)	0.35 × 0.25 × 0.20	0.45 × 0.40 × 0.25
$2\theta_{max}$ (°)	56.6	51.9
Reflections:		
collected	12144	25063
unique	4051 (R_{int} = 0.021)	4004 (R_{int} = 0.12)
Transmissions	1.00, 0.85	1.00, 0.49
No. of parameters	199	244
No. of restraints	0	3
S	1.036	1.053
R [*F*, $I>2\sigma(I)$]	0.0207	0.0632
wR [F^2, all data]	0.0519	0.1792
max Δ/σ	0.001	0.001
max ρ (e Å^{-3})	0.214	0.680
Absolute structure parameter	0.01(2)	

Table 3
Selected bond distances (Å) and angles (°) for complexes **1a** and **2b** [a]

	1a	**2b**	
Bond distances			
C(2)–Pd(1)	1.974(2)	Pd(1)–C(6)	1.949(6)
N(1)–Pd(1)	2.018(2)	Pd(1)–N(1)	2.015(5)
O(3)–Pd(1)	2.0371(18)	Pd(1)–O(3)	2.050(4)
Pd(1)–O(4) # 1	2.1388(18)	Pd(1)–O(4)	2.153(5)
Pd(1)–Pd(1) # 1	2.8653(3)	Pd(1)–Pd(1) # 2	2.8485(10)
C(3)–O(1)	1.385(3)	O(1)–C(3)	1.373(8)
C(4)–O(2)	1.375(4)	O(2)–C(4)	1.367(8)
C(14)–O(1)	1.416(4)	O(1)–C(14)	1.390(12)
C(14)–O(2)	1.424(5)	O(2)–C(15)	1.367(12)
C(1)–C(7)	1.439(4)	C(1)–C(7)	1.439(9)
C(7)–N(1)	1.286(3)	N(1)–C(7)	1.294(9)
C(8)–N(1)	1.474(3)	N(1)–C(8)	1.474(8)
Bond angles			
C(2)–Pd(1)–N(1)	81.51(9)	C(6)–Pd(1)–N(1)	81.2(2)
C(2)–Pd(1)–O(3)	94.39(10)	C(6)–Pd(1)–O(3)	93.8(2)
N(1)–Pd(1)–O(3)	175.90(8)	N(1)–Pd(1)–O(3)	174.0(2)
C(2)–Pd(1)–O(4) # 1	175.84(9)	C(6)–Pd(1)–O(4)	177.2(2)
N(1)–Pd(1)–O(4) # 1	94.69(8)	N(1)–Pd(1)–O(4)	96.5(2)
O(3)–Pd(1)–O(4) # 1	89.40(8)	O(3)–Pd(1)–O(4)	88.60(19)
C(2)–C(3)–O(1)	128.2(3)	O(1)–C(3)–C(2)	118.2(7)
C(5)–C(4)–O(2)	126.4(3)	O(2)–C(4)–C(5)	117.1(6)

[a] Symmetry transformations used to generate equivalent atoms: # 1 $-x+1$, $-y$, z; # 2 $-x+1$, $-y+3/2$, $z+0$.

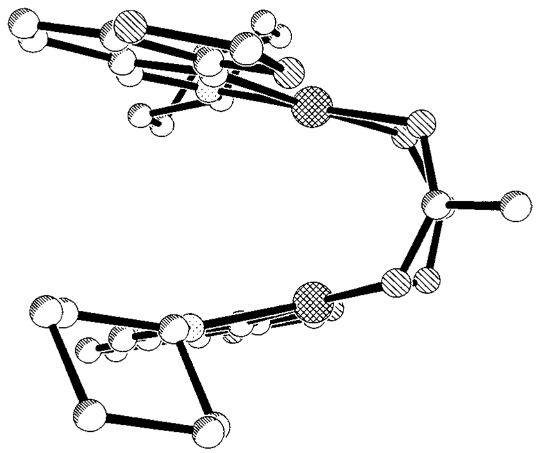


Fig. 4. The piperonal derivative, showing the non parallel nature of the cyclometallated moieties. The benzodioxan derivative is closely similar.

Except for the cyclohexyl and methyl groups, the Schiff base ligand is almost planar. The deviations from the least-squares mean plane at the coordination sphere of palladium (plane 1), the metallacycle (plane 2) and the phenyl ring (plane 3) are in the range 0.018–0.0358 Å. The angles between planes are as follows: plane 1/plane 2: 3.4°, plane 1/plane 3: 6.8°, plane 2/plane 3: 3.9° (**1a**), and: plane 1/plane 2: 1.7°, plane 1/plane 3: 2.7°, plane 2/plane 3: 1.0° (**2b**).

3. Conclusions

The results presented here are further examples of Schiff base ligands that possess two potential metallation sites, in a similar fashion as was found by us earlier for related ligands with methoxy and methyl groups. However, whereas in the latter case steric effects were claimed to be the inducement for the adoption of the metallation position, in the ligands of the present paper a ring size effect seems to operate. Whether it is due solely to electronic or to steric effects, or both operating together, we believe that further studies are needed in order to make a final judgement; these will be undertaken by us. Nevertheless, the experimental results shown here put forward the fact that careful selection of the phenyl ring substituents may conduct metallation towards the carbon atom of our choice.

4. Experimental

4.1. Materials and instrumentation

Solvents were dried according to the standard methods [23]. Palladium(II) acetate and (1,5-cyclooctadiene)dimethylplatinum(II) were 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 analyzer, 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}) or 85% H_3PO_4 (^{31}P-{^1H}) and were recorded on a Bruker AC 200F spectrometer.

The preparation of ligand **e** and complex **1e** were described in an earlier paper [13]. The synthesis of the Schiff base ligands **a**, **b**, **c**, **d** and **f** were performed by heating a chloroform solution of the appropriate quantities of piperonal or 1,4-benzodioxan-6-carboxaldehyde and the corresponding amine in a Dean–Stark apparatus under reflux.

3,4-{OCH_2O}$C_6H_3C(H){=}N(C_6H_{11})$ (**a**). Yield: 88.8%. Anal. Found: C, 72.6; H, 7.5; N, 6.1. Anal. Calc.: C, 72.7; H, 7.4; N, 6.1. IR: ν(C=N) = 1639s cm^{-1}. ^{13}C-{^1H}-NMR: δ157.7 (C=N); δ 149.5, 148.1 (C3, C4); δ 131.5 (C1); δ 124.0 (C5); δ 107.9, 106.7 (C2, C6); δ 101.3 (OCH_2O); C_6H_{11} group: δ 69.7 (C7), δ 34.4 (C8, C12), δ 25.6 (C10), δ 24.8 (C9, C11).

3,4-{OCH_2CH_2O}$C_6H_3C(H){=}N(C_6H_{11})$ (**b**). Yield: 87.0%. Anal. Found: C, 73.4; H, 7.6; N, 5.6. Anal. Calc.: C, 73.4; H, 7.8; N, 5.7. IR: ν(C=N) = 1630s cm^{-1}. ^{13}C-{^1H}-NMR: δ 157.7 (C=N); δ 145.5, 143.6 (C3, C4); δ 130.5 (C1); δ 121.6 (C5); δ 117.3, 116.7 (C2, C6); δ 64.5, 64.2 (OCH_2CH_2O); C_6H_{11} group: δ 69.8 (C7), δ 34.4 (C8, C12), δ 25.6 (C10), δ 24.8 (C9, C11).

3,4 - {OCH_2O}$C_6H_3C(H){=}NCH_2$(3,4-{OCH_2O}C_6H_3) (**c**). Yield: 85.0%. Anal. Found: C, 68.0; H, 4.5; N, 5.0.

Anal. Calc.: C, 67.8; H, 4.6; N, 4.9. IR: ν(C=N) = 1635s cm^{-1}. ^{13}C-{^{1}H}-NMR: δ 160.8 (C=N); δ 149.9, 148.3 (C3, C4); δ 147.7, 146.5 (C9, C10); δ 133.4 (C7); δ 131.0 (C1); δ 124.5 (C5); δ 121.0 (C11); δ 108.6, 108.2 (C8, C12); δ 108.0, 106.7 (C2, C6); δ 104.4, 100.9 (OCH_2O); δ 64.5 (NCH_2).

3,4-{OCH_2CH_2O}$C_6H_3C(H)$=NCH_2(3,4-{OCH_2O}-C_6H_3) (**d**). Yield: 85.0%. Anal. Found: C, 68.4; H, 5.0; N, 4.9. Anal. Calc.: C, 68.7; H, 5.1; N, 4.7. IR: ν(C=N) = 1630s cm^{-1}. ^{13}C-{^{1}H}-NMR: δ160.9 (C=N); δ 147.7, 146.5 (C9, C10); δ 145.9, 143.7 (C3, C4); δ 133.4 (C7); δ 130.4 (C1); δ 121.9, 121.0 (C5, C11); δ 117.3, 116.9 (C2, C6); δ 108.6, 108.2 (C8, C12); δ 100.9 (OCH_2O); δ 64.6, 64.5, 64.1 (OCH_2CH_2O, NCH_2).

3,4-{OCH_2CH_2O}$C_6H_3C(H)$=$NCH_2CH_2NMe_2$ (**f**). Yield: 83.9%. Anal. Found: C, 66.9; H, 7.6; N, 11.9. Anal. Calc.: C, 66.6; H, 7.7; N, 12.0. IR: ν(C=N) = 1635s cm^{-1}. ^{13}C-{^{1}H}-NMR: δ 160.9 (C=N); δ 145.8, 143.6 (C3, C4); δ 130.1 (C1); δ 121.7 (C5); δ 117.2, 116.8 (C2, C6); δ 64.5, 64.2 (OCH_2CH_2O); δ 60.2, 59.7 (NCH_2CH_2N), δ 45.8 (NMe_2).

4.2. Synthesis of complexes

Synthesis of [Pd{3,4-(OCH_2O)$C_6H_2C(H)$=N(C_6H_{11})-*C*2,*N*}(μ-O_2CMe)]$_2$ (**1a**). 3,4-(OCH_2O)$C_6H_3C(H)$=N-(C_6H_{11}) (0.550 g, 2.377 mmol) and palladium(II) acetate (0.500 g, 2.227 mmol) were added to 50 cm^3 of glacial acetic acid to give a yellow solution. After heating at 80°C for 3 h under argon the solution was cooled and the acetic acid removed in vacuo. The residue was diluted with water and extracted with dichloromethane. The combined extract was dried with anhydrous sodium sulfate, filtered and then concentrated in vacuo to give a yellow solid, which was column chromatographed on silica gel, eluting starting Schiff base with dichloromethane. Elution with dichloromethane–ethanol 1% gave a mixture of **1a** and **2a** in a 9:1 molar ratio. Compound **1a** could be obtained from the mixture in pure form by fractional recrystallization. The mixture was dissolved in 25 ml of warm chloroform, filtered, *n*-hexane carefully added and the resultant solution kept at −15°C for 48 h. Yellow crystals of **1a** were formed. The chloroform–*n*-hexane solution was evaporated to dryness giving a mixture of **1a**/**2a** in 2:1 ratio.

Overall yield: 90.7% (ca. 60% relative to **1a**). Anal. Found: C, 48.8; H, 4.4; N, 3.6. Anal. Calc.: C, 48.5; H, 4.8; N, 3.5. IR: ν(C=N) = 1610m, ν_{as}(COO) = 1588m, sh; ν_s(COO) = 1425m, sh cm^{-1}. ^{13}C-{^{1}H}-NMR (**1a**): δ 181.9 (O_2*C*Me); δ 167.7 (C=N); δ 151.4, 147.9, 142.5 (C2, C3, C4); δ 128.1 (C1); δ 122.6 (C5); δ 103.9 (C6); δ 100.2 (OCH_2O); δ 23.2 (O_2C*Me*); C_6H_{11} group: δ 64.1 (C7), δ 34.7 (C8, C12), δ 26.0 (C10), δ 25.7 (C9, C11). ^{13}C-{^{1}H}-NMR (**2a**): δ 181.0 (O_2*C*Me); δ 166.2 (C=N); δ 148.0, 146.6, δ 144.2 (C3, C4, C6); δ 138.5 (C1); δ 112.1, 106.3 (C2, C5); δ 100.5 (OCH_2O); δ 23.4 (O_2C*Me*); C_6H_{11} group: δ 64.0 (C7), δ 34.6 (C8, C12), δ 25.9 (C10), δ 25.6 (C9, C11).

Synthesis of [Pd-{3,4-(OCH_2CH_2O)$C_6H_2C(H)$=N-(C_6H_{11})-*C*6,*N*}(μ-O_2CMe)]$_2$ (**2b**). 3,4-{OCH_2CH_2O}-$C_6H_3C(H)$=N(C_6H_{11}) (0.585 g, 2.384 mmol) and palladium(II) acetate (0.500 g, 2.227 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 cooling to 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 to give the desired complex as yellow microcrystals.

Yield: 83.1%. Anal. Found: C, 49.5; H, 5.0; N, 3.3. Anal. Calc.: C, 49.8; H, 5.2; N, 3.4. IR: ν(C=N) = 1605 s, ν_{as}(COO) = 1585 m; ν_s(COO) = 1420 m, sh cm^{-1}. ^{13}C-{^{1}H}-NMR: δ 180.6 (O_2*C*Me); δ 166.3 (C=N); δ 146.9, 143.4, 140.1, 139.7, (C1, C3, C4, C6); δ 120.2(C5); δ 115.0 (C2); δ 64.6, 64.3 (OCH_2CH_2O); δ 25.2 (O_2C*Me*); C_6H_{11} group: δ 64.0 (C7), δ 34.6 (C8, C12), δ 25.9 (C10), δ 25.7 (C9, C11).

A similar procedure may be used to synthesize compound **1a**, which was obtained as a mixture of **1a**/**2a** in 2:1 molar ratio and purified as described before.

Synthesis of [Pd-{3,4-(OCH_2O)$C_6H_2C(H)$=NCH_2(3,4-{OCH_2O}C_6H_3)-*C*2,*N*}(μ-O_2CMe)]$_2$ (**1c**). Using a similar procedure as for compound **2b** a mixture of **1c** and **2c** in a 20:1 molar ratio was obtained.

Overall yield: 79.5%. Anal. Found: C, 48.3; H, 3.5; N, 3.2. Anal. Calc.: C, 48.2; H, 3.4; N, 3.1. IR: ν(C=N) = 1607 s, ν_{as}(COO) = 1580 m; ν_s(COO) = 1425 m, sh cm^{-1}. ^{13}C-{^{1}H}-NMR (**1c**): δ 182.2 (O_2*C*Me); δ 171.4 (C=N); δ 151.5, 148.5, 147.9, 147.4, 141.7 (C2, C3, C4, C9, C10); δ 128.5 (C7); δ 128.0 (C1); δ 123.4, 123.2 (C5, C11); δ 109.9, 108.4 (C8, C12); δ 104.3 (C6); δ 101.1, 100.3 (OCH_2O); δ 60.4 (NCH_2); δ 23.4 (O_2C*Me*). ^{13}C-{^{1}H}-NMR (**2c**): δ 181.8 (O_2*C*Me); δ 170.2 (C=N); δ 151.3, 147.2, 144.7 (C3, C4, C6, C9, C10); δ 137.8 (C1); δ 128.7 (C7); δ 123.1 (C11); δ 112.3, 106.8 (C2, C5); δ 100.7 (OCH_2O); δ 60.5 (NCH_2); δ 23.3 (O_2C*Me*).

Synthesis of [Pd-{3,4-(OCH_2CH_2O)$C_6H_2C(H)$=NCH_2(3,4-{OCH_2O}C_6H_3)-*C*6,*N*}(μ-O_2CMe)]$_2$ (**2d**). Compound **2d** was obtained following a similar procedure to compound **2b**.

Yield: 78.1%. Anal. Found: C, 49.7; H, 3.8; N, 3.2. Anal. Calc.: C, 49.4; H, 3.7; N, 3.0. IR: ν(C=N) = 1607 s, ν_{as}(COO) = 1590 m; ν_s(COO) = 1427 m cm^{-1}. ^{13}C-{^{1}H}-NMR: δ 181.1 (O_2*C*Me); δ 170.1 (C=N); δ 147.9, 146.5 (C9, C10); δ 147.5, 144.0, 140.6, 139.0 (C1, C3, C4, C6); δ 128.1 (C7); δ 123.6 (C5); δ 120.3 (C11);

115.8 (C2); δ 110.2, 108.4 (C8, C12); δ 101.1 (OCH_2O); δ 64.7, 64.0 (OCH_2CH_2O); δ 60.3 (NCH_2), δ 24.4 (O_2CMe).

Synthesis of [Pt-{3,4-(OCH_2CH_2O)C_6H_2C(H)=N-$CH_2CH_2NMe_2$-*C*6,*N*,*N*}(Me)] (**1f**). {3,4-(OCH_2CH_2O)-C_6H_3C(H)=$NCH_2CH_2NMe_2$ (0.077 g, 0.329 mmol) and (1,5-cyclooctadiene)dimethylplatinum(II) (0.100 g, 0.298 mmol) were added to 20 cm^3 of dry toluene to give a pale yellow solution which was heated at 90°C for 24 h under argon. After cooling at room temperature the solution was filtered to eliminate the small amount of black platinum formed. The solvent was concentrated until an orange crystalline precipitate appeared, the solid filtered off and washed with cold ethanol and *n*-hexane.

Yield: 60.0%. Anal. Found: C, 38.1; H, 4.5; N, 6.1. Anal. Calc.: C, 37.9; H, 4.5; N, 6.3. IR: ν(C=N) = 1619 m. ^{13}C-{^1H}-NMR: δ 166.2 (*C*=N), *J*(CPt) 93.6; δ 146.0 (C6), *J*(C6Pt) 1036.0; δ 143.7 (C1), *J*(C1Pt) 37.6; δ 138.8 (C3); δ 134.8 (C4), *J*(C4Pt) 31.2; δ 121.7 (C5), *J*(C5Pt) 105.7; δ 117.1 (C2), *J*(C2Pt) 49.7; δ 68.0 (αCH_2); δ 64.6, 64.1 (OCH_2CH_2O); δ 51.7 (βCH_2), *J*(CH_2Pt) 29.1; δ 48.5(NMe_2); δ 9.5 (PtMe).

4.3. Single-crystal X-ray diffraction analysis

Three-dimensional, room temperature X-ray data were collected in the θ range 1.56–28.29° for **1a** and 2.68–25.99° for **2b** on a Siemens Smart CCD diffractometer by the omega scan method. Reflections were measured from a hemisphere of data collected of frames each covering 0.3° in omega. Of the 12 144, **1a**; 25 063, **2b** 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, 3807, **1a**; 2726, **2b** 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 $R = 0.0207$, **1a**; 0.0632, **2b** ($wR_2 = 0.0519$, **1a**; 0.1792, **2b** for all 4051, **1a**; 4004, **2b** data, 199, **1a**; 244, **2b** parameters, mean and maximum $\delta/\sigma = 0.000, 0.001$) with allowance for thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density −0.214, **1a**; −0.718, **2b** and 0.209, **1a**; 0.680 **2b** e $Å^{-3}$. The structure solution and refinement were carried out using the program package SHELX-97 [24].

5. 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 **2b** available on request from author. The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre in CIF format. CCDC no. 117 008 for compound **1a** and no. 117 009 for compound **2b**.

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