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Cyclometallated complexes of bis(*N*-benzylidene)-1,4-phenylenediamines. Synthesis and crystal structure of $[1,4\text{-}\{\text{Pd}[2,3,4\text{-}(\text{MeO})_3\text{C}_6\text{HC(H)=N}](\text{Br})\}_2\text{C}_6\text{H}_4]_2$: a novel tetranuclear cyclometallated palladium(II) complex

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Abstract

Treatment of $1,4\text{-}\{2,3,4\text{-}(\text{MeO})_3\text{C}_6\text{H}_2\text{C(H)=N-}\}_2\text{C}_6\text{H}_4$ (**a**) or $1,4\text{-}\{4,5\text{-}(\text{OCH}_2\text{O})\text{C}_6\text{H}_3\text{C(H)=N-}\}_2\text{-C}_6\text{H}_4$ (**b**) with palladium(II) acetate gave the cyclometallated acetato-bridged complexes $[1,4\text{-}\{\text{Pd}[2,3,4\text{-}(\text{MeO})_3\text{C}_6\text{HC(H)=N}](\text{O}_2\text{CMe})\}_2\text{C}_6\text{H}_4]_n$ (**1a**) and $[1,4\text{-Pd}[4,5\text{-}(\text{OCH}_2\text{O})\text{C}_6\text{H}_2\text{C(H)=N}](\text{O}_2\text{CMe})\}_2\text{-C}_6\text{H}_4]_n$ (**1b**). These were converted into the analogous halide-bridged complexes by treatment with NaX (**2a**, **2b** X = Cl; **3a**, **3b** X = Br). Reaction of **a** or **b** with PdCl_2 also affords the chloro-bridged complexes **2a** and **2b**, which reacted with LiBr to give the bromo-bridged complexes **3a** and **3b**. The structure of **3a** is described. This is the first example of a structurally characterized tetranuclear cyclometallated bromo-bridged palladium(II) complex. Crystals are triclinic, space group $P\bar{1}$, with a 1109.1(4), b 1181.5(4), c 1481.5(5) pm, α 77.33(3), β 80.04(3), γ 82.50(3)°, U 1.857(1) nm^3, $Z = 1$, $R = 0.0558$ and $R_W = 0.0610$, for 3871 independent reflections with $I > 2.0\sigma(I)$. The structure is a centrosymmetric tetranuclear palladium(II) dimer with symmetrically bridging bromine atoms and non-bonding Pd $\cdots$ Pd distance of 366.2(5) pm.

Introduction

Cyclometallation reactions have been extensively studied in the past [1–5]. We have described the synthesis and chemistry of cyclometallated complexes derived from ligands with one nitrogen-donor atom such as Schiff bases [6,7] and phenylimidazoles [8], and more recently we have investigated cyclometallated complexes with ligands having two nitrogen-donor atoms, namely benzylidene hydrazones [9]

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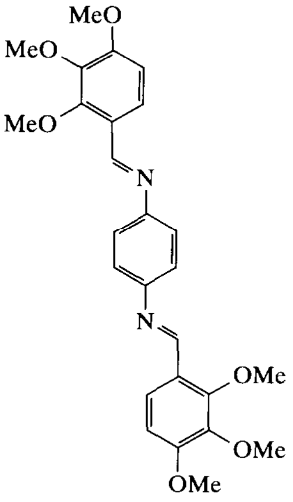
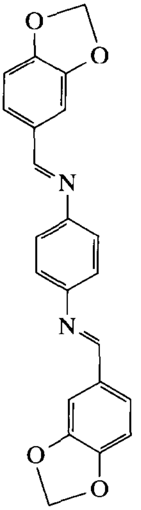
and terephthalaldehyde [10]. In such cases double cyclometallation is in principle possible, although preliminary results show that this seems not to be the case [11]. Double cyclometallation has been achieved before with diamines [12], benzylidene hydrazones [8,13], pyrazines [14], pyrimidines [15], pyrazoles [16] and diacetylbenzene dioximes [17] and to the best of our knowledge no cyclometallated complexes of the closely related diimines **a** and **b** have been reported.



(a)



(b)

Our aim was to try to double cyclometallate these and other related ligands, and also to investigate the nature of the complexes formed.

One interesting problem in the chemistry of cyclometallated complexes with mono-metallated as well as with double-metallated ligands, is to determine whether they are dimeric or polymeric. For mono-metallated ligands, such as Schiff bases, we have recently reported the X-ray crystal structure of a cyclometallated bromo-bridged palladium(II) complex, which was also the first example of a cyclometallated bromo-bridged dimer [7]. Similarly, complexes with double cyclometallated ligands, such as diamines [12], benzylidene hydrazones [13] and diacetylbenzene dioximes [17] have been reported. However, these complexes have been claimed to be polymeric and owing to their insolubility, the data are somewhat limited and in the majority of cases characterization was made on the basis of reaction products obtained when they react with tertiary phosphines, pyridine, sodium acetylacetonate or other nucleophiles.

In this paper we describe the synthesis of the first example of a tetranuclear palladium cyclometallated complex with double cyclometallated diimine ligands. It is a soluble non-polymeric complex for which full spectroscopic and structural data are now available. Related acetato- and halide-bridged complexes are also described.

Results and discussion

The reaction of bis-[(2,3,4-trimethoxy)benzylidene]-1,4-phenylenediamine (**a**) or of bis-[(4,5-methylenedioxy)benzylidene]-1,4-phenylenediamine (**b**) with palladi-

Table 1

Microanalytical, colour and IR data

	Colour	Analytical data (Found (calc.) (%))			IR data (cm^{-1})		
		C	H	N	ν(C=N) [a]	ν(COO) [b]	ν(Pd–Cl)
1a	Orange	45.3 (45.4)	4.2 (4.1)	3.6 (3.5)	1601m	1579s 1414s	
2a	Yellow	41.7 (41.8)	3.5 (3.5)	3.7 (3.6)	1605m		320m
3a	Yellow	37.5 (37.4)	3.3 (3.1)	3.3 (3.4)	1601m		
1b	Orange	44.5 (44.5)	3.1 (2.9)	4.2 (4.0)	1609m	1580s 1415s	
2b	Orange	40.3 (40.4)	2.1 (2.2)	4.2 (4.3)	1611m		340m
3b	Yellow	35.5 (35.6)	1.8 (1.9)	3.7 (3.8)	1610m		

[a] ν(C=N) values for **a** 1612m; **b** 1630m (cm^{-1}). [b] The higher value corresponds to ν_{as}(COO) and the lower one to ν_s(COO).

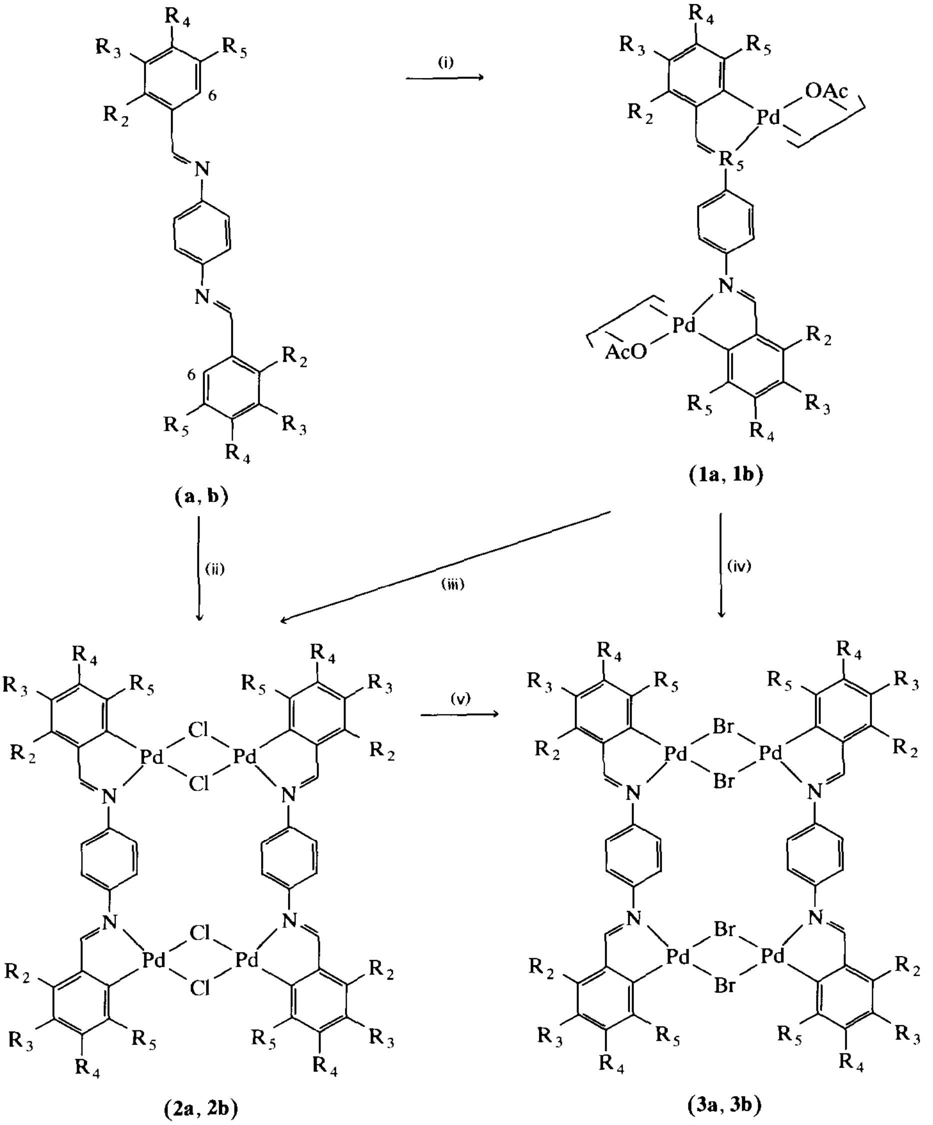
um(II) acetate in boiling glacial acetic acid under dinitrogen for 2 h gave the acetato-bridged complexes **1a** and **1b**, respectively, as air-stable solids (see Experimental section and Tables 1 and 2). Although both complexes have been fully characterized by elemental analyses (C, H and N), ^{1}H NMR and IR spectroscopy, neither mass spectra nor molecular weight measurements were possible. There-

Table 2

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

	δ(HC=N)	δ(H(6))	δ(H(5))	δ(MeO)	δ(OCH_2O)	δ(C_6H_4)	δ(O_2CMe)
a	8.56s	7.29d ^3J[H(5)H(6)] = 8.8	6.81d	3.91s 3.94s 3.99s		7.27s	
1a	8.05s		6.63s	3.87s 3.91s 3.95s		7.25s	2.10s 2.03s
2a	8.03s		6.70s	3.79s 3.95s 3.96s		7.21s	
3a	8.06s		6.86s	3.79s 3.95s 3.96s		7.20s	
		δ(H(2))	δ(H(3))				
b	8.40s	7.30d ^3J[H(2)H(3)] = 7.9	6.90dd		6.06s	7.25s	
1b	7.60s	7.20d ^3J[H(2)H(3)] = 7.1	7.06d		6.08s	7.24s	2.15s 2.08s
2b	7.34s	7.42d ^3J[H(2)H(3)] = 8.0	6.94d		6.09s	7.25s	
3b	7.35s	7.42d ^3J[H(2)H(3)] = 7.9	6.94d		6.08s	7.25s	

[a] Spectra measured at 250 MHz (*ca.* +20°C); chemical shifts (δ) in ppm (± 0.01) to high frequency of $SiMe_4$. Coupling constants in Hz. [b] s, singlet; d, doublet; dd, doublet of doublets. [c] δ(H(6)): **b**, 7.20d (^4J[H(2)H(6)] 1.4 Hz).



(a: $R_2 = R_3 = R_4 = \mathrm{MeO}$, $R_5 = \mathrm{H}$;
b: $R_2 = R_3 = \mathrm{H}$, $R_4\text{-}R_5 = \mathrm{OCH_2O}$)

Scheme 1. (i) $\mathrm{Pd(OAc)_2}$, glacial acetic acid, reflux; (ii) $\mathrm{PdCl_2}$, glacial acetic acid, reflux; (iii) NaCl in aqueous acetone; (iv) NaBr in aqueous acetone; (v) LiBr, in aqueous acetone.

fore, we assign these complexes the polymeric structures depicted in Scheme 1. The acetato-bridged complexes were converted into the halido-bridged analogues by treatment of **1a** or **1b** in acetone with aqueous sodium chloride or sodium bromide to give the chloro-bridged **2a**, **2b**, and bromine-bridged complexes **3a**, **3b**, respectively, as air-stable solids (see Experimental section and Tables 1 and 2). Alternatively, reaction of **a** and **b** with $\mathrm{PdCl_2}$ in boiling glacial acetic acid afforded the chloro-bridged complexes **2a** and **2b**, respectively. Treatment of **2a** or **2b** with an excess of LiBr gave the bromide-bridged species **3a** and **3b**, respectively. Elemental analyses are satisfactory (Table 1). The IR spectrum of complexes **1a** and **1b** exhibit the asymmetric and symmetric stretching modes of the acetate groups as strong absorptions at 1579, 1414 cm^{-1} (**1a**) and 1580, 1415 cm^{-1} (**1b**), which are absent in the halido-bridged species; the separation between them is consistent with bridging acetate ligands [18] as observed for other complexes [19]. The shift of the ν(C=N) vibration towards lower wavenumbers and the shift of the *H*C=N resonance towards lower frequency in the ^1H NMR spectrum (*ca.* 0.5–1.0 ppm) show that the palladium atom is bonded through the nitrogen atom of the C=N double bond [20] (see Tables 1 and 2).

The ^1H NMR spectra clearly demonstrate the formation of a Pd–C bond and in the case of complexes **1b**–**3b** show the regioselectivity of the metallation process. Thus, when ligand **a** is metallated the ^1H NMR spectra of the complexes show singlet resonances at δ 6.63 (**1a**), 6.70 (**2a**) and 6.86 (**3a**) ppm assigned to the H(5) proton, in each case (*cf.* δ 7.29 (1H, d, H(6)) and 6.81 (1H, d, H(5)) ^3J[H(6)H(5)] 8.8 Hz in **a**) (see Table 2). Palladation of ligand **b** may take place at the C(2) atom or at the C(6) atom, a mixture of isomers being possible. However, ^1H NMR data show that only one regioisomer is present. The ^1H NMR spectra of complexes **1b**–**3b** show that the site of palladation is clearly C(6) with H(3) and H(2) (AB pattern) appearing as doublets: δ 7.06 (**1b**), 6.94 (**2b**) and 6.94 (**3b**) ppm for H(3), and 7.20 (**1b**), 7.42 (**2b**), 7.42 (**3b**) ppm for H(2) (metallation of C(2) would give rise to singlet resonances for H(3) and H(6)). The three resonances at higher frequency are assigned to H(2), in each case, due to the anisotropic shielding of the C=N double bond [21]. This is in accordance with previously reported complexes [22] and contrasts to the situation reported by Dyke *et al.*, where metallation takes place through the C(2) atom [23].

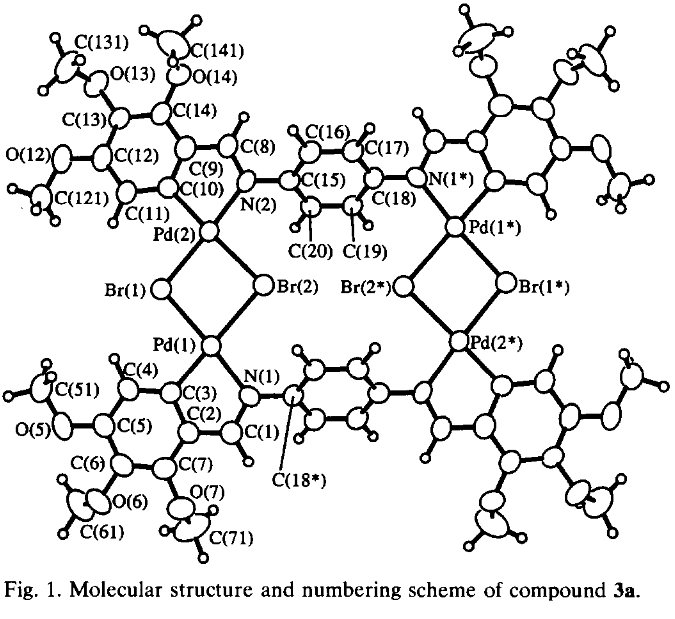


Fig. 1. Molecular structure and numbering scheme of compound **3a**.

Table 3

Non-hydrogen atom coordinates ($\times 10^4$) for compound **3a**

Atom	x	y	z
Pd(1)	4681.8(6)	7560.8(6)	3166.5(5)
Pd(2)	6577.2(6)	6309.7(6)	5003.4(5)
Br(1)	5908.6(9)	5730.7(8)	3697.8(7)
Br(2)	5558.4(11)	8326.5(9)	4384.9(8)
N(1)	3565(7)	9007(6)	2680(5)
C(1)	2932(8)	8862(8)	2056(6)
C(2)	3125(5)	7779(4)	1793(4)
C(3)	4002(5)	6976(4)	2214(4)
C(4)	4279(5)	5882(4)	1977(4)
C(5)	3678(5)	5591(4)	1319(4)
C(6)	2801(5)	6393(4)	897(4)
C(7)	2524(5)	7487(4)	1134(4)
O(5)	3916(7)	4580(6)	1011(5)
C(51)	4982(10)	3845(9)	1248(9)
O(6)	2187(6)	6116(6)	247(5)
C(61)	1348(12)	5242(12)	618(9)
O(7)	1751(7)	8312(6)	648(5)
C(71)	494(11)	8369(13)	959(9)
N(2)	7246(6)	6720(6)	6085(5)
C(8)	8003(8)	5902(7)	6471(6)
C(9)	8190(5)	4855(4)	6151(4)
C(10)	7525(5)	4792(4)	5449(4)
C(11)	7616(5)	3761(4)	5118(4)
C(12)	8371(5)	2793(4)	5490(4)
C(13)	9036(5)	2856(4)	6192(4)
C(14)	8946(5)	3887(4)	6523(4)
O(12)	8498(7)	1753(6)	5237(5)
C(121)	7848(13)	1587(10)	4551(8)
O(13)	9703(6)	1868(5)	6628(4)
C(131)	10793(12)	1482(12)	6094(10)
O(14)	9540(6)	3957(5)	7233(4)
C(141)	10811(12)	4025(14)	7002(9)
C(15)	7047(5)	7816(4)	6375(4)
C(16)	8045(5)	8382(4)	6445(4)
C(17)	7845(5)	9431(4)	6758(4)
C(18)	6648(5)	9915(4)	7001(4)
C(19)	5650(5)	9349(4)	6931(4)
C(20)	5849(5)	8300(4)	6618(4)

Although neither satisfactory mass spectra nor molecular weight measurements could be obtained for complexes **2a**, **2b** and **3b**, they were tentatively assigned a dimeric structure by analogy to **3a**, prepared by a similar route.

Crystal structure of 3a

Suitable crystals of compound **3a** were obtained by slowly evaporating a chloroform solution. The molecular structure and its numbering scheme are shown in Fig. 1. Final fractional coordinates are listed in Table 3 while selected interatomic distances and angles are given in Table 4.

Table 4

Selected bond lengths (pm) and angles (deg) [a] in compound **3a**

Br(1)-Pd(1)	245.0(3)	Br(2)-Pd(1)	256.4(4)
N(1)-Pd(1)	204.7(8)	Br(1)-Pd(2)	244.3(3)
Br(2)-Pd(2)	254.8(4)	N(2)-Pd(2)	204.8(8)
C(3)-Pd(1)	199.2(6)	C(10)-Pd(2)	199.7(6)
C(1)-N(1)	130.4(10)	C(8)-N(2)	129.5(10)
C(15)-N(2)	143.1(7)	C(18)-N(1')	143.2(10)
C(2)-C(1)	139.9(9)	C(9)-C(8)	139.8(9)
Pd(2) ··· Pd(1)	366.2(5)		
Br(2)-Pd(1)-Br(1)	85.1(1)	N(1)-Pd(1)-Br(1)	175.0(2)
N(1)-Pd(1)-Br(2)	99.5(3)	C(3)-Pd(1)-Br(1)	95.1(2)
C(3)-Pd(1)-Br(2)	179.6(1)	C(3)-Pd(1)-N(1)	80.2(3)
Br(2)-Pd(2)-Br(1)	85.6	N(2)-Pd(2)-Br(1)	176.1(2)
N(2)-Pd(2)-Br(2)	97.5(3)	C(10)-Pd(2)-Br(1)	96.2(2)
C(10)-Pd(2)-Br(2)	174.7(1)	C(10)-Pd(2)-N(2)	80.5(3)
Pd(2)-Br(1)-Pd(1)	96.9	Pd(2)-Br(2)-Pd(1)	91.5
C(1)-N(1)-Pd(1)	113.9(6)	C(8)-N(2)-Pd(2)	113.5(6)
C(2)-C(3)-Pd(1)	112.7(2)	C(9)-C(10)-Pd(2)	111.9(2)
C(4)-C(3)-Pd(1)	127.2(2)	C(11)-C(10)-Pd(2)	128.0(2)
C(18')-N(1)-Pd(1)	127.3(6)	C(15)-N(2)-Pd(2)	126.9(5)
C(18')-N(1)-C(1)	118.7(8)	C(15)-N(2)-C(8)	119.4(7)
C(2)-C(1)-N(1)	117.0(8)	C(9)-C(8)-N(2)	117.4(8)
C(20)-C(15)-N(2)	119.7(4)	C(16)-C(15)-N(2)	120.2(4)
C(19)-C(18)-N(1')	119.6(6)	C(17)-C(18)-N(1')	120.4(6)
C(3)-C(2)-C(1)	115.9(5)	C(7)-C(2)-C(1)	124.1(5)
C(10)-C(9)-C(8)	116.3(5)	C(14)-C(9)-C(8)	123.7(5)

[a] Primed atoms are related by the symmetry operator $(1.0 - x, 2.0 - y, 1.0 - z)$.

The complex, which crystallizes as a 1:4 chloroform solvate, is a centrosymmetric tetranuclear palladium dimer. The *cisoid* arrangement of the cyclopalladated ligands, confirmed unambiguously in this X-ray diffraction study, is further reflected in the geometry of the $PdBr_2Pd$ bridge. In particular, each bromine atom of the Pd_2Br_2 unit is *trans* either to two nitrogen atoms (Br(1)) or *trans* to two carbon atoms (Br(2)). The Pd–Br bond lengths for each bromine atom are Pd(1)–Br(1) 245.0(3), Pd(2)–Br(1) 244.3(3) pm and Pd(1)–Br(2) 256.4(4), Pd(2)–Br(2) 254.8(4) pm, a difference of *ca.* 11 pm between both pairs. The distinct values of the two sets of bond lengths result from the differing *trans* influences of the phenyl carbon and nitrogen atoms of the diimine ligand. The bromine bridges are therefore symmetrical in contrast to other related complexes where each halogen atom is *trans* to a carbon atom and a nitrogen atom simultaneously making the Pd_2X_2 unit asymmetrical [7,24,25]. Furthermore, the Pd–Br–Pd bond angles are clearly distinct, by over 5°, as a consequence of the different Pd(1)–[Br(1)]–Pd(2) and Pd(1)–[Br(2)]–Pd(2) distances in contrast to an asymmetrical Pd_2Br_2 unit where the Pd–Br–Pd bond angles were of the same value, *ca.* 93° [7]. In the present compound the C and N atoms of the cyclometallated moieties adopt a *cisoid* arrangement about the Pd_2Br_2 unit in contrast to previously reported molecules in which a *transoid* arrangement has been assumed [7,24,25]. Recently a *cisoid* arrangement has been tentatively assigned to a compound of formula $[LPd(\mu\text{-}Cl)_2PdL]$ (L = 2-phenylpyridine) [26].

Each palladium atom adopts a square-planar geometry, as expected for Pd^{2+}, with the distortion most noticeable in the C(3)–Pd(1)–N(1) and C(10)–Pd(2)–N(2) angles of 80.2(3) and 80.5(3)°, respectively; the sum of angles on each palladium is 360° (Pd(1)) and 359.7° (Pd(2)). The Pd–C bond lengths (Pd(1)–C(3), 199.2(6) and Pd(2)–C(10), 199.7(6) pm) are shorter than the expected value based on the covalent radius values of 131 pm for palladium and 77.1 pm for carbon [27]; this shortening, observed in related complexes [28], is probably due to partial multiple-bond character in the Pd–C linkage. The Pd–N bond lengths (Pd(1)–N(1), 204.7(8) and Pd(2)–N(2), 204.8(8) pm) are slightly longer than the single bond value of 201 pm calculated from the covalent radius of N(sp^2), 70 pm; palladium, 131 pm. The C=N distances (C(1)–N(1), 130.4(10) and C(8)–N(2), 129.5(10) pm) are somewhat longer than the value of 123.7(3) pm which is observed for a related imine free ligand [29]; this lengthening is typical of coordinated Schiff base anions where the nitrogen atom is involved in a σ bond to a metal atom [30], and has been observed by us before [7]. This compound shows an almost planar structure with the four palladium atoms and the four bromine atoms in the molecular plane. The methoxy groups are all twisted out of this plane, as to a lesser extent are both of the phenylene rings. The Pd–Pd distance between the two metal atoms linked by bromine is 366.2(5) pm, which excludes any metal–metal bonding. This Pd–Pd distance is greater than that found in previously described dibromo-bridged complexes (363.1(5) [7] and 354.9(9) pm [31]).

Experimental

Solvents were purified by the standard methods [32]. Chemicals were reagent grade. Palladium(II) acetate was purchased from Aldrich-Chemie. Microanalyses were carried out by Mr. J. Ulloa in the Servicio de Analisis Elemental of the University of Santiago using a Carlo–Erba Elemental Analyzer Model 1108. IR spectra were recorded as Nujol mulls or polythene discs on a Perkin–Elmer 1330 spectrophotometer. ^1H NMR spectra were obtained as $CDCl_3$ solutions, referred to the high frequency of $SiMe_4$, and recorded on a Bruker WM-250 spectrometer.

The synthesis of the organic ligands was performed by heating a chloroform solution of the appropriate quantities of the 1,4-phenylenediamine and of the corresponding aldehyde in a Dean–Stark apparatus under reflux.

Preparation of $[1,4\text{-}\{\overline{Pd[2,3,4\text{-}(MeO)_3C_6HC(H)=N]}(O_2CMe)\}_2C_6H_4]_n$ *(1a)*

A mixture of 1,4-{2,3,4-$(MeO)_3C_6H_2C(H)$=N-}$_2C_6H_4$ (0.5 g, 1.076 mmol) and palladium(II) acetate (0.508 g, 2.265 mmol) in glacial acetic acid (40 cm^3) was heated under reflux under dry nitrogen for 3 h. After cooling the mixture to room temperature the acetic acid was removed under vacuum. The residue was treated with water and extracted with dichloromethane. The combined extracts were dried over anhydrous sodium sulfate, filtered and concentrated *in vacuo* to give an orange oil. This was chromatographed on a column packed with silica gel. Elution with dichloromethane/ethanol(1%) removed unchanged starting material. Elution with dichloromethane/ethanol(4%) afforded the final product as an orange powder after concentration. Yield: 0.595 g, 66%.

Preparation of $[1,4\text{-}\overline{Pd[4,5\text{-}(OCH_2O)C_6H_2C(H)=N]}(O_2CMe)\}_2C_6H_4]_n$ *(1b)*

This was prepared similarly as an orange powder. Yield: 0.400 g, 62%.

Preparation of $[1,4\text{-}\{\overline{Pd[2,3,4\text{-}(MeO)_3C_6HC(H)=N]}(Cl)\}_2C_6H_4]_2$ *(2a) from 1a*

An aqueous solution of NaCl (*ca.* 10^{-2} *M*) was added dropwise to a solution of **1a** (0.106 g, 0.067 mmol) in acetone. The product immediately precipitated out as a yellow solid. After stirring for 1 h the solid was filtered off and dried *in vacuo*. Yield: 0.087 g, 87%.

The following three complexes were prepared in an analogous fashion to **2a** as yellow powders.

$[1,4\text{-}\{\overline{Pd[2,3,4\text{-}(MeO)_3C_6HC(H)=N]}Br\}_2C_6H_4]_2$ (**3a**), recrystallization from chloroform produced single crystals. Yield: 0.129 g, 94%.

$[1,4\text{-}\{\overline{Pd[3,4\text{-}(OCH_2O)C_6H_2C(H)=N]}Cl_2\}_2C_6H_4]_2$ (**2b**). Yield: 0.098 g, 91%.

$[1,4\text{-}\{\overline{Pd[3,4\text{-}(OCH_2O)C_6H_2C(H)=N]}Br_2\}_2C_6H_4]_2$ (**3b**). Yield: 0.122 g, 96%.

Preparation of 2a from **a** *and* $PdCl_2$

A mixture of **a** (0.500 g, 1.076 mmol) and of $PdCl_2$ (0.402 g, 2.265 mmol) in glacial acetic acid (25 cm^3) was heated under reflux under dry dinitrogen for 24 h. After cooling the mixture to room temperature the precipitate was filtered off, washed with ethanol and dried *in vacuo* over P_2O_5. Yield, 0.442 g, 55%. Compound **2b** could also be made in a similar fashion by this method.

Preparation of 3a from 2a and LiBr

To a suspension of **2a** (0.1 g, 0.067 mmol) in acetone (25 cm^3) an excess of aqueous LiBr was added and the mixture stirred for 12 h. Water was then added and the final product was filtered off and dried *in vacuo* over P_2O_5. Yield: 0.056 g, 53%.

Single-crystal X-ray diffraction analysis

All crystallographic measurements were made on a Nicolet P3/F diffractometer operating in the $\omega-2\theta$ scan mode using graphite monochromated Mo-K_α X-radiation ($\lambda = 71.069$ pm) following a standard procedure [33]. The data set was corrected for absorption empirically once its structure had been determined [34]. The structure of **3a** was determined by standard heavy-atom methods and was refined by full-matrix least-squares using the SHELX program system [35]. All non-hydrogen atoms were refined with anisotropic thermal parameters except for the non-hydrogen atoms of two disordered chloroform molecules which were refined with isotropic thermal parameters. The methyl and phenyl hydrogen atoms were included in calculated positions and assigned to an overall isotropic thermal parameter. The weighting scheme $w = [\sigma^2(F_o) + 0.00113(F_o)^2]^{-1}$ was used. Atomic coordinates are given in Table 3.

Crystal data. $C_{52}H_{52}Br_4N_4O_{12}Pd_4 \cdot 4CHCl_3$, $M = 2147.74$ (includes solvent molecules), triclinic, a 1109.1(4), b 1181.5(4), c 1481.5(5) pm, α 77.33(3), β 80.04(3), γ 82.50(3)°, U 1.857(1) nm^3, $Z = 1$, space group $P\bar{1}$, D_x 1.75 Mg m^{-3}, λ(Mo-K_α) 71.069 pm, μ 25.68 cm^{-1}, $F(000) = 1044$.

Data collection. Scan widths 2.0° + α-doublet splitting, scan speeds 2.0–29.3° min^{-1}, $4.0 < 2\theta < 45.0°$. 4972 data collected, 3871 with $I > 2.0\sigma(I)$ considered observed, T 290 K.

Structure refinement. Number of parameters = 406, $g = 0.0008$, $R = 0.0558$, $R_w = 0.0610$.

Tables of structure factors and complete listings of atomic coordinates and anisotropic temperature factors are available from the authors.

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