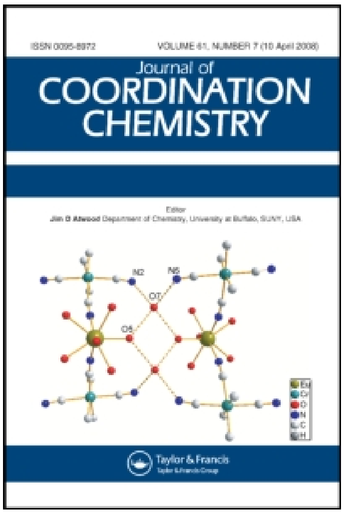

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SYNTHESIS OF CYCLOMETALLATED COMPOUNDS OF iV-(2-METHOXY)BENZYLIDENECYCLOHEXYLAMINE. THE STRUCTURE OF (PdI2-CH_3 OC_6 H_3 C(H)=N-C_6 H_{11}] $(CH_3COO))_2$

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SYNTHESIS OF CYCLOMETALLATED COMPOUNDS OF *N*-(2-METHOXY)BENZYLIDENECYCLOHEXYLAMINE. THE STRUCTURE OF $\{Pd[2\text{-}CH_3OC_6H_3C(H)=N\text{-}C_6H_{11}](CH_3COO)\}_2$

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The reaction of palladium(II)acetate with *N*-(2-methoxy)benzylidenecyclohexylamine in glacial acetic acid yields the acetato-bridged complex $\{Pd[2\text{-}CH_3OC_6H_3C(H)=N\text{-}C_6H_{11}](CH_3COO)\}_2$ (1). From it the halogeno-bridged dimers are synthesized. Treatment of the latter complexes with triphenylphosphine in a 1:2 molar ratio affords the correspondent monomers. The complexes have been characterized by i.r. and ^1H n.m.r. spectroscopy. The crystal structure of complex (**1**) was determined: $P2/c$; $a = 853.7(3)$, $b = 904.3(3)$, $c = 2118.6(3)$ pm, $\beta = 100.11(3)°$, $Z = 2$.

Keywords: Palladium(II), cyclometallation, Schiff bases, n.m.r., crystal structure

INTRODUCTION

Cyclometallated complexes form an interesting group of compounds that has been extensively studied and reviews covering complexes with different donor atoms have appeared.[1-3] The compounds provide novel routes in organic synthesis.[4] We have studied cyclometallated complexes derived from Schiff base ligands[5] and also from phenylimidazole ligands[6] with different metal atoms in each case. As a continuation of our work in this field we now report the synthesis and characterization of new cyclometallated complexes derived from *N*-(2-methoxy)benzylidenecyclohexylamine. A crystal structure determination has been carried out for an acetato-bridged dimer.

EXPERIMENTAL

The experimental techniques employed were the same as those reported in recent papers from this laboratory.[7]

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$[Pd\{2\text{-}MeOC_6H_3C(H)=N\text{-}C_6H_{11}\}(CH_3COO)]_2$ (1)

In a 100 cm^3 round-bottomed flask 0.36 g (1.66 mmol) of *N*-(2-methoxy)benzylidenecyclohexylamine and 0.35 g (1.56 mmol) of palladium(II) acetate were added to 25 cm^3 of glacial acetic acid to give a yellow solution. After refluxing for 1.5 h the solution was cooled to room temperature and the acetic acid removed under reduced pressure. 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 with dichloromethane to remove unchanged starting materials. Elution with dichloromethane/1% ethanol and removal of solvent gave the desired complex as a bright yellow solid. Recrystallization from dichloromethane/*n*-hexane afforded single crystals.

$\{Pd[2\text{-}CH_3OC_6H_3C(H)=NC_6H_{11}](X)\}_2$; X = Cl (2); X = Br (3)

To 0.1 g (0.13 mmol) of the acetato-bridged dimer dissolved in acetone (5 cm^3), giving a clear solution, a solution of sodium chloride or bromide in water (*ca* 10^{-2} mol l^{-1}) was added. A solid immediately precipitated. After stirring for 1 h at room temperature, the solid was filtered off and dried *in vacuo*.

$\{Pd[2\text{-}CH_3OC_6H_3C(H)=NC_6H_{11}](X)(PPh_3)\}$; X = Cl (4); X = Br (5)

To a suspension of 0.05 g (0.07 mmol, X = Cl; 0.06 mmol, X = Br) of the halogeno-bridged dimer in 5 cm^3 of acetone, triphenylphosphine was added in a dimer: phosphine 1:2 molar ratio (0.036 g, 0.14 mmol, X = Cl; 0.033 g, 0.12 mmol, X = Br) to give a clear solution. After stirring for 2 h at room temperature, a solution of acetone/water, 1:3 v/v was added and a solid precipitated. The solid was filtered off and dried *in vacuo*.

TABLE I
Analytical data, colours and yields of the complexes.

Compound	Colour	Yield (%)	Analytical data, found (calcd.) (%) C	H	N
1	Bright Yellow	65	50.7 (50.5)	5.4 (5.3)	3.6 (3.7)
2	Bright Yellow	97	47.0 (47.1)	4.8 (4.8)	3.7 (3.9)
3	Yellow	91	41.9 (41.9)	4.2 (4.3)	3.5 (3.5)
4	Pale Yellow	87	61.9 (62.0)	5.6 (5.2)	2.8 (2.2)
5	Pale Yellow	82	58.3 (57.9)	5.2 (4.9)	2.4 (2.1)

Analytical data, yields and colours of the complexes are given in Table I.

(**1**) crystallizes in the monoclinic space group *P*2/*c* with two molecules per unit cell. Crystal data and parameters for data collection and structure determination are summarized in Table II. Positional parameters are given in Table V, selected bond distances and angles in Table VI.

TABLE II
Crystal data and structure determination parameters.

Formula	$C_{32}H_{42}N_2O_6Pd_2$
Mol. wt.	763.5
Space group	$P2/c$ (No. 13)
Lattice parameters	$a = 853.7(3)$ pm,
	$b = 904.3(3)$ pm,
	$c = 2118.6(3)$ pm,
	$\beta = 100.11(3)°$
Cell volume	$V = 763.5 \times 10^6$ pm^3
Formula units	$Z = 2$
Density	$\rho_x = 1.575$ g cm^{-3}
$F(000)$	776
Diffractometer used	CAD4, ENRAF-NONIUS
Radiation	MoKα
Method of intensity measurement	$\theta/2\theta$
Range of h, k and l	$0 \rightarrow 10$, $0 \rightarrow 8$, $-25 \rightarrow 25$
Interval, std. reflections measured	1h, no intensity variation
Total No. of reflections measured; θ range	3443; 25°
No. of observed reflections	2002 with $I > 3\ \sigma(I)$
Absorption coefficient μ	11.447 cm^{-1}
Method used for absorption correction	DIFABS
Minimum absorption correction	0.8107
Maximum absorption correction	1.2431
Average absorption correction	0.9962
Methods used to solve structure	Patterson; subsequent Difference Fourier
Method of locating hydrogens	ΔF map
Method of refining hydrogens	positions refined with fixed $B_{iso} = 4 \times 10^4$ pm^2
Weighting scheme	$1/\sigma^2$
Parameters refined	254
Value of R	0.040
Value of wR	0.046
Error in an observation of unit weight	2.095
Secondary extinction coefficient	$1.19281(1) \times 10^{-7}$
Sources of atomic scattering factors	*International Tables*
Computer used	DEC MicroVAXII
Programs used	VAXSDP, Version 3.0 (1986)

Cell dimensions were determined on a CAD-4 four circle diffractometer by least-squares fitting of 25 high angle reflections. The intensity measurement in the range of $\theta = 1$–25° with $\theta/2\theta$-scan and MoKα radiation (graphite monochromator) resulted in 3443 intensities. After normal corrections and averaging 2002 independent intensities with $I > 3\sigma(I)$ were used for further calculations. For the structure determination the centrosymmetric space group $P2/c$ was assumed due to the observed extinctions. The position of the Pd atom could be obtained from a Patterson synthesis. The model was then completed by subsequent difference Fourier maps, which also showed the positions of all H atoms. They were included in the refinement with fixed isotropic temperature factors of $R_{iso} = 4 \times 10^4$ pm^2 whereas to all the other atoms anisotropic thermal parameters were applied resulting in a final R value of 0.040. Lists of hydrogen positions, anisotropic thermal parameters and observed and calculated structure factors have been deposited with the Editor.

RESULTS AND DISCUSSION

Synthesis and Properties

Reaction of *N*-(2-methoxy)benzylidenecyclohexylamine with palladium(II) acetate gave the acetato-bridged dimer as a bright yellow solid soluble in common organic solvents. Recrystallization from dichloromethane/*n*-hexane afforded crystals for X-ray diffraction determination (see Experimental and Table I) (Fig. 1).

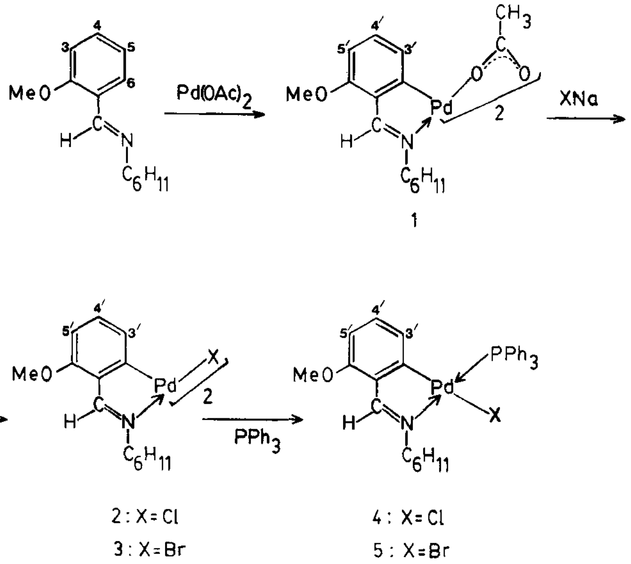

FIGURE 1 Reaction scheme for the complexes

TABLE III
I.r. data for the ligand and complexes (cm^{-1}).

	νC=N	νCH$_3$COO	νPd–X$_b$	νPd–X$_t$
Ligand	1637m			
1	1606s	1580s, 1413s		
2	1605s		328m, 240m	
3	1605vs		164m, 148m	
4	1612s			298m
5	1611s			208m

The i.r. spectrum shows two strong bands at 1580 and 1413 cm^{-1} assigned to ν(COO) of the acetato group (Table III). The separation between them shows that the acetato ligand acts as a bridging ligand.[8] The shift of the ν(C=N) band towards lower wave numbers and the shift of the imine proton signal towards low frequency (high field) in the ^{1}H n.m.r. spectrum suggest that the metal atom is bonded to the nitrogen atom.[9-11] The ^{1}H n.m.r. spectrum shows only one singlet (δ 2.13 p.p.m.,

TABLE IV

^{1}H n.m.r. data for the ligand and complexes.[a]

	δ (–C*H*=N–)	δ *H*6(2′)	δ *H*5(3′)	δ *H*4(4′)	δ *H*3(5′)	δ C*H*$_3$O	δ C*H*$_3$COO
Ligand	8.75s	7.95dd ^{1}J(H6–H5) = 7.7 ^{2}J(H6–H4) = 1.8	← 7.38–6.86m →			3.84s	
1	7.70s		6.45d ^{1}J(H3′–H4′) = 8.1	6.95t ^{1}J(H4′–H3′) = 8.1 ^{1}J(H4′–H5′) = 7.5	6.64d ^{1}J(H5′–H4′) = 7.5	3.76s	2.13s
2	8.08s		← 6.93–6.42m →			3.71s	
3	8.13s		6.43d ^{1}J(H3′–H4′) = 8.1	6.90t ^{1}J(H4′–H3′) = 8.1 ^{1}J(H4′–H5′) = 8.0	n.a.	3.72s	
4	8.56d ^{4}J(^{31}P–H) = 8.9		5.97t ^{1}J(H3′–H4′) = 8.0 ^{4}J(^{31}P–H3′) = 8.1	6.50t ^{1}J(H4′–H3′) = 8.0 ^{1}J(H4′–H5′) = 7.9	6.38d ^{1}J(H5′–H4′) = 7.9	3.77s	
5	8.58d ^{4}J(^{31}P–H) = 8.5		5.95t ^{1}J(H3′–H4′) = 7.8 ^{4}J(^{31}P–H3′) = 8.2	6.50t ^{1}J(H4′–H3′) = 7.8 ^{1}J(H4′–H5′) = 8.0	6.37d ^{1}J(H5′–H4′) = 8.0	3.76s	

[a] The numbers in parentheses represent the protons in the complexes (see Fig. 1); n.a., not assigned; s, singlet; d, doublet; dd, double doublet; t, triplet; m, multiplet; coupling constants in Hz.

Table IV) for both methyl acetato protons indicating that the two methyls are equivalent, so that the Schiff base ligands have a *trans* disposition with respect to the acetato groups. The H6 singlet (H2′ in the comlex) is absent upon metallation as expected (Table IV).

Treatment of the acetato-bridged dimer with sodium chloride or bromide in acetone gave the chloro-bridged dimer (**2**) and the bromo-bridged dimer (**3**), respectively, as solids insoluble in the more common organic solvents (only slightly soluble in dichloromethane and in chloroform) (see Experimental and Table I). The differnt *trans* influence of the phenyl carbon atom and of the nitrogen atom causes the bridging system (PdX_2Pd) to be asymmetric and thus two ($Pd–X_b$) bands appear in the i.r. spectrum (Table III). The lower frequency one may be attributed to the Pd–X bond *trans* to the phenyl carbon atom. We take the geometry of the halogeno-bridged complexes to be *trans* by comparison to others already reported.[12,13]

TABLE V
Positional parameters and equivalent isotropic thermal parameters U_{eq} [$pm^2 \times 10^4$]
$U_{eq} = 1/3(U_{11} + U_{33})$

Atom	x/a	y/b	z/c	U_{eq}
Pd	0.16914(6)	0.04677(6)	0.27833(3)	0.0384(3)
O1	0.1070(6)	−0.0974(6)	0.3443(2)	0.050(3)
O2	−0.1399(6)	−0.1341(6)	0.2876(2)	0.048(3)
O3	0.4036(8)	0.5657(7)	0.3166(3)	0.079(4)
N	0.2357(6)	0.1965(6)	0.2181(3)	0.040(3)
C1	−0.0257(9)	−0.1662(8)	0.3292(3)	0.049(4)
C2	−0.043(1)	−0.305(1)	0.3685(5)	0.074(6)
C3	0.2858(8)	0.3196(8)	0.2450(3)	0.046(4)
C11	0.2250(8)	0.2089(8)	0.3396(3)	0.043(4)
C12	0.2865(8)	0.3315(8)	0.3122(3)	0.045(4)
C13	0.3414(8)	0.4553(9)	0.3486(3)	0.052(4)
C14	0.3352(9)	0.458(1)	0.4136(4)	0.058(5)
C15	0.273(1)	0.335(1)	0.4399(4)	0.063(6)
C16	0.2202(8)	0.2109(9)	0.4050(3)	0.050(5)
C21	0.2204(8)	0.1696(8)	0.1490(3)	0.041(4)
C22	0.3557(9)	0.0702(9)	0.1358(3)	0.053(5)
C23	0.327(1)	0.030(1)	0.0642(4)	0.074(6)
C24	0.306(1)	0.163(1)	0.0208(4)	0.071(6)
C25	0.178(1)	0.265(1)	0.0372(4)	0.065(6)
C26	0.2074(9)	0.3086(9)	0.1084(4)	0.056(5)
C31	0.452(1)	0.700(1)	0.3483(5)	0.082(7)

Reaction of the halogeno-bridged complexes with triphenylphosphine in acetone in a 1:2 molar ratio yields the mononuclear species (**4**) and (**5**) (see Experimental and Table I). The i.r. spectra show a rather low value for $\nu(Pd–X_t)$ indicating the halogen ligand must be *trans* to the carbon atom[14,15] (Table III). The ^1H n.m.r. spectra for complexes (**4**) and (**5**) show a doublet at *ca* 8.6 p.p.m. due to the imine proton coupled to the ^{31}P atom [$^4J(PH)$ *ca* 9 Hz] (Table III). A doublet at *ca* 6.4 p.p.m. is observed in the ^1H n.m.r. spectrum of complexes (**1**) and (**3**) assigned to H3′

(complex (**2**) gave an unresolved multiplet), due to coupling with H4′ (coupling to H5′ was not observed). However, in the case of complexes (**4**) and (**5**) a triplet appears at *ca* 6 p.p.m. which we also assign to H3′ now coupled to H4′ [^2J(HH) *ca* 8 p.p.m.] and to the ^{31}P atom [^4J(PH) *ca* 8 p.p.m.]

TABLE VI
Selected distances (pm) and angles (°) with e.s.d.'s
(Symmetry operator i: $-x$, y, $1/2 - z$).

Pd–O1	204.7(3)	O1–Pd–O2^i	86.8(1)
Pd–O2^i	213.7(3)	O1–Pd–N	176.5(2)
Pd–N	200.9(4)	O1–Pd–C11	95.0(2)
Pd–C11	196.2(5)	O2^i–Pd–N	96.6(2)
O1–C1	128.3(6)	O2^i–Pd–C11	172.7(2)
O2–C1	122.9(6)	N–Pd–C11	81.6(2)
O3–C13	136.5(7)	Pd–O1–C1	117.5(3)
O3–C31	141.1(8)	Pd^i–O2–C1	129.5(3)
N–C3	128.9(6)	C13–O3–C31	119.9(5)
N–C21	146.8(6)	Pd–N–C3	114.3(3)
C1–C2	152.5(9)	Pd–N–C21	122.4(3)
C3–C12	142.7(7)	C3–N–C21	123.3(4)
		O1–C1–O2	128.2(5)
Pd . . . Pd^i	292.6(1)	O1–C1–C2	115.4(5)
		O2–C1–C2	116.4(5)
		N–C3–C12	116.7(5)
		Pd–C11–C12	112.5(4)
		Pd–C11–C16	128.5(4)

Structure of (1)

The structure of [Pd{2-MeOC$_6$H$_3$C(H)=N-C$_6$H$_{11}$}(CH$_3$COO)]$_2$ (**1**) is shown in Fig. 2. The two Pd atoms are bridged by two acetato groups in a *cis*-arrangement. In addition, every Pd atom is bound to one Schiff base ligand by its N and Cl atoms forming a five membered metallacycle. The complex possesses C_2 symmetry with the twofold axis perpendicular to the Pd–Pd vector. As expected for Pd^{2+} the coordination is square-planar with bond angles at the Pd atom of between 81.6° and 96.6° (Table VI). The smallest angle is determined by the chelate ring. The coordination geometry is almost planar. The greatest deviation from the best plane through Pd, O1, O2, C11 and N is for the C11 atom (7(1) pm). Within the dimeric complex the two coordination planes form an interplanar angle of 33.9(1)°. No Pd-Pd interactions are present as indicated by the distance 292.6 pm.

The Pd–O1 and Pd–O2 distances are of approximately equal length and comparable with values in the trimer [Pd(CH$_3$COO)$_2$]$_3$.[16] They represent single bonds. The distances Pd–Cl (196.2 pm) and Pd–N (200.9 pm) are also in agreement with single bond interactions.

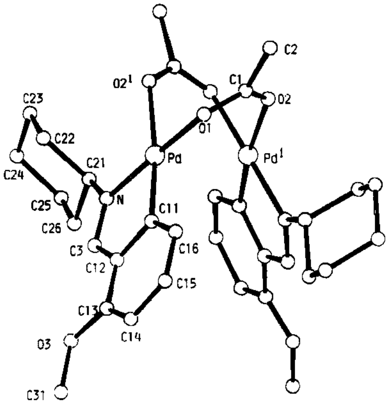

FIGURE 2 Structure of $\{Pd[2\text{-}CH_3OC_6H_3C(H){=}N\text{-}C_6H_{11}](CH_3COO)\}_2$

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