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Reaction of folded acetate-bridged *ortho*-palladated complexes with CH_2Cl_2. Crystal structure of $[\{Pd(C_6H_5-CH_2-N=C-(COC_6H_5)-C_6H_4)(\mu\text{-}Cl)\}_2]$

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Abstract

Folded acetate-bridged *ortho*-palladated complexes of benzoylbenzylideneamines react with CH_2Cl_2 to afford unfolded chloro-bridged *ortho*-palladated complexes. This finding is supported by an X-ray crystallographic study of the complex $[\{Pd(C_6H_5-CH_2-N{=}C-(COC_6H_5)-C_6H_4)(\mu\text{-}Cl)\}_2]$.

Key words: Palladium; X-ray structure; Ortho metallation; Dinuclear

1. Introduction

The reaction of *N*-(4-methoxyphenyl)-α-benzoylbenzylideneamine (**1a**) with palladium(II) acetate under various conditions allowed us to isolate two acetate-bridged *ortho*-metallated atropisomers with a folded structure (**2a**). The purification of these complexes by chromatography using CH_2Cl_2 and CH_2Cl_2-EtOH as eluents allowed us to isolate a further minor product (< 10%), as we have indicated previously [1].

In order to clarify the structure and the origin of this minor product and to check if similar products could be formed from other benzoylbenzylideneamines, we have investigated the mixtures obtained by reaction between palladium(II) acetate and *N*-(4-chlorophenyl)-(**1b**) [2], *N*-benzyl-(**1c**) [3], and *N*-phenylethyl-α-benzoylbenzylideneamine (**1d**) [3] (Scheme 1).

In this paper we report the results which demonstrate that CH_2Cl_2, usually considered an inert solvent, is able to transform the folded acetate-bridged complexes in the corresponding unfolded chloro-bridged *ortho*-metallated complexes.

2. Results and discussion

The reaction mixtures containing the folded acetate-bridged *ortho*-palladated complexes **2a–d** [1–3], were chromatographed with CH_2Cl_2 and CH_2Cl_2-EtOH. This allowed us to separate the orange folded acetate-bridged cyclopalladated complexes **2a–d**, and also two new yellow complexes **3a–d** and **4a–d**.

The microanalytical data of **4a–d** are consistent with the empirical formula [LPdCl]. These complexes are insoluble in organic solvents (except DMSO and DMF). The IR spectra exhibit two asymmetric stretching absorptions at 312 and 308 cm^{-1} in **4a**; 319 and 295 cm^{-1} in **4b**; 315 and 294 cm^{-1} in **4c** and 307 and 240 cm^{-1} in **4d**, which can be assigned to ν (Pd–Cl) bridging vibra-

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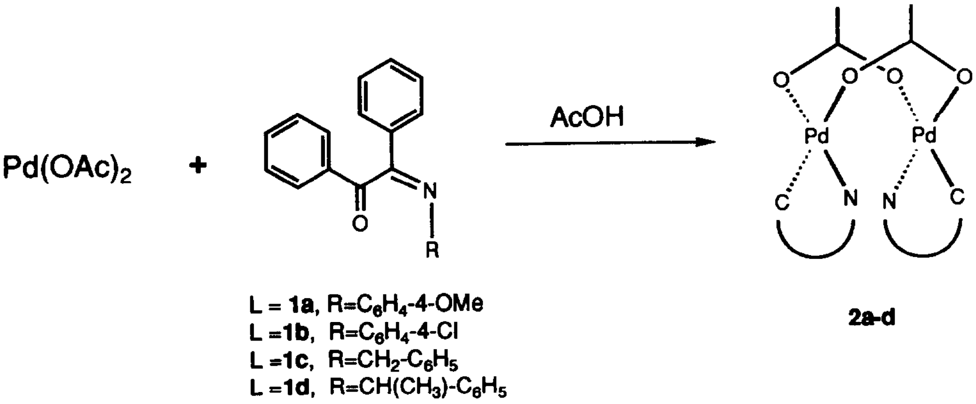

2a-d

Scheme 1.

tions, which indicates that these complexes are dinuclear. The ^1H NMR spectra show well-resolved separated signals in the aromatic region, contrary to what is observed for the folded acetate-bridged complexes **2a–d**. These compounds are chloro-bridged cyclopalladated complexes with an unfolded structure [4 *].

The complexes **3a–d** are soluble in organic solvents. The microanalytical data of these complexes are not reproducible, and always show values intermediate between those corresponding to [LPdCl] and to [LPdOAc]. The ^1H NMR spectra (Table 1) show well-resolved separated signals in the aromatic region, very similar to those of the unfolded chloro-bridged complexes **4a–d**, but in contrast to those of the folded acetate-bridged complexes **2a–d**, which suggests that the structures of complexes **3a–d** should be similar to **4a–d**. In the aliphatic region of the spectra of **3a–d** we observed a signal at *ca.* 1.25 ppm assigned to the acetate methyl group which is more shielded than in **2a–d** [5 *]. This fact is consistent with the resolution of the aromatic proton signals. The intensities of these last signals decrease, in solution as two new signals at *ca.* 1.60 and 3.70 ppm appear. However, there is no change in the aromatic region.

Similar changes (which do not affect the cyclometallated ligand) are also observed in the ^{13}C NMR spectra (Table 1). In general, the carbon chemical shifts are similar to those observed in other cyclometallated complexes [1–3]. The more significant differences in the ^{13}C NMR spectra concern the chemical shift of the acetate methyl group which initially appears at *ca.* 30 ppm (correlating with the ^1H signal at *ca.* 1.25 ppm), more deshielded than for **2a–d** (at *ca.* 24 ppm). This signal intensity decreases at the same time as that of a new signal at *ca.* 43 ppm (correlating with the ^1H signal at *ca.* 3.70 ppm) increases.

After the chromatographic fraction containing **3c** was concentrated, a single crystal was isolated. Crystal structure determination confirmed that the compound was the corresponding chloro-bridged cyclometallated complex **4c** (see below), which demonstrates that **3c** had evolved into **4c** during the concentration process. All the above facts suggest that compounds **3a–d** are unstable intermediates in the formation of the stable chloro-bridged complexes **4a–d**. They exhibit structures intermediate between those of **2a–d** and **4a–d** [6 *].

When the chromatographic purification of complexes **2a–d** was carried out with acetone/hexane as eluent, we never observed complexes **3a–d** and **4a–d**. Furthermore, if a solution of complexes **2a–d** in CH_2Cl_2 is stirred for several days, we observed partial transformation to **3a–d** and finally to **4a–d**. Both facts suggest that CH_2Cl_2 is responsible for the evolution of **2a–d** into **3a–d** and **4a–d**.

The X-ray diffraction studies of acetate-bridged cyclopalladated complexes with the folded structures **2a–d** have shown that the two parallel square-planar units are situated opposite one another and that the Pd–Pd distances (2.927–3.047 Å) [1,2] are consistent with a metal–metal interaction [7]. To rationalize the transformation **2a–d** → **4a–d**, we note that generally the d^8 binuclear complexes with metal–metal bond show an important photochemical reactivity. A molecular orbital model for Pd–Pd systems allows one-electron excitation from an antibonding orbital ($d\sigma^*$) unconnected with the Pd–Pd bond into a bonding orbital ($p\sigma$) yielding an excited state with diradical structure [8]. Our complexes **2a–d** should be similar and also give rise to diradical structures. This implies an increase in reactivity, and particularly the possibility of intermolecular electronic transfer reactions, as when

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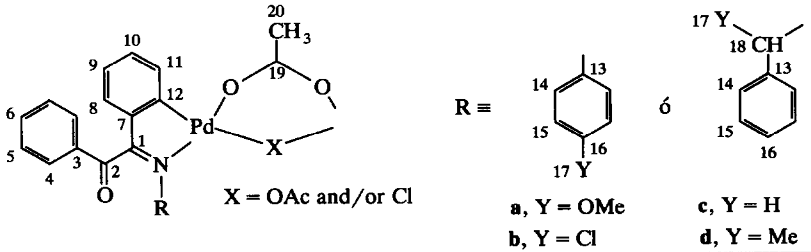
* Reference number with asterisk indicates a note in the list of references.

TABLE 1. NMR Spectra (ppm) of the complexes **3a–d**



	^{1}H NMR				^{13}C NMR		
	3a	**3b**	**3c**	**3d** [a]	**3a**	**3b**	**3c**
1					180.1	182.2	182.5
2					192.4	191.4	190.9
3					136.2	133.4	132.6
4,4′	7.74, m, 2H	7.75, m, 2H	7.87, m, 2H	7.95, m, 2H	129.1	129.1	129.7
5,5′	7.38, m, 2H	7.41, m, 2H	7.47, m, 2H	7.46, m, 2H	129.4	128.7	129.3
6	7.56, m, 1H	7.59, m, 1H	7.65, m, 1H	7.63, m, 1H	135.5	135.4	135.6
7					145.6	145.5	146.2
8	6.56, br, 1H	6.93, dd (2.0, 7.2), 1H	6.77, dd (1.4, 7.1), 1H	6.61, d (7.8), 1H	128.3	129.2	128.2
9	7.01, m, 1H	6.98, t (7.2), 1H	6.95, dt (1.4, 7.1), 1H	6.92, t (7.8), 1H	124.4	125.1	124.9
10	7.14, m, 1H	7.09, m, 1H	7.08, t (7.1), 1H	7.04, m, 1H	131.0	132.2	131.1
11	7.31, br, 1H	7.32, m, 1H	7.46, m, 1H	7.42, m, 1H	133.0	134.1	134.1
12					154.8	155.7	155.1
13					137.8	143.7	136.2
14,14′	6.94, [b] 2H	7.20–7.14, m	7.43, [c] m, 2H	7.35–7.15, m	125.5	125.5	128.4
15,15′	6.68, [b] 2H	7.20–7.14, m	7.19, [c] m, 2H	7.35–7.15, m	113.1	128.7	128.4
16			7.40, m, 1H	7.35–7.15, m	158.1	133.1	127.7
17	3.72, s, 3H			1.84, m, 3H	55.2		
18			4.80, br, 2H	4.48, m, 1H			58.9
19					179.8	181.5	180.2
Others [d]	1.23, s	1.26, s	1.25, s	1.25, s	30.8	29.7	29.7
	1.59, s	1.60, s	1.58, s	1.65, s	n.o.	28.3	n.o.
	3.78, s	3.75, s	3.74, s	3.68, s	n.o.	n.o.	43.4

[a] The low yield obtained for the complex **3d** prevented us from recording its ^{13}C NMR spectrum. [b] AA′BB′ system. [c] Assigned unambiguously. [d] The integral of these protons is not invariant. Abbreviations: br, broad; s, singlet; d, doublet; t, triplet; dd, double doublet; dt, double triplet; m, multiplet; n.o., not observed.

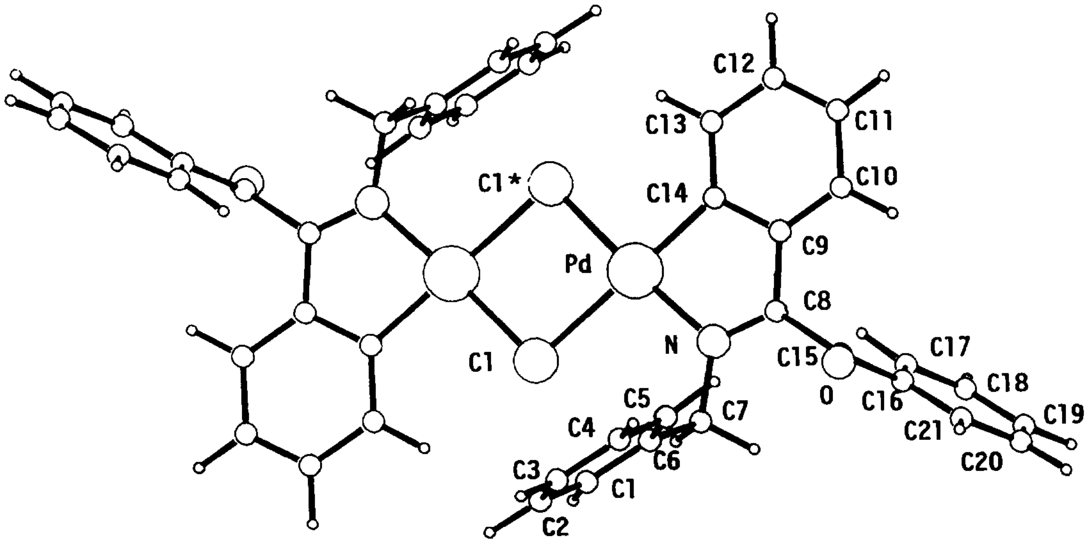


Fig. 1. The molecular structure of **4c** showing the atom numbering scheme.

the folded acetate *ortho*-palladated complexes are eluted with CH_2Cl_2 [6 *].

2.1. Crystal structure of the complex 4c

X-ray diffraction shows that complex **4c** is a chloro-bridged cyclometallated dimer, in which each palladium atom is bonded to an imine nitrogen, the *ortho* carbon of the phenyl ring supporting the imine carbon (*endo* structure) and two chlorine atoms in a square-planar coordination, with Pd 0.016 Å out on the mean plane passing through the C14, N, Pd, Cl and Cl* atoms. The five-membered chelate ring is planar, the maximum displacement from the best-fit plane being 0.010 Å (C14).

The atom labelling scheme is shown in Fig. 1. Atomic parameters for the non-hydrogen atoms are listed in Table 2. Selected bond distances and bond angles are listed in Table 3.

The Pd–N and Pd–C14 bond lengths of 2.026(4) and 1.967(5) Å, respectively, are similar to those in analogous cyclometallated complexes [1–3]. The Pd–Pd intra- and inter-molecular distances of 3.553(4) Å and 8.613(5) Å, respectively, indicate there are no metal–metal interactions. The N–C8–C15–O torsion angle is −86.7(1)°.

TABLE 2. Final atomic coordinates (×1000) and B_{eq} values for the non-hydrogen atoms and their estimated standard deviations for compound **4c**

	x	*y*	*z*	B_{eq} [a]
Pd	4172(3)	7522(2)	11651(4)	3.02(2)
Cl	6547(15)	3258(7)	−10539(15)	4.24(5)
O	3240(5)	2838(2)	3638(7)	7.18(22)
N	1309(4)	1714(2)	1351(5)	3.51(14)
C1	3560(7)	1280(4)	−391(8)	5.30(29)
C2	4849(8)	979(4)	−105(10)	6.05(36)
C3	5955(8)	1029(5)	1275(12)	6.71(40)
C4	5762(8)	1365(4)	2379(11)	6.59(35)
C5	4447(7)	1652(4)	2134(8)	5.30(27)
C6	3337(6)	1619(3)	713(7)	4.36(22)
C7	1923(6)	1960(3)	367(6)	4.24(21)
C8	1301(5)	2101(2)	2419(5)	3.69(17)
C9	677(6)	1782(3)	3326(6)	4.06(19)
C10	589(7)	2102(3)	4546(8)	5.22(26)
C11	38(8)	1735(4)	5391(7)	6.02(32)
C12	−446(8)	1067(4)	4989(7)	5.48(32)
C13	−368(6)	740(3)	3747(7)	4.57(28)
C14	177(5)	1097(3)	2911(6)	3.60(18)
C15	1988(6)	2821(3)	2794(7)	4.48(20)
C16	1131(5)	3450(2)	2217(6)	3.66(18)
C17	−325(6)	3409(3)	1372(7)	4.69(22)
C18	−1091(7)	4009(4)	883(9)	6.14(29)
C19	−443(8)	4660(3)	1294(9)	6.10(31)
C20	1001(8)	4698(3)	2141(9)	5.87(31)
C21	1785(6)	4104(3)	2616(7)	4.45(23)

[a] $B_{eq} = (8\pi^2/3)\Sigma_{ij}U_{ij}a_i a_j a_i^* a_j^*$.

TABLE 3. Selected bond distances and angles for compound **4c**

Distances (Å)	
Pd–N	2.026(4)
Pd–C14	1.967(5)
Pd–Cl	2.457(1)
Pd–Cl [a]	2.317(1)
N–C8	1.295(6)
C8–C9	1.448(8)
C8–C15	1.520(7)
C9–C10	1.393(9)
C9–C14	1.400(7)
C10–C11	1.39(1)
C11–C12	1.36(1)
C12–C13	1.416(9)
C13–C14	1.369(8)
C15–O	1.214(6)
C15–C123	1.458(7)
Pd–Pd [a]	3.553(4)
Angles (deg)	
N–Pd–C14	80.9(2)
N–Pd–Cl	99.5(1)
C14–Pd–Cl [a]	95.7(1)
Cl–Pd–Cl [a]	83.9(1)
Pd–N–C8	115.3(4)
N–C8–C9	115.5(4)
C8–C9–C14	114.6(5)
Pd–C14–C9	113.6(4)
Pd–Cl–Pd [a]	96.1(1)

[a] (−x, −y, −z).

The Pd–Cl bond *trans* to the aromatic carbon atom is significantly longer, 2.457(1) Å, than Pd–Cl*, 2.317(1) Å, which is *trans* to the imine nitrogen, a consequence of the different *trans* influences of these atoms [9]. All distances and angles within the aromatic groups are normal.

The aromatic rings joined to methylene groups in this structure are perpendicular to the plane containing the Pd–Cl bonds. If the complexes **3a–d** are unfolded, like complex **4c**, the shielding of the acetate methyl groups observed in ^1H NMR spectra could be due to through-space interactions of the overlying rings.

3. Experimental section

IR spectra were recorded in Nujol mulls and KBr pellets in the 4000–200 cm^{-1} range with a Perkin Elmer Model 283 spectrophotometer. NMR spectra were recorded on a Bruker WP-200-SY (200 MHz) spectrometer in $CDCl_3$ with TMS, as internal standard. The C, H, and N analyses were carried out with a Perkin Elmer 240B microanalyzer.

All solvents were purified prior to use by standard methods [10]. CH_2Cl_2 was carefully dried with CaH_2. Palladium(II) acetate was purchased from Strem. The syntheses of other compounds follow published methods [11].

TABLE 4. Crystal Analysis Parameters of Compound **4c**

Crystal data	
Formula	$C_{42}H_{32}N_2O_2Cl_2Pd_2$
Symmetry	Monoclinic, $P2_1/n$
Unit cell dimensions: a, b, c(Å)	10.406(2), 19.053(3), 9.932(1)
β(°)	115.07(1)
Packing: V(Å^3), Z, D_c (g cm^{-3})	1783.7(8), 2, 1.639
M, F(0, 0, 0), μ(cm^{-1})	879.7, 880, 11.79
Experimental data	
Number of reflections:	
Measured	5638
Observed	3863
Standard reflections	3 reflections every 120 min, no variation
Solution and refinement	
Solution	Patterson
Refinement	Least-squares on F_{obs}
H atoms	Geometric calculations
R, R_w	0.061, 0.066

Dimers **2a–d** were prepared according to refs. 1–3. When the crude residue was column chromatographed (SiO_2) eluting with CH_2Cl_2 and CH_2Cl_2-EtOH (99 : 1), three separate bands became visible, yielding the complexes **2a–d** (orange), complexes **3a–d** (yellow) and **4a–d** (yellow). Eluting with acetone-hexane produced only one band, yielding the complexes **2a–d** (orange).

3.1. Structure determination and refinement of the complex 4c

Slow evaporation from a CH_2Cl_2 solution of complex **3c** produced yellow crystals. A prismatic crystal (0.1 × 0.1 × 0.2 mm) was selected and mounted on an Enraf-Nonius CAD4 diffractometer. Unit cell parameters were determined from automatic centring of 25 reflections ($16 \le \theta \le 21°$) and refined by least-squares method. The data, the details of the data collection and structure analyses are summarized in Table 4. Intensities were obtained with graphite monochromated Mo Kα radiation, using $\omega/2\theta$ scan technique. 5638 reflections were measured in the range $2 \le \theta \le 3°$, 3863 of which were assumed as observed applying the condition $I \ge 2.5\ \sigma(I)$. Three reflections were measured every two h as orientation and intensity control, significant intensity decay was not observed. Lorentz-polarization, but no absorption corrections were made.

The structure was solved by Patterson synthesis, using SHELXS [12] and refined by a full-matrix least-squares method, with the SHELX76 [13]. The function minimized was $\Sigma w \| F_o | - | F_c \|^2$, where $w = (\sigma^2(F_o) + 0.010 | F_o |^2)^{-1}$. f, f′ and f″ were taken from International Tables of X-ray Crystallography [14]. The position of all H atoms was computed and refined with an overall isotropic temperature factor, using a riding model and the remaining atoms being treated anisotropically. The final R factor was 0.061 (Rw = 0.066) for all observed reflections. The number of refined parameters was 227. Max. shift/e.s.d = 0.1. Max. and min. peaks in final difference synthesis were 0.3 and −0.3 e Å^{-3}, respectively.

Acknowledgment

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Supplementary material

Listings of anisotropic thermal parameters for non-hydrogen atoms, positional and isotropic thermal parameters for hydrogen atoms, and all bond distances and angles for **4c** are available from the Cambridge Crystallographic Data Centre.

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4 These complexes are identical to those obtained by metathetical reaction of complexes **2a–d** with NaCl in acetone, or by reaction of $PdCl_2$ with the corresponding ligand in MeOH. Microanalytical, ^1H and ^{13}C NMR and IR data are collected in refs. 2, 3 and J.L. García-Ruano, I. López-Solera, J.R. Masaguer, M.A. Monge, C. Navarro-Ranninger and J.H. Rodríguez, *J. Organomet. Chem., 476* (1994) 111.

5 A similar greater shielding has been inferred when carboxylato-bridged orthopalladated azine complexes are converted in asymmetric-bridge compounds with chlorothiolate implying opening up of the open-book structure (P. Espinet, personal communication).

6 Because the microanalytical and NMR data of these compounds are not reproducible, but always exhibit values intermediate between those of the folded acetate complexes and unfolded chloro-complexes, the species **3a–d** could be formed by more than one compound. Each would be a different intermediate involved in the transition **2a–d** → **4a–d**. Radical (or nucleophilic) attack of Pd on the CH_2Cl_2 (with simultaneous Pd ··· Pd bond-splitting, marking the transition from a folded to an unfolded structure) could be the initial step of this transformation. Species containing the fragments OAc, CH_2Cl and Cl (which might explain the signals at *ca.* 1.25 and 3.7 ppm in ^1H NMR spectra as well as those at *ca.* 30 and 43 ppm in ^{13}C NMR spectra) could be formed successively during the acetate-chloride exchange.

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