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Orthometalation reactions of substituted benzylideneamines by palladium(II) chloride

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Abstract

Carbon–metal σ-bonded complexes have been synthesized by reaction of various substituted benzylideneamines with $PdCl_2$. The chloro-bridged complexes formed have been studied by spectroscopic methods and by thermogravimetric analyses.

The number of articles on organometallic intramolecular coordination compounds is increasing [1–5]. Benzylideneamines also afford many types of organometallic intramolecular complexes having five-membered ring structures in which the ligand is π-bonded to the metal or the five-membered ring is formed by coordination of a lone pair of the ligand atom [6–8].

With these compounds, formation of the metal-carbon σ bond usually occurs more or less readily by direct interaction of the ligand and metal substrate, and elimination of the hydrogen in combination with a suitable leaving group. The cyclometalation reaction is facilitated by choice of a good leaving group in the metal complex, which combines with the hydrogen atom displaced from the metalated carbon atom.

We present here the results of a study of the coordination behaviour of *N*-phenylbenzoylbenzylideneamines and its substituted derivatives towards palladium(II) dichloride.

Experimental

Starting materials. Solvents of commercial quality were purified and dried by standard methods. Palladium chloride (Merck) was used without further purification. The ligands *N*-phenylbenzoylbenzylideneamine (PBI), *N*-(1-phenylmethyl)ben-

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zoylbenzylideneamine (PMBI), and *N*-(1-phenylmethoxy)benzoylbenzylideneamine (PXBI) were kindly supplied by Drs. J. Plumet, G. Escobar and R. Pérez Alvarez-Ossorio (Universidad Complutense de Madrid).

Preparation of the complexes. All complexes were obtained as yellow solids by the following procedure. To a solution containing 2 mmol of $PdCl_2$ in 5 ml of ethanol was added an ethanol solution of 2 mmol of ligand. The mixture was stirred for several hours, and the precipitate then filtered off, washed with methanol then diethyl ether, and vacuum-dried at room temperature.

$[Pd(PBI)X]_2$. Found: C, 55.85; H, 3.45; N, 3.13; Pd, 24.77. Calcd.: C, 56.17; H, 3.51; N, 3.27; Pd, 24.90%.

$[Pd(PMBI)X]_2$. Found: C, 56.71; H, 3.80; N, 3.31; Pd, 23.75. Calcd.: C, 57.11; H, 3.85; N, 3.17; Pd, 24.11%.

$[Pd(PXBI)X]_2$. Found: C, 55.58; H, 3.69; N, 3.21; Pd, 24.00. Calcd.: C, 55.11; H, 3.71; N, 3.06; Pd, 23.26%.

Physical methods. The infrared spectra were recorded in Nujol and KBr pellets in the 4000–200 cm^{-1} range with a Perkin–Elmer model 283 spectrophotometer. NMR spectra were recorded with $CDCl_3$ solutions with TMS as internal standard ($\delta = 0$ ppm), and were recorded on a Bruker WP-200-SY (200 MHz) spectrometer.

Thermogravimetric measurements were made on a Mettler HE 20 thermobalance, with a DTA accessory fitted. The analytical constants were DTA range 20 $\mu V = 0.33$ kcal s^{-1}; TG range 20 mV; heating rate 5 °C min^{-1}; recording rate, 40 cm h^{-1}; thermocouple, Pt/Pt–Rh 10%; the sample (~ 20 mg) was placed on a platinum crucible standing on the thermocouple. The instrument was calibrated by use of indium (purity 99.99%) as standard substance. The analyses were carried out in a dynamic air atmosphere. Data on the temperatures or thermal transitions and the mass-loss determinations are shown in Table 4, and the TG/DTA curves are shown in Fig. 2.

DSC measurements were performed with a Mettler TA 3000 system with a differential scanning calorimeter model DSC 20. Samples of about 5 mg were used so as to make insignificant any temperature non-uniformity within the sample. An aluminium pan was used under a dynamic air atmosphere. The scanning rate was 5 °C min^{-1}, and the instrument calibration was checked periodically with standard samples of indium.

The results are shown in Table 4.

Results and discussion

The IR spectral data for ligands and complexes in the range 1550–1700 cm^{-1} are given in Table 1.

The spectra of the free benzylideneamines show four bands in this region. The band at ca. 1664 cm^{-1} is assigned to the C=O stretching mode, that at ca. 1620 cm^{-1} to the C=N stretching mode, and those at 1586, 1574 cm^{-1} to aromatic stretching modes. As Table 1 shows, the frequency of the C=O absorption band in the spectra of ligands was not shifted to lower frequencies on formation of the palladium-ligand complexes, which indicates that oxygen-to-metal bonds were not present. However, coordination of the benzylideneamines to palladium always results in a slight shift of the C=N stretching mode to lower frequencies, if complexation occurred through the π-system a substantial decrease in the C=N

Table 1

Azomethine, carbonylo, and aromatic ring stretching modes (cm^{-1})

R	Ligand			Complex		
	ν(C=N)	ν(C=C)	ν(C=O)	ν(C=N)	ν(C=C)	ν(C=O)
H	1620s	1586, 1572s	1664s	1605sh	1586, 1563s	1664s
CH_3	1615s	1586, 1574s	1660s	1600sh	1585, 1563s	1663s
OCH_3	1624s	1586, 1575s	1669s	1615sh	1588, 1563s	1670s

stretching frequency would be expected (ca. 150 cm^{-1}) [4,9], whereas in our complexes, the decrease averages only about 15 cm^{-1}. The position of the aromatic ring stretching frequency is approximately constant. Thus the coordination of the benzylideneamines is almost certainly through the lone pair and not through the azomethine π-system. There seems to be no simple relation between the electronic character of the substituent and the change in the azomethine stretching frequency.

The presence of an *ortho*-substituted aromatic ring is shown by the presence in the infrared spectrum of extra bands (compared with the number in the ligand) in the 700–800 and 1100 cm^{-1} regions [4,10,11]. These bands are clearly observed in all the complexes prepared.

Finally, two ν(Pd–Cl) bands are apparent for each compound (see Table 2). On the basis of the higher *trans*-influence of a σ-bonded carbon compared with that of a nitrogen atom, the higher frequency band was attributed to the stretching vibration ν(Pd–Cl) *trans* to the nitrogen atom, and the lower frequency one to ν(Pd–Cl) *trans* to the σ-bonded carbon.

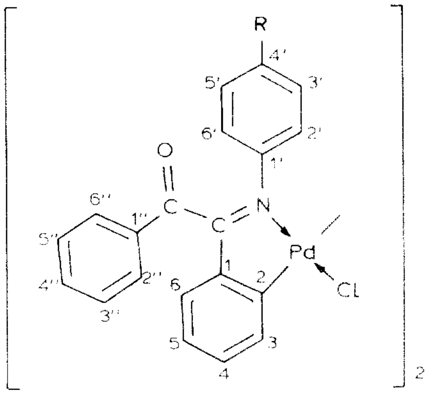
These data are all consistent with the proposed structure [12]. Conclusive confirmation of the *ortho* substitution could not be obtained from the NMR spectrum of the di-μ-chlorobis[*N*-(1-phenylmethoxy)benzoylbenzylideneamine)]dipalladium(II), $[Pd(PXBI)Cl]_2$ because the disappearance of the H(2) proton upon palladation cannot be clearly observed owing to coupling of H(2) in the ligand with the other ring protons [8].

For the same reason, and also because of the presence of the other two aromatic rings, the expected upfield shift of the H(3) signal after metallation is not clearly seen. However, the downfield shifts of the methoxy group and of the protons of the iminomethoxy *p*-disubstituted aromatic ring (H2′–6′)) seem to be in agreement with the coordination of the metal atom to the organic moiety through the nitrogen lone pair (see Fig. 1 and Table 3). Unfortunately, the other complexes are too insoluble in chloroform for their NMR spectra to be obtained.

Table 2

Stretching frequencies (cm^{-1}) in complexes $[PdLCl]_2$

	ν(Pd–Cl)	ν(Pd–N)
$[Pd(PBI)Cl]_2$	335s 240m	310m
$[Pd(PMBI)Cl]_2$	338s 260m	295m
$[Pd(PXBI)Cl]_2$	335s 245m	290w



R = H , CH_3 , OCH_3

Fig. 1.

Figure 2 shows the DSC (to 600 °C), DTA (600–1000 °C) and TG curves corresponding to di-μ-chlorobis(*N*-phenylbenzoylbenzylideneamine)dipalladium(II), $[Pd(PBI)Cl]_2$.

It can be seen that there are three endothermic peaks with maxima at 250, 267, and 804 °C, respectively. There is also a very marked exothermic effect, with a maximum at 440 °C, and a shoulder centred at 484 °C.

From the TG plot it appears that decomposition starts at about 180 °C, and although there are no clear steps in this curve, the information given by the DSC and DTA curves helps to reveal what is happening. Between 180 and 305 °C there are two overlapping endothermic processes with peak temperatures of 250 and 267 °C. The weight loss recorded up to the end of the second endothermic process at 380 °C is 12.50%, and can be attributed to the loss of a benzoyl radical of one ligand, the calculated weight loss for this being 12.28%. The enthalpy of this process is ΔH 303.85 ± 0.78 kJ mol^{-1}.

At higher temperatures, there is further loss of weight corresponding to an exothermic peak between 342–473 °C and a shoulder between 473–644 °C. The first process may be due to elimination of the ligands and concomitant formation of $PdCl_2$ and PdO, but this process cannot be clearly separated from oxidation of the palladium halide (eq. 1), which is responsible for the exothermic shoulder centred at

$$PdCl_2 + \tfrac{1}{2}O_2 \rightarrow PdO + Cl_2 \qquad (1)$$

484 °C. An interesting aspect on this process is that according to eq. 1 there should

Table 3

^1H NMR data for the ligand PXBI and the complex $[Pd(PXBI)Cl]_2$

	H(2,6,2″,6″)	H(3,4,5,3″,4″,5″)	H(2′,3′,5′,6′)	OCH_3
1	7.8–7.6	7.4–7.1	6.8–6.5	3.5
2	8.0–7.0		6.9–6.6	3.8

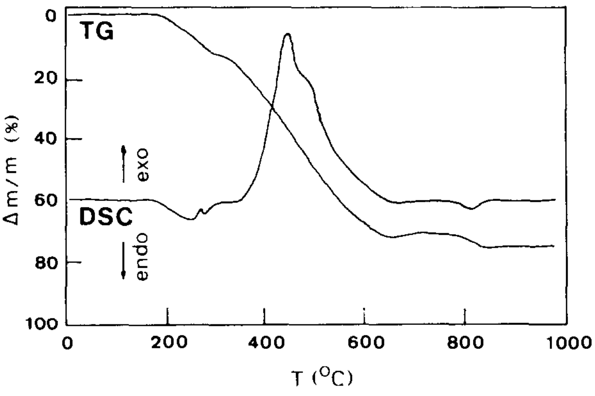


Fig. 2.

be a total net weight loss of 67.34%, whereas it can be seen that after 692° C there is a weight gain on the TG curve, and this suggests that the $PdCl_2$ is totally decomposed before the resulting palladium metal is completely oxidized. The weight gain in this oxidation will then be responsible for the slight mass increase up to 692° C (loss found 67.08%). The total enthalpy of these processes is $\Delta H = 4786.6 \pm 2.8$ kJ. mol^{-1}.

Table 4

Thermal data

Compound	Temperature (° C)	Peak temperature (° C)	Mass loss (Found (calcd.) (%))	Process	ΔH (kJ mol^{-1})	Identified compound
$[Pd(C_{20}H_{15}NO)Cl]_2$	180–305	250; 267	12.50 (12.28)	Endothermic	303.85 ± 0.78	$[Pd_2(C_{20}H_{15}NO)(C_{13}H_{10}N)]Cl_2$
	342–692	440; 484	67.08 (67.34)	Exothermic	4786.6 ± 2.8	PdO
	781–827	804	13.12 (13.07)	Endothermic	6.53 ± 0.04	Pd
$[Pd(C_{21}H_{17}NO)Cl]_2$	235–290	255; 266; 273; 281	12.00 (11.90)	Endothermic	178.63 ± 0.28	$[Pd_2(C_{21}H_{17}NO)(C_{14}H_{12}N)]Cl_2$
	348–674	451; 479	68.87 (68.51)	Exothermic	4423.97 ± 3.1	PdO
	774–819	800	13.10 (13.07)	Endothermic	6.46 ± 0.02	Pd
$[Pd(C_{21}H_{17}NO_2)Cl]_2$	208–295	248; 253; 286	11.00 (11.48)	Endothermic	164.59 ± 0.34	$[Pd_2(C_{21}H_{17}NO_2)(C_{14}H_{12}NO)]Cl_2$
	357–703	432; 490	70.04 (69.76)	Exothermic	3945.75 ± 3.6	PdO
	798–825	812	12.89 (13.07)	Endothermic	6.31 ± 0.07	Pd

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The last endothermic process (781–827 °C), with a maximum peak temperature at 804 °C, represents the decomposition of the PdO previously formed, according to:

$$\mathrm{PdO} \rightarrow \mathrm{Pd} + \tfrac{1}{2}\mathrm{O_2}$$

The calculated weight loss (13.07%) is in fair accord with the experimental value (13.12%). The enthalpy of this endothermic process is $\Delta H = 6.53 \pm 0.04$ kJ mol^{-1}.

The thermoanalytical curves for the other two complexes $[\mathrm{Pd(PMBI)Cl}]_2$ and $[\mathrm{Pd(PXBI)Cl}]_2$ were analogous to those discussed for $[\mathrm{Pd(PBI)Cl}]_2$. The results obtained are shown in Table 4. If the values of the enthalpies for the three complexes are compared it can be seen that the values are highest for the complex with PBI as ligand and lowest for that with PXBI as ligand the enthalpies of all three processes. This sequence is consistent with the findings from infrared spectroscopy.

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