Transition Metals Complexes to Ordered Mesophases. Synthesis and Mesomorphic Properties of Cyclopalladated Complexes Formed from *p*-Alkoxy-*p*′-alkyl-azobenzenes

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In order to prepare new materials for liquid-crystal display devices some recent investigations are dealing with the synthesis of coordination or organometallic complexes having mesomorphic properties. As far as species containing palladium are concerned, either coordination [1] or organometallic compounds arising from the orthometallation of azobenzene esters [2] have been described.

In this paper we report the extension of our work to the synthesis, characterisation and mesomorphic behaviour of some cyclopalladated complexes formed by reaction between *p*-alkoxy-*p*′-alkylazobenzenes and $Pd(PhCN)_2Cl_2$.

Experimental

Preparation of Compounds

The *p*-alkyl-*p*′-alkoxyazobenzenes (**L1**–**L5**) [3–5] and the starting complex $Pd(PhCN)_2Cl_2$ [6] were prepared as described in the literature.

[PdCl(L-H)]₂

The reactions were performed in an oxygen-free nitrogen atmosphere. In a typical preparation, to 25 ml of an ethanolic solution containing 1 mmol of the appropriate ligand **L** was added 1 mmol of $Pd(PhCN)_2Cl_2$. The resulting orange mixture was stirred at room temperature for 12 h. The yellow precipitate formed was collected by filtration, washed with ethanol and dried under vacuum. The crude product was chromatographed on a Kieselguhr column using mixtures of reagent grade diethylether and dichloromethane. The solvent was removed under reduced pressure and the remaining solid product dissolved in dichloromethane and precipitated by adding to hexane. *Anal.* Compound **1**, $[PdCl(\mathbf{L1}\text{-H})]_2$, yield 60% (Found: C, 46.40; H, 3.44; N, 7.59. Calc. for $C_{28}H_{26}N_4Cl_2O_2Pd_2$: C, 45.80; H, 3.57; N, 7.63%). Compound **2**, $[PdCl(\mathbf{L2}\text{-H})]_2$, yield 52% (Found: C, 46.55; H, 3.93; N, 7.10. Calc. for $C_{30}H_{32}N_4Cl_2O_2Pd_2$: C, 47.14; H, 4.22; N, 7.33%). Compound **3**, $[PdCl(\mathbf{L3}\text{-H})]_2$, yield 55% (Found: C, 52.67; H, 5.52; N, 5.96. Calc. for $C_{40}H_{50}N_4Cl_2O_2Pd_2$: C, 53.23, H, 5.58; N, 6.20%). Compound **4**, $[PdCl(\mathbf{L4}\text{-H})]_2$, yield 45% (Found: C, 57.04; H, 6.82; N, 5.34. Calc. for $C_5H_{70}N_4Cl_2O_2Pd_2$: C, 57.58; H, 6.76; N, 5.37%). Compound **5**, $[PdCl(\mathbf{L5}\text{-H})]_2$, yield 48% (Found: C, 57.75; H, 6.94; N, 4.96. Calc. for $C_{52}H_{76}N_4Cl_2O_2Pd_2$: C, 58.21; H, 7.13; N, 5.22%).

Physical Measurement

Infrared spectra were recorded on a Perkin-Elmer model 1330 spectrometer as KBr pellets. ^{1}H NMR spectra were recorded on a Varian XL-100 spectrometer in $CDCl_3$ solutions. The thermal behaviours were monitored with a Mettler FP 800 thermosystem equipped with a FP 84 Microscopy Cell, heating rate 4 °C/min. The textures of the various mesophases have been observed by means of a Reichert Thermovar polarizing microscope equipped with an heating stage. Elemental analyses were carried out by the Microanalysis Laboratory of the Istituto di Farmacia dell'Università di Pisa, Italy.

Results and Discussion

The azobenzenes **L1**–**L5**, of general formula $(p\text{-}RCH_2O)C_6H_4\text{–}N\text{=}N\text{–}C_6H_4$ (p'-R'), were synthe-

TABLE I. Selected ^{1}H NMR data (δ/ppm)[a] for the ligand L and the complexes $[PdCl(L\text{-H})]_2$

Ligand	δ(R–*CH*₂–O–)	δ(R′)	Complex	δ(R–*CH*₂–O–)		δ(R′)	
				A	B	A	B
L1 (R = H; R = CH_3)	3.91	2.44	**1**	3.90	3.88	2.37	2.44
L2 (R = R′ = CH_3)	4.12	2.42	**2**	4.11	4.09	2.36	2.43
L3 (R = C_6H_{13}; R′ = CH_3)	4.02	2.42	**3**		4.17		2.43
L4 (R = $C_{11}H_{23}$; R′ = CH_3)	4.06	2.46	**4**	4.07[b]		2.36	2.44
L5 (R = $C_{11}H_{23}$; R′ = C_2H_5)	4.04	2.74[c]	**5**	4.02[b]		2.64	2.73[c]

[a] All values are relative to $Si(CH_3)_4$. [b] Broad signal. [c] Methylenic protons.

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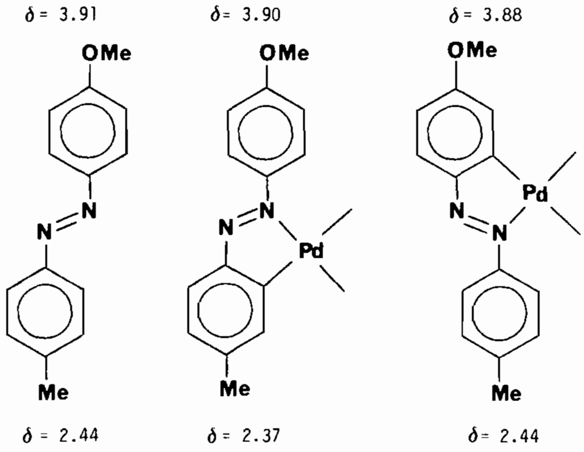
sized following the usual procedure [3–5], and characterized by elemental analysis, IR and ^{1}H NMR spectroscopy (Table I).

The dinuclear cyclometallated palladium complexes $[PdCl(L\text{-}H)]_2$ (**1**–**5**) were obtained in 45–60% yield by reaction of $Pd(PhCN)_2Cl_2$ with the appropriate ligand and characterized by elemental analysis, IR and ^{1}H NMR spectroscopy ('Experimental' and Table I). The microanalytical data account for the expected stoichiometry.

On the other hand the literature reports that in similar reactions carried with asymmetrically substituted azobenzenes the metallation can occur on both the aromatic rings [7]. In the present case the identification of the metallated ring was obtained by ^{1}H NMR spectroscopy. Thus, for example, in the spectrum of **1**, wherein the reacted ligand was *p*-methoxy-*p*'-methylazobenzene, two distinct resonances for each methyl group are present (Table I), of relative intensity approximately 1:1:1:1. In particular, both for CH_3O- and CH_3- group one signal is found in the same position of the uncomplexed **L1**, while the other one results downfield shifted. These data are consistent with a nearly statistical metallation on both benzene ring of the ligand, as shown in Scheme 1.



1 **A** **B**

Scheme 1. Ligand **L1** and Complex **1** (**A** and **B** forms).

The ^{1}H NMR spectra of **2** and **4** confirm the presence of a distribution of **A** and **B** forms about 1:1 as estimated from the integral of the R' methyl signals. The same feature is found for the product **5** ($R = C_{11}H_{23}$; $R' = C_2H_5$) whose protonic spectrum contain a broad triplet, due to the $R-CH_2-O-$ hydrogens, and two very close quartets arising from the R' methylenic protons (Table I). Surprisingly **L3** gives the form **B** only, complex **3** in Table I, the reason of such a reactivity we are not able to explain.

The thermal behaviour of both the ligands **L1**–**L5** and the species **1**–**5** is reported in Table II. The azobenzenes **L2**–**L5**, accordingly with their molecular structures [8], display mesomorphism in which nematic textures are present. Their cyclopalladated derivatives, either as mixtures (**2**, **4** and **5**) or as single species (**3**) retain this mesogenic nature. In this context, noteworthy is the behaviour of **1** which shows a nematic phase, lacking in the parent ligand **L1**. Finally, compounds **2**–**5** are thermally very stable, so that an extensive physical characterisation of these new materials is under way.

TABLE II. Transition[a] temperatures (°C) for the ligands L and the species $[PdCl(L\text{-}H)]_2$ (**1**–**5**)

Ligands		Complexes	
L1	K ⟶ 180(I)	1	K → 230(N) → 255(dec.)
L2	K ⟶ 119(I) 91(K) ← 92(N) ⟵	2	K → 215(N) → 260(I)
L3	K ⟶ 76(I) 58(K) ← 68(N) ⟵	3	K → 175(N) → 195(I)
L4	K ⟶ 77(I) 72(K) ← 76(N) ⟵	4	K → 150(N) → 171(I)
L5	K ⟶ 71(I) 61(K) ← 67(N) ⟵	5	K → 162(N) → 168(I)

[a] K, crystal; N, nematic; I, isotropic; dec., decomposition.

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