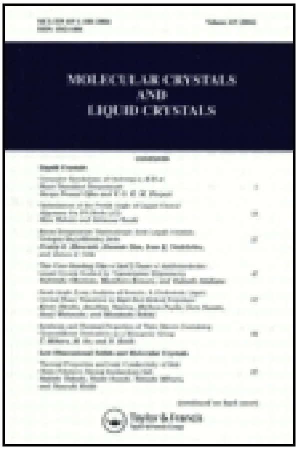

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Transition Metals Complexed to Ordered Mesophases: Palladium-Azo Complexes

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Transition Metals Complexed to Ordered Mesophases: Palladium-Azo Complexes

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The synthesis and characterization of palladium (II) complexes with liquid crystal azobenzene ligands is reported. The new organometallic compounds, having a σ metal-carbon bond and a metal-metal chloro bridge, display ordered mesophases. The temperatures of the K-N phase transition, in the region of 200°C, are some 130° higher than those for the related free ligands.

INTRODUCTION

One of the more interesting aspects of homogeneous catalysis is that of obtaining high selectivity by varying the properties of the ligands around the transition metal. The selectivity that can be induced by electronic or steric effects is usually the result of a cooperative effect of both, but in some particular reactions, i.e., stereospecific syntheses, the geometrical environment of the catalytic site determines the conformation of the reaction product.[1] In this perspective we are interested in the study of the properties and reactivity of transition metals in highly ordered media such as liquid crystals.

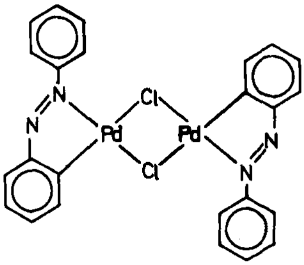
Since any attempt to dissolve an organometallic complex in a nematic phase generally gives rise to a loss of the ordered texture, because the guest complex is too large with respect to the host molecules, our efforts have been focused on the synthesis of new organometallic complexes, in which the transition metal is directly bonded to an organic liquid crystal moiety.

Some examples of organometallic liquid crystals, demonstrating that transition metal complexes can have smectic or nematic mesophases, have been recently reported in the literature,[2,3] thus encouraging us about our project.

As the first part of this study we report the results on the reaction of tetrachloropalladate with organic liquid crystal materials containing the azobenzene frame.

RESULTS AND DISCUSSION

In organometallic chemistry, it is known that azobenzenes undergo *ortho*-metallation by reaction with $PdCl_4^{2-}$ giving complexes like I.[4]



In the same way, liquid crystal materials such as compounds **1–4** (Table I) and tetrachloropalladate interact giving, in good yields, orange precipitates (**5–8**). The microanalytical values obtained for these materials are in agreement with those of compounds containing ligand, palladium, and chlorine in a 1 : 1 : 1 ratio. Far infrared investigations show the presence of a Pd—Cl bridge[5] (three bands, see Table II). On the basis of these data and taking into account the behavior of the strictly related ligand azobenzene, we suggest for complexes **5–8** a structure containing palladium and carbon σ bonded as in I.

The presence of a Pd—C σ bond and the dinuclear nature of these complexes have been confirmed by the analysis and characterization of the products obtained by reaction of the complexes **5–8** with one equivalent of triphenylphosphine. The neutral ligand triphenylphosphine is able to cleave the chlorine bridge,[6] but not the Pd—C bond or the Pd—N bond. The complexes **9–12** formed by this reaction give microanalytical data and spectra in the far

TABLE I

Liquid crystal ligands.

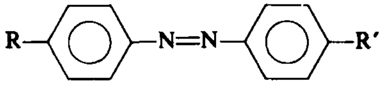
	R	R'
1	C_2H_5O	C_4H_9COO
2	C_2H_5	$C_5H_{11}COO$
3	C_2H_5O	$C_6H_{13}COO$
4	C_2H_5O	$CH_2{=}CH(CH_2)_8COO$

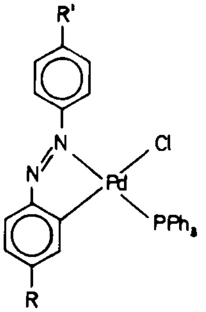
TABLE II

Analytical and far-infrared data for metallated liquid crystals.

Compound[a]	Yield %	Found (Calc.) % C	H	N	ν(Pd—Cl) cm^{-1}
5 (Pd(1—H)Cl)$_2$	60	48.6(48.8)	4.4(4.5)	6.0(6.0)	345, 319, 245
6 (Pd(2—H)Cl)$_2$	58	50.4(51.6)	4.8(5.0)	6.2(6.0)	341, 319, 241
7 (Pd(3—H)Cl)$_2$	55	50.8(50.9)	5.3(5.1)	5.8(5.7)	341, 320, 242
8 (Pd(4—H)Cl)$_2$	40	54.7(54.7)	5.6(5.7)	5.3(5.1)	359, 318, 250
9 Pd(1—H)(PPh$_3$)Cl	85	60.5(61.0)	5.1(5.0)	3.9(3.8)	309
10 Pd(2—H)(PPh$_3$)Cl	77	62.0(61.4)	5.0(5.1)	3.5(3.8)	311
11 Pd(3—H)(PPh$_3$)Cl	78	62.1(61.7)	5.5(5.4)	3.7(3.7)	310
12 Pd(4—H)(PPh$_3$)Cl	80	64.0(63.6)	5.9(5.8)	3.6(3.4)	309

[a] The ligands (1—H), (2—H), etc. refer to the numbered compounds of Table I less one hydrogen atom in each case.

infrared region (one band, see Table II) in agreement with the general formula II:



Previous studies carried out on azo-benzenes bearing para-substituents[7] have demonstrated that metallation occurs at the more electron-rich ring, so that we can suggest for complexes **5–8** the following geometry (III):

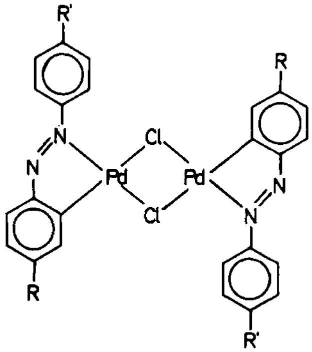


TABLE III

Mesophases and transition temperatures (°C) of uncomplexed liquid crystals and palladium-azocomplexes.

Free liq. cryst.[a]		Related complex		$\Delta t = (t_C - t_F)^b$
1	78–126	**5**	K ↔ 212(N) ↔ 215(I)	134
2	73–127	**6**	K ↔ 210(N) ↔ 225(I) ↑140 ↘ 190(S_B) ← 200(S_A)	137
3	59–112	**7**	K ↔ 190(N) ↔ 205(I)	131
4	64–107	**8**	K ↔ 165(N) ↔ 185(I)	101

[a] Temperature interval of existence of mesophases.

[b] t_C = transition temperature (K—N) complex; t_F = transition temperature (K—N) free liquid crystal.

Investigations by hot stage polarized microscopy on the mesomorphic properties of the palladium azo-complexes show that only the binuclear compounds **5–8** exhibit mesophases (see Table III), while compounds **9–12** simply decompose.

All the complexes **5–8** show enantiotropic nematic mesophases which give a *schlieren* threaded texture with high birifrangence. They tend to be spontaneously oriented homeotropically and to give macroscopic, homeotropic domains without any surface treatment. Complex **6**, in addition, gives monotropic smectic A and B phases; the smectic A phase spontaneously gives a homeotropic texture with a few focal-conic regions, while the smectic B phase tends to adopt a typical polygonal texture.

Although the complexing agents do not belong to a strictly homologous series, the following general trends may be recognized:

i) the metal complexes display remarkable increases in the transition temperatures at which the phases are formed from the solid state (from +137° in **6** to +101° in **8**).

ii) the phase transition temperature decreases with increase in the R′ chain.

iii) complexing dramatically reduces the temperature range in which the compounds exist in an ordered liquid crystal structure—from approx. 53° for **1–4** to approx. 15° for **5–8**. That is, $T_{N\text{-}I}$ increases less than the m.p. on complex formation.

Unfortunately point (*i*) limits the scope of this investigation to probe the potential calamitic (discotic) nature of complexes such as **5–8**. Since a knowledge of the influence of structure on m.p. is crucial in order to select appropriate complexing agents which will allow these transition temperatures to be reduced, further studies are in progress. Only in this way can the potential applications of this new class of organometallic liquid crystal be tested.

EXPERIMENTAL

General procedure for preparation of complexes **5–8**. In a typical preparation, potassium tetrachloropalladate (1mmol) and the stoichiometric amount of the appropriate liquid crystal (**1–4**) were dissolved in a mixture (1:1) of dioxan and water (10 ml) and stirred at room temperature for a week. The orange precipitate formed was filtered off, washed with ethanol and diethyl ether, and dried under vacuum.

General procedure for preparation of complexes **9–12**. To a suspension of 0.1 mmol of the appropriate complex **5–8** in diethyl ether (10 ml), the stoichiometric amount of triphenylphosphine was added. The mixture was stirred for 2 h at room temperature and then filtered. The yellow or orange precipitate was washed with diethyl ether and dried under vacuum.

Apparatus. Infrared spectra were recorded using a Perkin-Elmer 580 instrument nujol mulls of the solid samples. Elemental analyses were determineted by the Microanalysis Laboratory of the Istituto di Farmacia of the University of Pisa, Pisa, Italy.

Acknowledgment

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