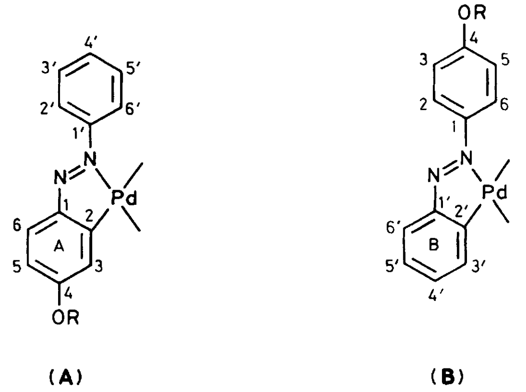
Synthesis and Characterisation of Binuclear Cyclopalladated *p*-Alkoxyphenylazo Complexes: Preparation of New Mesogenic Materials

Mauro Ghedini,* Salvatore Armentano, and Francesco Neve
Dipartimento di Chimica, Università della Calabria, I 87030 Arcavacata (CS), Italy
Silvia Licoccia
Dipartimento di Scienze e Tecnologie Chimiche, II Università di Roma, I 00173 Roma, Italy

In order to investigate new materials with liquid-crystalline properties, the synthesis, characterisation, and thermal behaviour of binuclear complexes of Pd^{II} with *p*-alkoxyphenylazobenzene ligands are reported. Whilst none of the free ligands displays ordered mesophases, some of their cyclopalladated derivatives show smectic phases at temperatures below 130 °C. Possible explanations of the function of the metal–halide bridge in determining the mesomorphism are provided.

The preparation of new materials having liquid-crystalline properties is of both theoretical and industrial interest.[1] While many investigations have dealt with organic mesomorphic compounds, little attention has been paid to similar co-ordination or organometallic species.[2–5]

We previously reported the thermotropic properties of a number of palladium(II) orthometallated complexes with *p,p'*-disubstituted azobenzenes.[6–9] Stable mesophases have been observed for binuclear halide-bridged compounds, as well as for mononuclear compounds containing a neutral molecule such as pyridine or quinoline. These complexes contained ligands possessing liquid-crystalline properties. We have now tested a series of *p*-alkoxyphenylazobenzenes, compounds lacking thermotropic properties,[10] with the aim of gaining insight into the roles played by the organic moiety and the metal atom with respect to the possible thermotropic behaviour of the resulting organometallic complexes.



(A) (B)

Scheme 1. Possible cyclopalladations of the ligands L^1—L^5

Results and Discussion

Synthesis and Characterisation.—Condensation of nitrosobenzene with *p*-alkoxyaniline, *p*-$C_nH_{2n+1}OC_6H_4NH_2$ (n = 1, 7, 10, 12, or 14), affords the *p*-substituted azobenzene ligands L^1—L^5 respectively which were characterised by i.r. and ^1H n.m.r. spectroscopy. By reaction of these ligands with $[Pd(PhCN)_2Cl_2]$, cyclopalladated compounds $[\{PdCl(L - H)\}_2]$, (**1**)—(**5**), are obtained.

In principle, the palladation of asymmetrically substituted azobenzenes can take place on either of the phenyl rings, and therefore products containing the moiety (**A**) or (**B**) (Scheme 1) can form.

In a recent investigation on cyclopalladated *p*-alkoxy-*p'*-alkylazobenzenes, the identification of the metallated ring was performed through the analysis of their ^1H n.m.r. spectra in the region of the resonances of the aliphatic protons.[9] Now, for compounds (**1**)—(**5**), a similar determination has been accomplished, taking into account the aromatic signals. This spectral analysis shows that two distinct metallated azobenzene moieties are present, one of them contained in compound (**2**) as traces only. Therefore, for (**2**), by means of simple decoupling experiments it was possible both to assign the signals of the aromatic region (Table 1) and to identify the metallated ring [(**A**) in Scheme 1]. Moreover, the presence of a unique species in (**2**) prompted us to record its $^{13}C-\{^1H\}$ n.m.r. spectrum. In Table 2 are reported the assignments of the aromatic signals of both the complexed ligand and of the parent diazo compound L^2. As far as the carbon resonances of the metallated ring are concerned, it is important to note, even if the assignments were not unambiguous, the C^2 resonance at *ca.* 160 p.p.m., since this relevant downfield shift, with respect to the whole uncomplexed aromatic region, is further evidence of the Pd–C^2 σ-bond formation.[11,12]

The results obtained for (**2**) helped to distinguish in the proton n.m.r. spectra of (**1**) and (**3**)—(**5**) two groups of signals due to the palladated and to the free phenyl rings respectively, which arise from mixtures containing both the fragments (**A**) and (**B**) (Scheme 1). The ^1H n.m.r. data for the metallated rings and the approximate measurement of the ratio between the metallated forms (**A**) and (**B**), estimated from the integrals of some selected signals for the different species, are reported in Table 1.

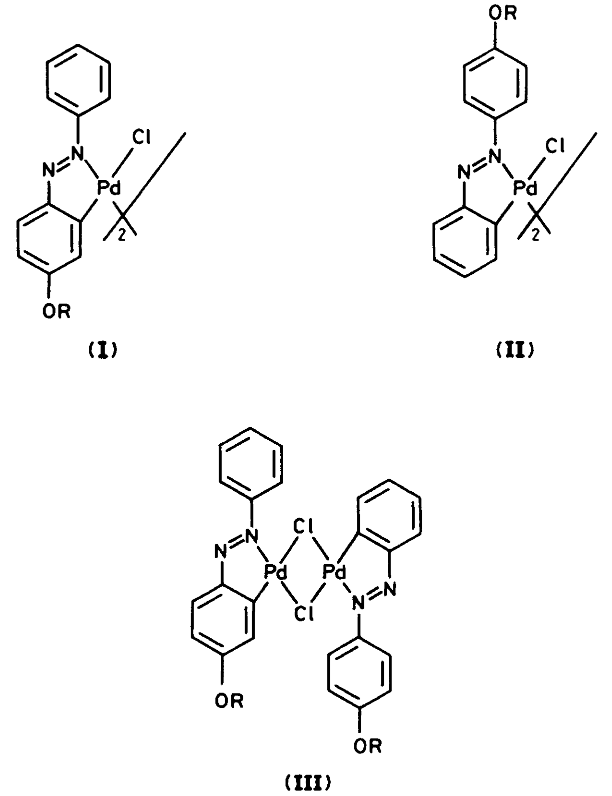
Thermal Properties.—Thermal properties of both the *p*-alkoxyphenylazobenzene ligands L^1—L^5 and of the related complexes (**1**)—(**5**) are reported in Table 3. The ligands L^1—L^5 do not display mesomorphic properties and melt at temperatures ranging from 52—54 (L^1) to 75 °C (L^5). Their cyclopalladated derivatives were tested by hot-stage optical microscopy, increasing the temperature until the isotropic phases were obtained, then cooling to the solid crystalline state. The products (**1**) and (**2**) melt at 245 and 185 °C respectively, while (**3**)—(**5**) show mesomorphism, but on cooling only. The textures of the mesophases, as seen optically, appear to be smectic[13] and stable over ranges of temperature of 38, 21, and 5 °C respectively. Remarkably, compounds (**3**)—(**5**) maintain the above described liquid-crystalline behaviour even after many heating and cooling cycles.

Conclusions

The cyclopalladated compounds (**1**)—(**5**), separated by filtration from the reaction mixtures, were recovered in about 50% yields. The isolated products (**1**) and (**3**)—(**5**), analysed by ^{1}H n.m.r. spectroscopy, were metallated at the alkoxy-substituted benzene ring (**A**) as well as at the unsubstituted ring (**B**). The isomer ratios, for a number of preparations carried out under the same experimental conditions, are roughly constant (± 0.1) and fall in the range from 1.2 for (**4**) to 2.0 for (**3**). Surprisingly, in compound (**2**) only the ring (**A**) is σ bonded to the palladium atom, (**A**):(**B**) > 99:1. Therefore, the cyclopalladation reactions are in accord with the previously reported data.[14]

The present investigation was devoted to the synthesis of new materials having thermotropic liquid-crystalline properties, so that no attention was paid to the separation of the different isomers and the products (**1**)—(**5**) were tested as they were recovered from the reaction mixtures. In spite of this, their thermal behaviour can enable a first elucidation of the role played by the metal–halide bridge in the formation of mesomorphic species.

It is well known that molecular structures containing a strong polar group near to the centre of the molecule, and along the longest molecular axis, favour liquid crystallinity.[10] Therefore the influence of the metal atom might be related either to an increased structural anisotropy or to an appropriate effect on the molecular shape as seems supported by the observation that the mono-*p*-substituted azobenzenes do not possess the thermotropic properties shown by the *p,p'*-disubstituted azobenzenes because of the absence in their molecular structure of one group bonded to the azobenzene moiety in position *p'*.



Scheme 2. Possible structures of the cyclopalladated complexes $[\{PdCl(L-H)\}_2]$ (**1**)—(**5**)

Table 1. Proton n.m.r. data[a] for the palladated rings in complexes (**1**)—(**5**)

Compound	(**A**):(**B**) Ratio	Form (**A**)	Form (**B**)[b]
(**1**)[c]	1.5	7.87 (d, H^6) 6.87 (br s, H^3) 6.73 [dd, H^5, $J(H^5H^6)$ = 8.6, $J(H^3H^5)$ = 2.5]	7.82 (br d, $H^{6'}$) 7.23 [vt, $H^{4'}$, $J(H^{3'}$-$H^{4'})$ = $J(H^{4'}H^{5'}) \approx$ 7.4] 7.12 (m, $H^{5'}$)
(**2**)	>99	7.77 (d, H^6) 6.84 (br s, H^3) 6.71 [dd, H^5, $J(H^5H^6)$ = 8.6, $J(H^3H^5)$ = 2.5]	
(**3**)	2.0	7.87 (d, H^6) 6.85 (br s, H^3) 6.71 [dd, H^5, $J(H^5H^6)$ = 8.6, $J(H^3H^5)$ = 2.6]	7.82 [br d, $H^{6'}$, $J(H^{5'}H^{6'})$ = 7.5] 7.22 [vt, $H^{4'}$, $J(H^{3'}$-$H^{4'})$ = 7.6, $J(H^{4'}H^{5'})$ = 7.4, $J(H^{4'}H^{6'})$ = 1.7] 7.10 (m, $H^{5'}$)
(**4**)	1.2	7.79 (d, H^6) 6.77 (br s, H^3) 6.63 [dd, H^5, $J(H^5H^6)$ = 8.6, $J(H^3H^5)$ = 2.0]	7.74 [br d, $H^{6'}$, $J(H^{5'}H^{6'})$ = 7.74] 7.14 [vt, $H^{4'}$, $J(H^{3'}H^{4'})$ = $J(H^{4'}H^{5'}) \approx$ 7.3] 7.03 (m, $H^{5'}$)
(**5**)	1.7	7.87 (d, H^6) 6.85 (br s, H^3) 6.71 [dd, H^5, $J(H^5H^6)$ = 8.5, $J(H^3H^5)$ = 2.3]	7.82 [br d, $H^{6'}$, $J(H^{5'}H^{6'})$ = 7.7] 7.22 (m, $H^{4'}$) 7.10 (m, $H^{5'}$)

[a] In $CDCl_3$ at 30 °C; chemical shifts (δ) are relative to internal $SiMe_4$, *J* values in Hz. Assignments and coupling constants are given in parentheses. [b] For all the complexes, the signal of $H^{3'}$ was obscured by other resonances. [c] $\delta(OCH_3)$ 3.91 and 3.89.

Table 3. Thermal properties of the ligands L^1—L^5 and of their cyclopalladated complexes (**1**)—(**5**)

Ligand	M.p. (°C)	Complex	Mesophases * and transition temperatures (°C)
L^1	52—54	(**1**)	245 (I)
L^2	70	(**2**)	185 (I)
L^3	63	(**3**)	153 (I) ⟶ 118 (S) ⟶ 115 (S) ⟶ 80 (C)
L^4	69	(**4**)	150 (I) ⟶ 136 (S) ⟶ 115 (C)
L^5	75	(**5**)	170 (I) ⟶ 103 (S) ⟶ 98 (C)

* C = Crystal, S = smectic, and I = isotropic.

Table 2. ^{13}C-$\{^1H\}$ N.m.r. data[a] for ligand L^2 and complex (**2**)

Compound	C^1	C^2	C^3	C^4	C^5	C^6	$C^{1'}$	$C^{2'}$	$C^{3'}$	$C^{4'}$	$C^{5'}$	$C^{6'}$
L^2	147.20	124.64[b]	114.86[c]	161.82			153.11	122.51[d]	128.85[e]	130.04		
(**2**)	158.98[f]	160.17[f]	131.90	161.92[f]	114.89	120.12	152.50	124.26[d]	129.00[e]	130.64		

[a] In $CDCl_3$; chemical shifts (δ/p.p.m.) are relative to internal $SiMe_4$. [b] $C^{2,6}$. [c] $C^{3,5}$. [d] $C^{2',6'}$. [e] $C^{3',5'}$. [f] Not unambiguously assigned.

As far as this latter aspect is concerned, we note that the cyclopalladated complexes (**1**)—(**5**) can assume the three different geometries (**I**), (**II**), and (**III**) in Scheme 2, arising from the combinations of the moieties (**A**) and (**B**) (Scheme 1), *i.e.* (**A**)(**A**), (**B**)(**B**), and (**A**)(**B**) respectively.

Complex (**2**) is almost completely metallated according to the form (**A**), hence its molecular structure should be like (**I**). Compounds (**1**) and (**3**)—(**5**) are mixtures of isomers where, since form (**A**) is dominant, (**A**):(**B**) > 1:1, one isomer is (**I**) while the other may be (**II**) and/or (**III**). Although on the basis of our data we are not able to distinguish (**II**) and (**III**), nevertheless it seems reasonable to assume, particularly for compounds (**3**)—(**5**), that the steric hindrance due to the long aliphatic chains [R = $C_{10}H_{21}$ in (**3**), $C_{12}H_{25}$ in (**4**), and $C_{14}H_{29}$ in (**5**)] can favour structure (**II**). Both structures (**I**) and (**II**) exhibit the alkoxy substituents on the opposite side of the Pd–Pd axis, so giving rise to molecular shapes analogous to a *p,p'*-disubstituted azobenzene.

Finally, the lack of mesomorphism found for (**1**) and (**2**) can probably be ascribed to the length of the aliphatic chain being too short to provide the proper entropic contribution to the thermodynamic stability of the mesophases.[10]

Further investigations on both the synthesis and the physical characterisation of new mesogenic materials containing transition metals are in progress.

Experimental

Apparatus.—Infrared spectra were recorded on a Perkin-Elmer model 1330 spectrometer as KBr pellets, proton and $^{13}C-\{^{1}H\}$ n.m.r. spectra on a Bruker WH 300 spectrometer in $CDCl_3$ solutions. Thermal behaviour was monitored by means of a Mettler FP 800 thermosystem equipped with a FP 84 microscopy cell, at a heating rate of 4 °C min^{-1}. The textures of the various mesophases were observed by means of a Reichert Thermovar polarising microscope equipped with a heating stage. Elemental analyses were carried out by the Microanalysis Laboratory of the Istituto di Farmacia dell'Università di Pisa.

The preparations of the palladium complexes were performed in a oxygen-free nitrogen atmosphere.

Preparation of the p-*Alkoxyphenylazobenzenes* L^1—L^5.—The *para*-substituted azobenzenes were obtained in good yields by condensation of nitrosobenzene (Fluka A.G.) with the appropriate *p*-substituted aniline following the procedure reported for *p*-phenylazobenzoic acid.[15] *p*-Alkoxyanilines were synthesised as described[16] using the appropriate n-alkyl bromide (Aldrich Chemical Co.). Crude products were purified by chromatography on a silica gel column eluted with diethyl ether. The *p*-alkoxyazobenzenes L^1—L^5 were characterized by i.r. and ^1H n.m.r. spectroscopy.

Preparation of the Dinuclear Cyclopalladated Complexes $[\{PdCl(L-H)\}_2]$ (**1**)—(**5**).—The general procedure was as follows: to a suspension of $[Ph(PhCN)_2Cl_2]$[17] (1.30 mmol) in ethanol (20 cm^3) was added a solution containing the appropriate azobenzene (1.15 mmol) in absolute ethanol (20 cm^3). The resulting red mixture was stirred at room temperature for 48 h. The dark red precipitate was collected by filtration, washed with diethyl ether, and dried under vacuum.

Yields are about 50% [Found for (**1**): C, 43.55; H, 3.10; N, 7.30. Calc. for $C_{26}H_{22}Cl_2N_4O_2Pd_2$: C, 44.20; H, 3.15; N, 7.95. Found for (**2**): C, 52.35; H, 5.20; N, 6.15. Calc. for $C_{38}H_{46}Cl_2N_4O_2Pd_2$: C, 52.20; H, 5.30; N, 6.40. Found for (**3**): C, 55.40; H, 6.30; N, 5.85. Calc. for $C_{44}H_{58}Cl_2N_4O_2Pd_2$: C, 55.10; H, 6.10; N, 5.85. Found for (**4**): C, 56.25; H, 6.40; N, 5.10. Calc. for $C_{48}H_{66}Cl_2N_4O_2Pd_2$: C, 56.90; H, 6.55; N, 5.55. Found for (**5**): C, 58.10; H, 7.05; N, 5.05. Calc. for $C_{52}H_{74}Cl_2N_4O_2Pd_2$: C, 58.30; H, 6.95; N, 5.25%].

Acknowledgements

This work was financed by the C.N.R. project 'Chimica Fine e Secondaria.'

References

1 G. W. Gray, *Proc. R. Soc. London, Ser. A*, 1985, **402**, 1.
2 A. M. Girond-Godquin, J. M. Latour, and J. C. Marchon, *Inorg. Chem.*, 1985, **24**, 4452 and refs. therein.
3 D. W. Bruce, D. A. Dunmur, E. Lalinde, P. M. Maitlis, and P. Styring, *Nature (London)*, 1986, **323**, 791 and refs. therein.
4 C. Sulin, L. Bosio, and J. Simon, *J. Chem. Soc., Chem. Commun.*, 1987, 379 and refs. therein.
5 C. Carfagna, V. Caruso, A. Roviello, and A. Sirigu, *Makromol. Chem., Rapid Commun.*, 1987, **8**, 345.
6 M. Ghedini, M. Longeri, and R. Bartolino, *Mol. Cryst. Liq. Cryst.*, 1982, **84**, 207.
7 M. Ghedini, S. Licoccia, S. Armentano, and R. Bartolino, *Mol. Cryst. Liq. Cryst.*, 1984, **108**, 269.
8 A. M. Manotti Lanfredi, F. Ugozzoli, M. Ghedini, and S. Licoccia, *Inorg. Chim. Acta*, 1984, **86**, 165.
9 M. Ghedini, S. Armentano, and F. Neve, *Inorg. Chim. Acta*, 1987, **134**, L23.
10 H. Kelker and R. Hatz, 'Handbook of Liquid Crystals,' Verlag Chemie, Weinheim, 1980.
11 J. F. Van Baar, K. Vrieze, and S. J. Stufkens, *J. Organomet. Chem.*, 1975, **85**, 249.
12 J. Granell, S. Sainz, J. Sales, X. Solans, and M. Font-Altaba, *J. Chem. Soc., Dalton Trans.*, 1986, 1785.
13 D. Demus and L. Richter, 'Textures of Liquid Crystals,' Verlag Chemie, Weinheim, 1978.
14 M. I. Bruce, B. L. Goodall, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1978, 687.
15 H. D. Anspon, *Org. Synth.*, 1955, **Coll. Vol. 3**, 711.
16 P. Keller and L. Liebert, 'Liquid Crystals,' Academic Press, New York, 1978, p. 24.
17 M. S. Karash, R. C. Seyler, and F. R. Mayo, *J. Am. Chem. Soc.*, 1938, **60**, 882.

Received 29th June 1987; *Paper* 7/1163