Mesogenic cyclopentadienyl cyclopalladated azobenzene complexes

Mauro Ghedini,* Daniela Pucci and Francesco Neve

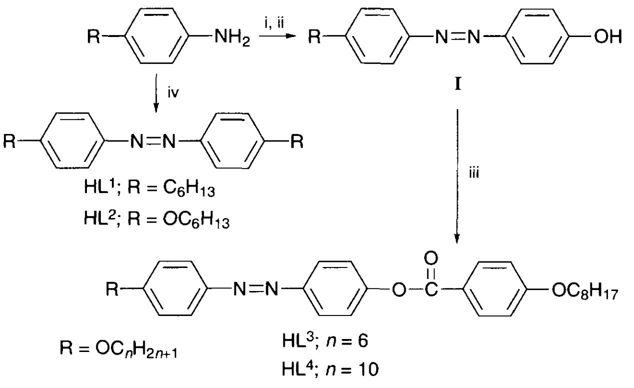
Dipartimento di Chimica, Università della Calabria, I-87030 Arcavacata (CS), Italy

The novel coordinatively saturated cyclopentadienyl palladium complexes [PdL^n(η^5-C_5H_5)] (HL^n = thermotropic 4-R,4′-R′-azobenzene; n = 1, R = R′ = C_6H_{13}; n = 2, R = R′ = $C_6H_{13}O$; n = 3, R = $C_6H_{13}O$, R′ = $C_8H_{17}OC_6H_4CO_2$; n = 4, R = $C_{10}H_{21}O$, R′ = $C_8H_{17}OC_6H_4CO_2$) are dark red solids which melt into isotropic fluids for n = 1,2, whereas for n = 3,4 liquid crystalline properties are exhibited with a stabilization of melting and clearing temperatures as high as 70 °C.

Thermotropic mesomorphism in organometallic palladium complexes (palladium mesogens) was firstly reported for the cyclometallated dinuclear halo-bridged species arising from substrates such as azobenzenes, imines, azines or phenylpyrimidines.[1] These roughly planar complexes possess a molecular structure referred as 'H-shaped' and their mesomorphism appears at temperatures some 100 °C higher than those of the parent mesogenic ligands. Since practical applications require liquid-crystalline materials with transition temperatures close to room temperature, investigations have been focused to reach this goal. In particular, the remarkable results obtained for mononuclear cyclopalladated acetylacetonate compounds[2–4] and for azoxy–mercury complexes[5] suggested that a molecular asymmetry, as it is found in these 'P-shaped' molecules, could lead to the desired result. Following such an approach, herein we report on the synthesis and mesomorphic properties of η^5-cyclopentadienyl cyclopalladated azobenzene complexes.

The 4-R,4′-R′-azobenzenes, HL^n (n = 1, R = R′ = C_6H_{13}; n = 2, R = R′ = $C_6H_{13}O$; n = 3, R = $C_6H_{13}O$, R′ = $C_8H_{17}OC_6H_4CO_2$; n = 4, R = $C_{10}H_{21}O$, R′ = $C_8H_{17}OC_6H_4$-CO_2) were prepared following standard methods (Scheme 1) and were characterized by elemental analyses and ^{1}H NMR spectroscopy.

These ligands, on reaction with [Pd(PhCN)$_2$Cl$_2$], afforded cyclopalladated chloro-bridged dimers [{Pd(μ-Cl)L^n}$_2$][6] in 80–90% yield. The corresponding mononuclear derivatives [PdL^n(η-C_5H_5)], **1–4**, were obtained by treatment with Tl(C_5H_5), according to a procedure previously described for unsubstituted azobenzenes.[7] The compounds **1–4**, separated in good yields (60–70%) after recrystallization from *n*-pentane, are dark red, air-stable solids.

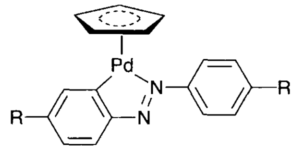


Scheme 1 *Reagents and conditions*: i, HCl, NaNO$_2$, in H$_2$O; ii, PhOH, NaOH (2 mol dm^{-3}) in H$_2$O; iii, *n*-octyloxybenzoic acid, DCC, 4-pyrrolidinopyridine, CH$_2$Cl$_2$, 56 h; iv, CuCl, py, 48 h. Yields: HL^1 = 80%, HL^2 = 80%, HL^3 = 65%, HL^4 = 75%

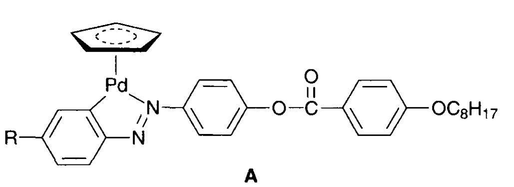
The elemental analyses of both the di- and mono-nuclear complexes accounted for the appropriate stoichiometry, although ^{1}H NMR spectra suggested evidence of different behaviour of HL^n ligands upon palladation. In particular, while the spectra of the complexes arising from the symmetrically substituted azobenzenes HL^1 and HL^2 were as expected, those of compounds derived from HL^3 and HL^4 displayed signals attributable to a mixture of products **A** and **B** (**B** being the minor isomer) formed by non-selective palladation of the asymmetrically substituted azobenzenes.† The molecular structures of mononuclear derivatives **1–4** were suggested by analogy with the cyclopentadienyl cyclopalladated azobenzene whose structure has been determined by single-crystal X-ray analysis.[8]

All the HL^n compounds are thermotropic (Table 1) and exhibited a nematic phase (enantiotropic in HL^2, HL^3, and HL^4 or monotropic in HL^1) with a marbled texture on heating and a schlieren one on cooling. In addition, only for HL^4 was an enantiotropic smectic C phase observed, which showed characteristic transition bars at the N–S$_C$ transition.

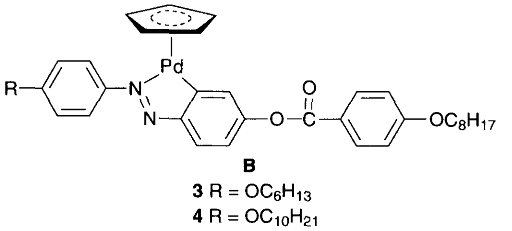
These mesomorphic properties changed in depth by complexation of the Pd(η^5-C_5H_5) fragment. Indeed, complexes **1** and **2** did not exhibit any liquid-crystalline phase and upon heating they melted (**1**, 43.5 °C; **2**, 113 °C) into isotropic fluids at temperatures similar to those of the parent ligands. By contrast, compounds **3** and **4** were found to be nematic (enantiotropic mesophase; schlieren and marbled textures for **3** and **4**, respectively) with melting and clearing temperatures as reported in Table 1. Moreover, on cooling the isotropic liquid, the nematic phase of either **3** or **4** was frozen in the glassy state. The glass transition was observed by DSC on second heating (Table 1). Further heating afforded a crystallization process



1 R = C_6H_{13}
2 R = OC_6H_{13}



A



B

3 R = OC_6H_{13}
4 R = $OC_{10}H_{21}$

followed by melting and clearing at temperatures unaffected with respect to the first run.

With reference to the molecular structure, the main difference between **1** or **2** and **3** or **4** resides in the additional benzoate group present in the azobenzene moiety of the liquid crystalline compounds **3** and **4**. It is thus possible to assume that the mesogenic rod-like cyclopalladated azobenzenes can tolerate a large lateral substituent only when the rigid molecular core is properly enlarged.[9]

It must be also noted that the clearing temperatures of **3** and **4** are significantly lower than those of the parents HL^3 and HL^4 [namely 67 °C (**3**) and 73 °C (**4**)], while the mesomorphic range becomes narrower [*i.e.* from 103 °C (HL^3) to 26 °C (**3**) and from 107 °C (HL^4) to 56 °C (**4**)]. In one case (**4**) a significant lowering of the melting temperature of the ligand was observed upon complexation.

The aim of this study was to test the effectiveness of the bulky η-C_5H_5 as a possible alternative to the previously considered flat acac ligand in molecular architectures which favour low transition temperatures. In this framework it has been proved that η-C_5H_5 is very useful, whereas other aspects than the geometrical features differentiate η-C_5H_5 from acac. In particular, as far as the bonding mode is concerned, the acac and the η-C_5H_5 ligands act as four- and six-electron donors in the homologous series $[PdL^n(acac)]$[2,4] and $[PdL^n(\eta^5\text{-}C_5H_5)]$, respectively. Hence, the electronic configuration of the Pd metal, which has 16 valence electrons in the former series, will have 18 valence electrons in the latter series. The palladium centre in **1–4** is therefore coordinatively saturated and, even though other examples of $18e^-$ metallomesogens were previously reported,[10–13] **1–4** are the only palladium mesogens reported up to now sharing such a feature. Notably, in square-planar $16e^-$ palladium mesogenic complexes, axial intermolecular interactions are often considered responsible for high transition temperatures.[1] In this context, the $18e^-$ configuration allowed by the η-C_5H_5 ligand could be a further contribution to the synthesis of thermally stable and processable palladium mesogens. Physical properties which depend on electron density or polarizability should also benefit from the overall improvement.

Table 1 Optical and thermal properties of the HL^n ligands and $[PdL^n(\eta^5\text{-}C_5H_5)]$ complexes

Compound	Transition[a]	T/°C	ΔH/kJ mol^{-1}[b]
HL^1	C–N	25.0[c]	
	N–I	33.0[c]	
HL^2	C–N	104.3	41.4
	N–I	115.7	1.2
	I–N	113.1	1.2
	N–C′	98.5	
	C′–C	97.8	41.4[d]
HL^3	C–N	107.9	24.3
	N–I	210.9	1.6
	I–N	207.9	1.9
	N–C	81.6	21.5
HL^4	C–Sc	94.6	26.0
	Sc–N	133.6	1.4
	N–I	201.5	2.1
	I–N	199.2	2.1
	N–Sc	131.2	1.4
	Sc–C	80.6	21.2
1	C–I	43.5[c]	
2	C–I	113.0[c]	
	I–C	91.0[c]	
3[e]	C–N	117.4	12.0
	N–I	143.6	1.2
	I–N	141.0	1.4
4[f]	C–N	72.5	10.2
	N–I	128.5	0.9
	I–N	127.2	1.1

[a] C = Crystal, N = Nematic, S = Smectic, I = Isotropic. [b] Data from DSC (Perkin Elmer DSC-7) for second heating cycle. [c] Data from optical observations (Zeiss Axioscop polarized microscope equipped with a Linkam CO600 heating stage). [d] Overall value for both transitions. [e] T_g −2.1 °C. Recrystallization occurs at 86.0 °C. [f] T_g −9.9 °C. Recrystallization occurs at 50.5 °C.

Financial support from Italian Ministero per l'Università e la Ricerca Scientifica e Tecnologica (MURST) e Consiglio Nazionale della Ricerche (CNR) is gratefully acknowledged.

Footnote

† Comparing the relative abundances of species **A** and **B**, as calculated from the pertinent $[PdL^n(\eta^5\text{-}C_5H_5)]$ and $[\{Pd(\mu\text{-}Cl)L^n\}_2]$ (n = 3,4) ^1H NMR spectra, one observes that the mixtures **3** and **4** are richer in component **A** than the mixtures of the parent cyclopalladated dimers. Although different explanations could be considered, we suggest that the observed trend merely reflects a different solubility of the starting dinuclear materials in $CDCl_3$.

References

1 S. A. Hudson and P. M. Maitlis, *Chem. Rev.*, 1993, **93**, 861.
2 M. Ghedini and D. Pucci, *J. Organomet. Chem.*, 1990, **395**, 105.
3 M. J. Baena, P. Espinet, M. B. Ros and J. L. Serrano, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 711.
4 M. Ghedini, D. Pucci, E. Cesarotti, O. Francescangeli and R. Bartolino, *Liq. Cryst.*, 1994, **16**, 373.
5 A. Omenat and M. Ghedini, *J. Chem. Soc., Chem. Commun.*, 1994, 1309.
6 A. Crispini, M. Ghedini, S. Morrone, D. Pucci and O. Francescangeli, *Liq. Cryst.*, in press.
7 G. K. Anderson, R. J. Cross, S. Fallis and M. Rocamora, *Organometallics*, 1987, **6**, 1440.
8 G. K. Anderson, R. J. Cross, K. W. Muir and L. Manojlovic-Muir, *J. Organomet. Chem.*, 1989, **362**, 225.
9 D. W. Bruce, *Adv. Mater.*, 1994, **6**, 699.
10 (*a*) J. Malthête and J. Billard, *Mol. Cryst. Liq. Cryst.*, 1976, **34**, 117; (*b*) L. Ziminski and J. Malthête, *J. Chem. Soc., Chem. Commun.*, 1990, 1495.
11 G. Lattermann, S. Schmidt, R. Kleppinger and J. H. Wendorff, *Adv. Mater.*, 1992, **4**, 30.
12 D. W. Bruce and X. H. Liu, *J. Chem. Soc., Chem. Commun.*, 1994, 729.
13 R. Deschenaux and J. W. Goodby, in *Ferrocenes*, ed. A. Togni and T. Hayashi, VCH Verlagsgesellschaft, Weinheim, 1995, p. 471 and references therein.

Received, 3rd August 1995; Com. 5/05190H