

***trans*-(η^2 -Alkene)(4'-alkyloxy-4-stilbazole)dichloroplatinum; Low Melting Organometallic Mesogens**

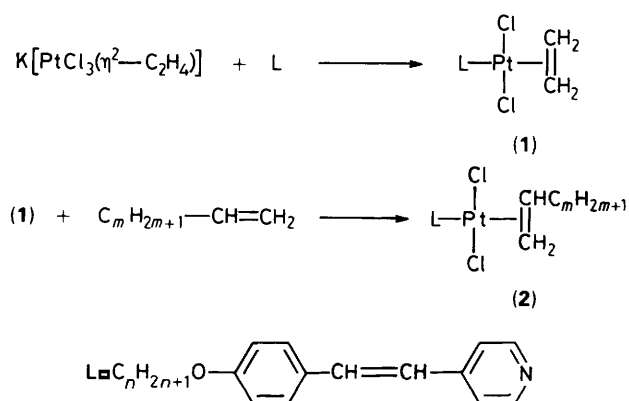
Jon P. Rourke, Francesco P. Fanizzi, Nicholas J. S. Salt, Duncan W. Bruce, David A. Dunmur, and Peter M. Maitlis*

Department of Chemistry, The University, Sheffield S3 7HF, U.K.

trans-[PtCl₂(C_nH_{2n+1}OC₆H₄CH=CHC₅H₄N)(η^2 -CH₂=CHC_mH_{2m+1})] (2) form stable smectic A mesophases on heating (for $n \geq 7$, $m \geq 7$; $n \geq 8$, $m \geq 5$; $n \geq 9$, $m \geq 2$; and $n \geq 11$, $m \geq 0$); melting temperatures below 50 °C can easily be achieved.

Metallomesogens (thermotropic liquid crystals containing co-ordinated metals) of a variety of types have been reported.¹⁻⁷ Most are conventional co-ordination complexes, but a few organometallic mesogens are known,⁴⁻⁷ mostly cyclometallated palladium complexes.^{4,5}

Incorporation of a metal centre into a liquid crystal introduces useful properties (*e.g.*, higher anisotropy, increased birefringence²) but a frequent side effect is to raise the melting and clearing temperatures over those for related organic mesogens. An important target is, therefore, to make metallomesogens with low transition temperatures. Less symmetric molecules (lacking a centre of symmetry, for example) should pack less easily and give rise to lower lattice energies, and hence lower transition temperatures. Unfortunately, many complexes disproportionate (*e.g.*, 2 [MLL'X₂]



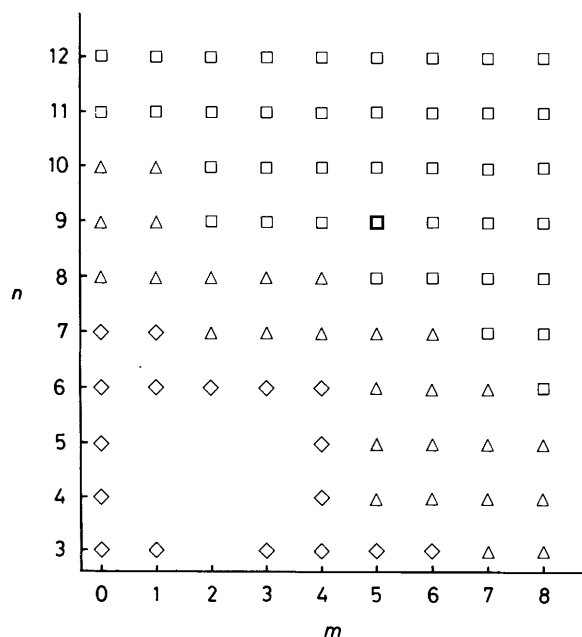


Figure 1. Phase behaviour of (2). \diamond Non-mesogenic, Δ monotropic, \square enantiotropic.

$\rightleftharpoons [ML_2X_2] + [ML'_2X_2]$; thus inert metal centres are required for stable complexes of reduced symmetry. We here describe new rod-like alkene-platinum mesogens with such characteristics.

Complexes (1), from Zeise's salt by reaction with the stilbazole (L),⁸ and (2) [by replacement of ethene in (1) by another alkene], are formed in high yields,[†] do not disproportionate easily, and are stable below ca. 110 °C.

The ethene complexes (1) with long alkyloxy chains (n) on L showed enantiotropic smectic A (S_A) phases[‡] (102–109 and 93–116 °C for $n = 11$ and 12 respectively). Those with alkoxy chains, $n = 8$ – 10 , only showed monotropic S_A phases[‡] (*i.e.*, only on cooling), and those with $n \leq 7$ showed no mesophase behaviour. Extension of the alkene chain length ($m \geq 5$) for example, in complexes (2), $n = 8$, induced enantiotropic mesophases (S_A) and lowered the transition temperatures.

Increasing the alkene chain length (m) stabilised, and also brought in S_A phases, for shorter alkyloxy chains (n) on the stilbazole. The phase behaviour of the series (2), summarised in Figure 1, shows that enantiotropic mesomorphism (only S_A) occurs above the diagonal, approximately from $n = 11$ and $m = 0$ to $n = 6$ and $m = 8$. No mesomorphism at all was found in the shorter chained molecules ($m = 0$ and $n = 3$ – 7 ; $n = 6$ and $m = 0$ – 4 ; $m = 4$ and $n = 3$ – 6 ; or $n = 3$ and $m = 0, 1$, and 3 – 6), and monotropic (S_A) behaviour was found for complexes which lay in the band between the non-mesogenic and the enantiotropic regions. No nematic phases were observed.

Although this appears to be the first series of metallo-mesogens where m and n were varied independently, related data have been reported for the organic compounds, $C_nH_{2n+1}OC_6H_4CH=NC_6H_4C_mH_{2m+1}$.⁹ Here again, an increase in the stability of the smectic phases with increasing chain length was found.

[†] Complexes (1) and (2) gave microanalyses, ¹H NMR and IR [*e.g.*, ν (*trans*-PtCl₂) 342 cm⁻¹] spectra in full agreement with the proposed structures.

[‡] Enantiotropic materials show a thermodynamically stable mesophase (both on heating and cooling); monotropic mesophases are not thermodynamically stable and appear only on cooling.

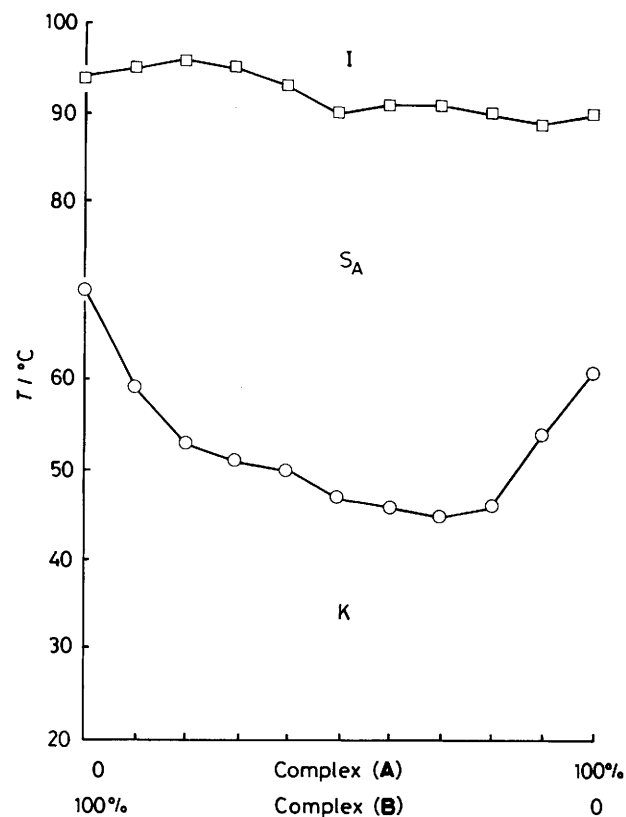


Figure 2. Phase behaviour of mixtures of complex (A) [PtCl₂(C₁₂H₂₅OC₆H₄CH=CHC₅H₄N)(CH₂=CHC₃H₇)] and complex (B) [PtCl₂(C₁₂H₂₅OC₆H₄CH=CHC₅H₄N)(CH₂=CHC₆H₁₃)].

By mixing two complexes, (2, $n = 12$, $m = 3$; K $\xrightarrow{61^\circ\text{C}}$ S_A $\xrightarrow{90^\circ\text{C}}$ I) [complex (A)] with (2, $n = 12$, $m = 6$; K $\xrightarrow{70^\circ\text{C}}$ S_A $\xrightarrow{94^\circ\text{C}}$ I) [complex (B)], in a 70:30 ratio, the melting points were substantially further reduced to 45 °C, without affecting the clearing temperature (K $\xrightarrow{45^\circ\text{C}}$ S_A $\xrightarrow{91^\circ\text{C}}$ I) (Figure 2).

Low temperature crystal to S_A phase transitions were recently reported for the iridium(I) complexes *cis*-[Ir(CO)₂Cl(ROC₆H₄N=CHC₅H₄N)]¹⁰ and have also been found for the related stilbazole, rhodium, and iridium complexes, *cis*-[M(CO)₂Cl(ROC₆H₄CH=CHC₅H₄N)]¹¹. These data suggest that low melting points are a property of the molecular shape, and support the view that less symmetric complexes are advantageous.

We have also examined the effects of changing co-ligands, since this changes melting points as well. For example the 4-alkyloxy-4'-stilbazole complexes, [PdL₂X₂] (L = C_nH_{2n+1}OC₆H₄CH=CHC₅H₄N), showed no mesophases for X = Cl and $n = 8, 10$, and high-temperature smectic phases (K $\xrightarrow{280^\circ\text{C}}$ S) for $n = 12$. Replacement of Cl by hexanoate gave complexes which showed nematic phases and at much lower temperatures (K \rightarrow N, N \rightarrow I: 156, 164; 146, 159; and 144, 164 °C respectively for $n = 8, 10, 12$, and X = O₂CC₅H₁₁). Despite the improvement, melting temperatures were still high and the complexes slowly decomposed in the mesophases. It is thus apparent that building in asymmetry is probably the preferred way to obtain low melting points.

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