Synthesis and Properties of (±)-*trans*-(η^2-Alkene)(4-alkyloxy-4'-stilbazole)dichloroplatinum: a Remarkable Family of Low-melting Metallomesogens†

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A novel series of low-melting metallomesogens (metal-containing liquid crystals) has been prepared and characterised. Reaction of Zeise's salt $K[PtCl_3(\eta^2\text{-}CH_2{=}CH_2)]$ with the 4-*n*-alkyloxy-4'-stilbazole ligands ($L = C_nH_{2n+1}OC_6H_4CH{=}CHC_5H_4N$; n = 3–12) yielded *trans*-$[PtCl_2(\eta^2\text{-}CH_2{=}CH_2)L]$ **1**, which react with alk-1-enes ($CH_2{=}CHC_mH_{2m+1}$, m = 1–8, 10 or 12) to give *trans*-$[PtCl_2(CH_2{=}CHC_mH_{2m+1})L]$ **2**. The complexes where $(m + n) \geqslant$ *ca.* 8 are generally liquid crystalline (smectic A mesophases); those with shorter tails [$(m + n)$ = 8 to *ca.* 13] show monotropic mesophases, while those with longer tails [$(m + n) >$ *ca.* 13] show enantiotropic behaviour. The melting temperatures are lower than would be anticipated for metallomesogens of this size, reflecting the non-centrosymmetric molecular structures which make the crystal packing less easy. A 70:30 mixture of the complexes **2** (n = 12, m = 3; $K \longrightarrow S_A$ at 61 °C) and (n = 12, m = 6; $K \longrightarrow S_A$ at 70 °C) shows the transition into the mesophase, $K \longrightarrow S_A$, at 45 °C, an unusually low temperature. The mesophase to isotropic ($S_A \longrightarrow I$) transition temperatures remain rather constant at 92 ± 4 °C for all compositions.

Materials formed by the incorporation of metals into liquid crystals, known as metallomesogens, are attracting increasing attention. They allow the combination of the anisotropic supramolecular arrays of liquid crystals (of such great utility in electronic displays, sensors and other fields), with the variety of electronic environment, shape, and colour offered by the presence of a metal (especially of the d-block elements). Such metallomesogens have been reviewed recently.[1] Those which change phase with temperature (thermotropics) and which have overall rod-like shapes have so far elicited the most interest. Although Vorländer[2] in 1910 already recognised lamellar mesophases in the alkali-metal carboxylates, the first researchers to seek advanced materials among such compounds were Giroud and Müller-Westerhoff,[3] who reported the mesogenic nickel and platinum dithiolenes in 1977.

Many of the properties of metallomesogens, the overall shape of which is dominated by that of the large organic ligands, mimic those of the ligands, and thus similar mesophase behaviour is often observed. Positive consequences of the incorporation of the metal which have already been found include sharp increases in the birefringence[4] and in the electronic polarisability,[5] as well as a high linear dichroism.[6] A less desirable result of incorporation of a metal is a sharp rise in the temperatures both of melting (from the crystal into the mesophase) and of clearing (from the mesophase into the isotropic liquid). This not only takes such liquid crystals out of the range of many useful applications, but also severely restricts the range of physical measurements which can be performed on them. For this reason a prime concern of workers in the field has been to devise strategies to bring down the transition temperatures, especially the melting point, in order to make the mesophase more accessible.

There are several possible means of accomplishing this. The method we focus on here is to introduce more asymmetry into the molecules so that they will pack less favourably and hence crystallise with greater difficulty.[7] Other methods include (*i*) changing the coligands (for example by replacing hard coligands such as chloro by amphiphilic ones such as alkylcarboxylato), (*ii*) adjusting the hydrocarbon tails of the organic ligands and (*iii*) by mixing two or more related complexes, which show similar phase behaviour.

However, rod-like complexes with a central metal atom (A–M–B) but lacking a centre of symmetry can be difficult to isolate since they have a strong tendency to disproportionate [equation (1)]; thus an inert metal is called for. We have chosen

$$2A\text{–}M\text{–}B \longrightarrow A\text{–}M\text{–}A + B\text{–}M\text{–}B \qquad (1)$$

Pt^{II} for that reason and here report the synthesis, characterisation and mesomorphic behaviour of the *trans*-(η^2-alkene)(4-alkyloxy-4'-stilbazole)dichloroplatinum complexes, which are an accessible and relatively stable series of non-centrosymmetric compounds, which have low melting points. A part of the work has been described in a communication.[8]

Results and Discussion

Synthesis of (±)-trans-(η^2-*Alkene*)*dichloro*(*stilbazole*)*platinum*(II).—Reaction of Zeise's salt $K[PtCl_3(C_2H_4)]$, with the stilbazole ligands ($L = C_nH_{2n+1}OC_6H_4CH{=}CHC_5H_4N$; n = 3–12) gave the complexes *trans*-$[PtCl_2(\eta^2\text{-}CH_2{=}CH_2)L]$ **1** in greater than 90% yield (Scheme 1). The products were of analytical purity and were characterised by microanalysis and spectroscopy. They were shown to be *trans* isomers by the presence of only one ν(Pt–Cl) band in the appropriate region (340–342 cm^{-1}) of the far-IR spectrum, as expected from the closely related *trans*-dichloro(η^2-ethene)(pyridine)platinum(II) made by a similar route.[9]

Of the ten members of the homologous series synthesised, compounds **1** (n = 11 and 12) exhibited enantiotropic (thermodynamically stable) smectic A phases at temperatures between 90 and 120 °C, while those with n = 8–10 exhibited monotropic (thermodynamically unstable) smectic A phases at tem-

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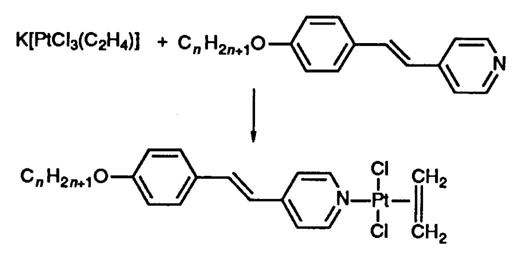
† Throughout this paper the letter n is used to indicate the number of carbons in the alkyloxy chain of the stilbazole (4-styrylpyridine), and m to indicate the number of carbon atoms in the alkyl chain of the alkene; thus ethene has m = 0.

Supplementary data available (No. SUP 56894, 19 pp.): microanalysis and phase characterisation data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.



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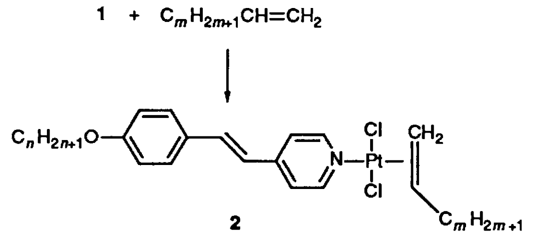
Scheme 1



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Scheme 2

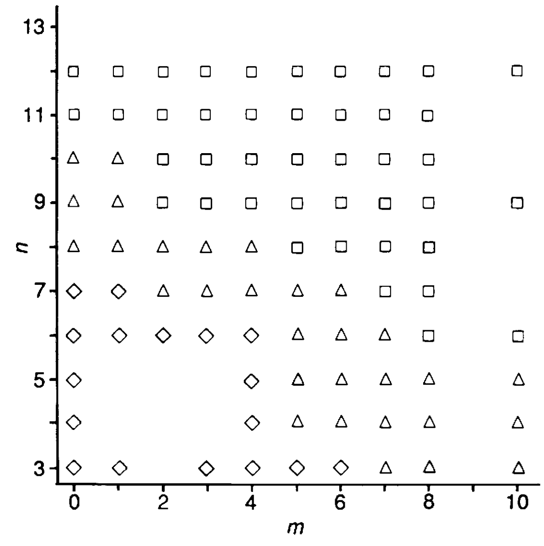


Fig. 1 Diagram illustrating the limits of mesophase behaviour for complexes **1** and **2** as a function of tail lengths, *m* and *n*: ◇, non-mesogenic; △, monotropic; □, enantiotropic

peratures below 95 °C [Fig. 2(*a*)]. Complexes **1** with *n* between 3 and 7 did not exhibit any mesomorphic behaviour. The longer-tailed members of the series show the greatest smectic stability, presumably as a direct result of the increased structural anisotropy of these compounds compared with their lower homologues.

In order to increase still further the structural anisotropy of the molecules and also to increase the range of compounds, complexes **1** were treated with stoichiometric amounts of the appropriate alk-1-enes ($CH_2{=}CHC_mH_{2m+1}$; m = 1–8, 10 or 12) in diethyl ether, to give *trans*-$[PtCl_2(CH_2{=}CHC_mH_{2m+1})L]$ **2**, again in essentially quantitative yield and analytical purity (Scheme 2). These complexes were also shown to be the *trans* complexes by far-IR spectroscopy. Since the *n*-alk-1-enes have a prochiral face their co-ordination to the platinum gives a chiral molecule; compounds **2** were all obtained as racemic mixtures.

Compounds **2** were isolated as yellow microcrystalline powders, indefinitely stable in air at room temperature. At higher temperatures (100 °C; in air, nitrogen or argon), however, decomposition occurred. This thermal decomposition was inhibited, and did not occur until 125 °C, under an ethene atmosphere, and it is thus probable that it involves loss of alkene to give the chloride-bridged dimer $[Pt_2Cl_4L_2]$. Some of this material was isolated after prolonged heating (12 h, 100 °C) of compound **2** (n = 9, m = 3): the microanalysis and far-IR [ν(Pt–Cl$_{term}$) 340vs, ν(Pt–Cl$_{bridge}$) 310s cm^{-1}] indicated its identity, but it proved too insoluble for solution NMR spectroscopy.

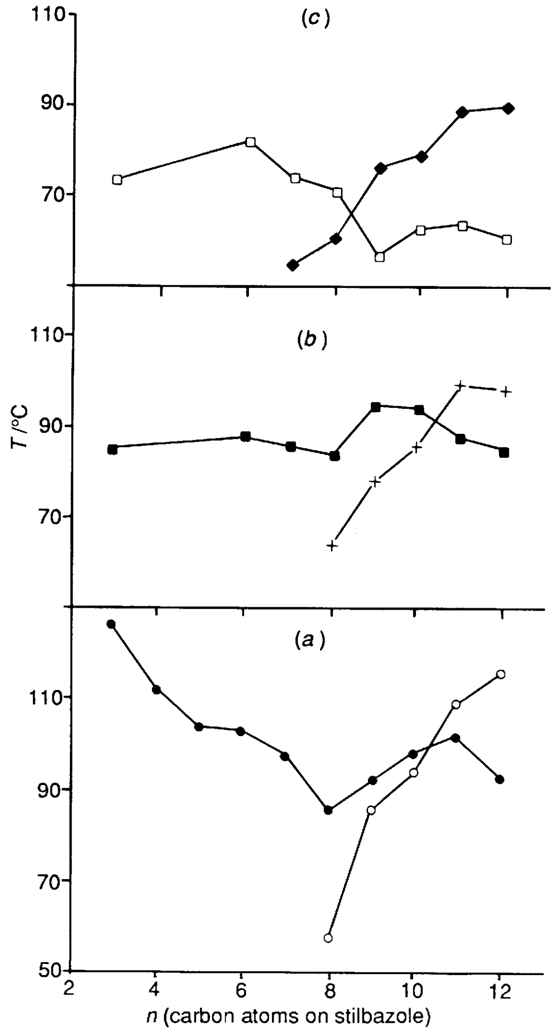


Fig. 2 Phase behaviour of the ethene (*a*), prop-1-ene (*b*) and but-1-ene (*c*) complexes $[PtCl_2(CH_2{=}CHC_mH_{2m+1})(C_nH_{2n+1}OC_6H_4CH{=}CH\text{-}C_5H_4N)]$ **1** (m = 0–2) as a function of the length of the alkyloxy tail, *n*, on the stilbazole. Symbols for (*a*), (*b*), (*c*): ●, ■, □, K ⟶ S$_A$, I; ○, +, ◆, S$_A$ ⟶ I

A total of 82 compounds of the type **2** were synthesised and characterised. A smectic A phase was invariably identified (by optical microscopy) for those which showed mesomorphic behaviour; no other phases were observed. Fig. 1 summarises the limits that have been found for the existence of mesogenic compounds in such series, and, not unexpectedly, shows that the complexes with the longer tails favour smectic mesomorphism. Compounds which are described as 'non-mesomorphic' have, in this context, no phase stable at, or above, room temperature. It is however possible that if such a compound were rapidly cooled to lower temperatures a monotropic phase could occur before it became glassy.

In the isotropic state compounds **2** were very fluid. Both the isotropic liquids and the smectic A phases supercooled very easily, and it was possible to supercool the compounds to as low as −30 °C for several hours, and to room temperature for many days, without any crystallisation occurring, though a glass did form. The full phase behaviour of compounds **2** is summarised in Figs. 2–4 and is tabulated in SUP 56894.

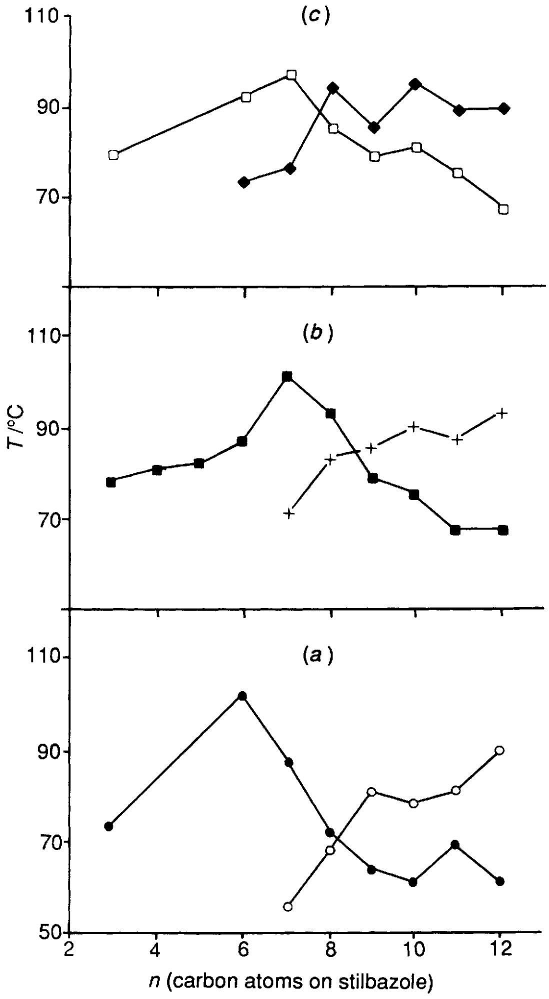


Fig. 3 Phase behaviour of the pent-1-ene (*a*), hex-1-ene (*b*) and hept-1-ene (*c*) complexes **1** (m = 3–5) as a function of the length of the alkyloxy tail, n, on the stilbazole. Symbols as in Fig. 2

These data show that increasing n and m have the twin effects of decreasing the stability of the crystal phase (lowering the melting point) and of increasing the clearing temperature, thus increasing the range of smectic phase stability. This observation is not surprising; smectic phases are promoted by increasing alkyl chain lengths, but since long hydrocarbon chains often increase the disorder in the crystal they also cause the lowering of the melting point. These effects begin to plateau out with combined chain lengths $n + m$ of around 14 units. The S_A (smectic) ⟶ I (isotropic) transitions, especially in the oct-1-ene complex [Fig. 4(*a*)], show classic alternation of clearing temperature with hydrocarbon tail length ('odd-even' effect).

By contrast to complexes **2**, the known bis(stilbazole)platinum complexes $[MCl_2L_2]$ are exceedingly high melting and show no mesomorphism, while the only palladium complex in the series to show mesomorphism, *trans*-$[PdCl_2(C_{12}H_{25}OC_6H_4CH{=}CH\text{-}C_5H_4N)_2]$, does so at very high temperatures [K (crystal) ⟶ S at 280, S ⟶ N (nematic) at 290 and N ⟶ I at 315 °C].[1,10]

We have also recently examined another series of non-centrosymmetric rod-like metallomesogens, the rhodium(I) and iridium(I) complexes, *cis*-$[ML(CO)_2Cl]$ **3**, again based on the same stilbazoles, L, used here.[11] These complexes also show quite low melting points (*ca.* 85 °C), but rather higher clearing points (120–140 °C) than do **2**. However, by contrast to the platinum complexes **2**, which only show S_A mesophases, the rhodium and iridium complexes exhibit nematic phases when the stilbazoles have short tails.

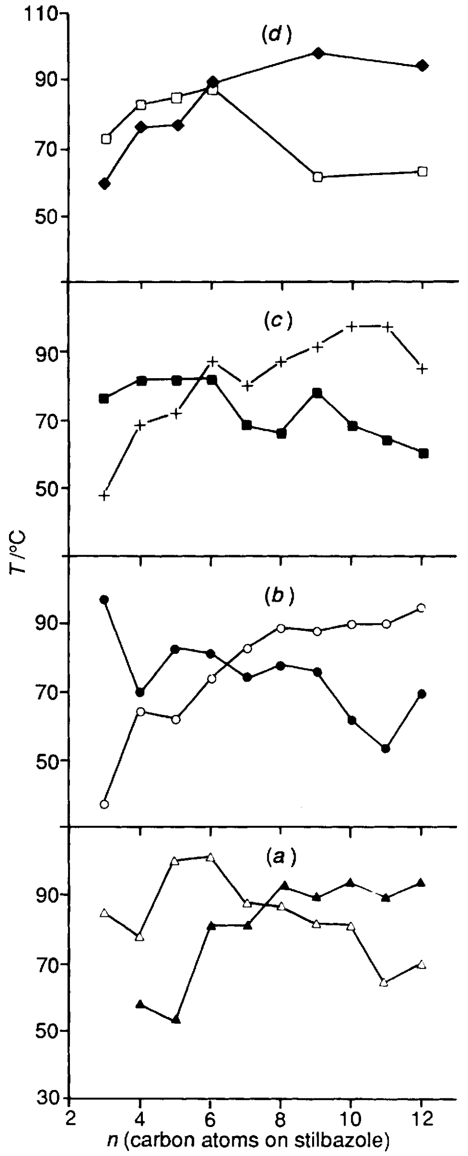
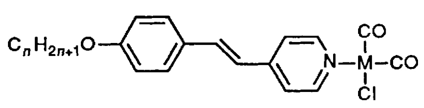


Fig. 4 Phase behaviour of the oct-1-ene (*a*), non-1-ene (*b*), dec-1-ene (*c*) and dodec-1-ene (*d*) complexes **1** (m = 6–8 or 10) as a function of the length of the alkyloxy tail, n, on the stilbazole. Symbols for (*a*), (*b*), (*c*), (*d*): △, ●, ■, □, K ⟶ S_A, I; ▲, ○, +, ◆, S_A ⟶ I



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Low-angle X-Ray Scattering.—Low-angle X-ray scattering experiments were carried out at the Daresbury synchrotron radiation source (SRS) on compounds **2** (n = 9, m = 5) and (n = 12, m = 16) in the mesophase. The resulting photographs showed a single sharp ring (with harmonics), the pattern expected from smectic A mesophases, and allowed the calculation of the S_A layer spacings in the two materials as 31.4 and 42.5 Å respectively. CPK (Corey–Pauling–Koltun) models indicate the lengths of the two molecules to be around 36 and 52 Å, respectively, when stretched out. The fact that the observed layer spacings are less suggests that either the S_A layers are interdigitated or that the hydrocarbon tails are folded back along the length of the molecule, or disordered.[12] In view of the observation of an odd-even effect, the second possibility is the more likely since such an effect would not be expected with an interdigitated structure. It has not, so far, proved possible to obtain a crystal suitable for a single-crystal X-ray structure analysis.

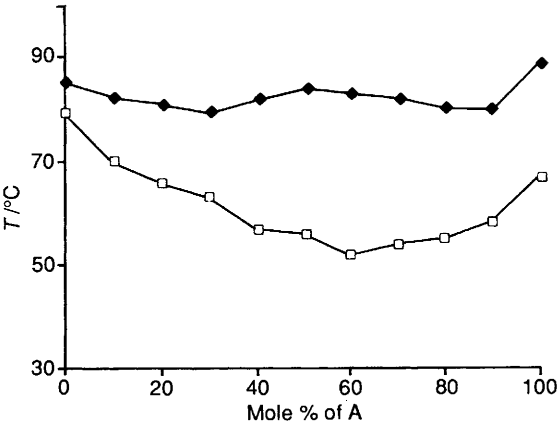


Fig. 5 Phase behaviour of mixtures of the complexes *trans*-$[PtCl_2(CH_2{=}CHC_5H_{11})(C_{12}H_{25}OC_6H_4CH{=}CHC_5H_4N)]$ A and *trans*-$[PtCl_2(CH_2{=}CHC_5H_{11})(C_9H_{19}OC_6H_4CH{=}CHC_5H_4N)]$ B: □, $K \longrightarrow S_A$; ◆, $S_A \longrightarrow I$

Table 1 Phase behaviour of mixtures of the complexes *trans*-$[PtCl_2(CH_2{=}CHC_5H_{11})(C_{12}H_{25}OC_6H_4CH{=}CHC_5H_4N)]$ A and *trans*-$[PtCl_2(CH_2{=}CHC_5H_{11})(C_9H_{19}OC_6H_4CH{=}CHC_5H_4N)]$ B

Proportion (%)		Transition		$\Delta H/J\ g^{-1}$
A	B	$K \longrightarrow S_A$	$S_A \longrightarrow I$	$(S_A \longrightarrow I)$
0	100	79	85	3.4
10	90	70	82	5.0
20	80	66	81	5.2
30	70	63	79	5.0
40	60	57	82	3.4
50	50	56	84	3.8
60	40	52	83	4.0
70	30	54	82	3.2
80	20	55	80	4.0
90	10	58	80	3.9
100	0	67	89	6.0

Table 2 Phase behaviour of mixtures of the complexes *trans*-$[PtCl_2(CH_2{=}CHC_3H_7)(C_{12}H_{25}OC_6H_4CH{=}CHC_5H_4N)]$ C and *trans*-$[PtCl_2(CH_2{=}CHC_6H_{13})(C_{12}H_{25}OC_6H_4CH{=}CHC_5H_4N)]$ D

Proportion (%)		Transition		$\Delta H/J\ g^{-1}$
C	D	$K \longrightarrow S_A$	$S_A \longrightarrow I$	$(S_A \longrightarrow I)$
0	100	70	94	6.5
10	90	59	95	6.0
20	80	53	96	4.7
30	70	51	95	5.2
40	60	50	93	5.1
50	50	47	90	4.2
60	40	46	91	4.4
70	30	45	91	3.8
80	20	46	90	4.0
90	10	54	89	3.4
100	0	61	90	4.5

Mixing Experiments.—The mixing of two mesogenic compounds generally reduces the melting point of the mixture relative to that of the pure components. Thus in order to increase the mesomorphic range of the metallomesogens **2** two series of mixing experiments were carried out. Equimolar stock solutions of the two different compounds were prepared, the appropriate measured volumes of each were mixed together, and the solvent was evaporated to leave a solid mixture.

In the first experiment, two compounds **2** with the same alkene ($m = 5$), but different stilbazoles ($n = 9$ or 12) were mixed (Table 1 and Fig. 5). The crystal to smectic A transition ($K \longrightarrow S_A$) was lowered to 52 from 79 °C for pure **2** ($n = 9$) and 67 °C for pure **2** ($n = 12$) for a mixture containing the two in a 40:60 ratio. There was little variation in the clearing point ($S_A \longrightarrow I$, 84 ± 5 °C). Thus, by comparison with the better of the two, **2** ($n = 12$), which had a smectic range of 22 °C, the mixture had a range of 41 °C, almost double.

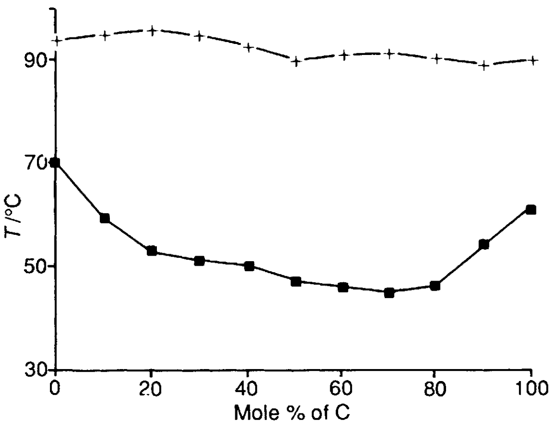


Fig. 6 Phase behaviour of mixtures of the complexes *trans*-$[PtCl_2(CH_2{=}CHC_3H_7)(C_{12}H_{25}OC_6H_4CH{=}CHC_5H_4N)]$ C and *trans*-$[PtCl_2(CH_2{=}CHC_6H_{13})(C_{12}H_{25}OC_6H_4CH{=}CHC_5H_4N)]$ D: ■, $K \longrightarrow S_A$; +, $S_A \longrightarrow I$

In the second experiment two compounds **2** with the same stilbazole ($n = 12$), but different alkenes ($m = 3$ or 6), were mixed (Table 2 and Fig. 6). A reduction to 45 °C was observed in the $K \longrightarrow S_A$ transition for a 70:30 mixture, from 61 for **2** ($m = 3$) and 70 °C for **2** ($m = 6$). There was very little change in $S_A \longrightarrow I$ which remained at 92 ± 4 °C, and here again the smectic range was enhanced by mixing, from 26 or 29 to 46 °C.

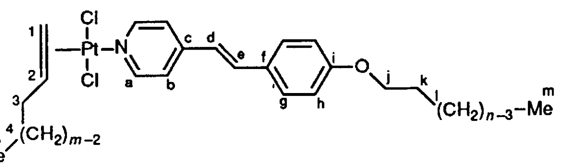
Thus substantial enhancements of the liquid-crystal ranges of the complexes **2** may be effected by the simple step of mixing. The conditions have not been optimised, and there seems no reason to suppose that by judicious choice of the components a metallomesogen mesomorphic at or even below ambient temperature could not be produced.

Other Olefin Complexes.—In order to investigate the effect on properties of changes in the olefin, a number of analogous platinum olefin complexes **4** were made, in addition to **2**. Mesomorphism could be detected only in two cases.

Thus the complexes $[PtCl_2(C_9H_{19}OC_6H_4CH{=}CHC_5H_4N)(CH_2{=}CHPh)]$ and $[PtCl_2(C_{10}H_{21}OC_6H_4CH{=}CHC_5H_4N)(CH_2{=}CHCH_2Ph)]$ decomposed before they melted (114 and 128 °C respectively). Similarly the C_9 stilbazole derivative with allyl alcohol $[PtCl_2(C_9H_{19}OC_6H_4CH{=}CHC_5H_4N)(CH_2{=}CHCH_2OH)]$ melted cleanly at 87 °C, and showed no monotropic phases on cooling. The esters methyl oleate, *cis*-$Me(CH_2)_7CH{=}CH(CH_2)_7CO_2Me$, and methyl elaidate, *trans*-$Me(CH_2)_7CH{=}CH(CH_2)_7CO_2Me$, were treated with **1** ($n = 3$ or 12) to form the complexes $[PtCl_2(C_3H_7OC_6H_4CH{=}CHC_5H_4N)(ester)]$ and $[PtCl_2(C_{12}H_{25}OC_6H_4CH{=}CHC_5H_4N)(ester)]$. All four compounds were isotropic liquids at room temperature, and showed no sign of any other phases, even on examination by DSC, when cooled to −30 °C.

The branched alkene 2,3-dimethylbut-1-ene was treated with complex **1** to give the alkene complex $[PtCl_2(C_{12}H_{25}OC_6H_4CH{=}CHC_5H_4N)(CH_2{=}CHCMe_3)]$. The pure compound melted into a smectic A phase (95 °C) and then decomposed before clearing (110 °C).

Of the functionalised olefins which were investigated, only the allyl ethyl ether complex $[PtCl_2(C_{12}H_{25}OC_6H_4CH{=}CHC_5H_4N)(CH_2{=}CHCH_2OEt)]$ behaved in a manner similar to its alk-1-ene analogue: it formed a smectic A phase at 83 °C, and cleared into the isotropic liquid at 104 °C [*cf.* K (67 °C) $\longrightarrow S_A$ (93 °C) $\longrightarrow$ I for **2** ($n = 12, m = 4$)].



Thus, incorporation of a more bulky alkene (such as 2,3-dimethylbut-1-ene) leads to an increase in transition temperatures. Aromatic alkenes (styrene or allylbenzene) raise the transition temperatures above the decomposition point of the molecule. Co-ordination of the internal alkenes, methyl oleate and methyl elaidate, reduces efficient packing in the crystal, and thus the products are isotropic liquids, even at ambient temperature.

Conclusion

The compounds described in this paper form a versatile metal-containing mesogenic system. The complexes **2** contain an alkyloxy chain on the stilbazole and an alkyl on the olefin, which can be varied independently. This has allowed the synthesis of some ninety compounds, and is the first time that such a systematic variation has been possible in a metal-containing system. Complexes **2** exhibited smectic A phases at very accessible temperatures (< 100 °C), amongst the lowest yet discovered for metallomesogens. This may largely be ascribed to the lack of a centre of symmetry in the molecules. Attempts to make metallomesogens with other olefins co-ordinated to the platinum lead us to conclude that alk-1-enes form the best mesomorphs here.

Experimental

Microanalyses were carried out by the University of Sheffield Microanalytical Service. Infrared spectra were recorded on a Perkin Elmer PE680 spectrometer, as Nujol mulls, between Polythene plates, NMR spectra on a Bruker AM250 FT spectrometer, ^{1}H (250.13 MHz) and ^{13}C (62.896 MHz), using $CDCl_3$ as both solvent and reference. Optical characterisation was performed using covered microscope slides on a Zeiss Labpol polarising microscope equipped with a Linkam TH600 hot-stage and PR600 temperature controller. Differential scannning calorimetry (DSC) measurements were made in sealed aluminium pans, on a Perkin Elmer DSC7 system (7700 data station and TAS7 software). Temperatures of transitions are quoted from the onset of the transitions in the DSC and were all confirmed on the microscope at a heating rate of 1 K min^{-1}; whenever possible they were confirmed on the cooling and second heating cycles. There were, in general, no differences in the temperatures when measured in air or in an inert atmosphere; however, the decomposition of complexes **2** was significantly retarded under an ethene atmosphere.

The 4-alkyloxy-4′-stilbazoles and Zeise's salt were prepared by literature methods.[13,14] All other reagents were commercially available, and used as supplied. Typical synthetic methods are given below for the preparation of complexes **1**, **2** and **4**. Microanalysis data are in SUP 56894 Supplementary Tables. Melting point behaviour is shown in Figs. 2–6, and as SUP 56894.

(±)-trans-(η^2-*Ethene*)*dichloro*(*stilbazole*)*platinum*(II) *Complexes* $[PtCl_2(CH_2{=}CH_2)(C_nH_{2n+1}OC_6H_4CH{=}CHC_5H_4N)]$ **1**.—Zeise's salt (500 mg, 1.29 mmol) was dissolved in acetone (10 cm^3) and a solution of 4-dodecyloxy-4′-stilbazole (457 mg, 1.29 mmol) in acetone (10 cm^3) was added. The mixture was stirred (15 min), and the solvent was then removed *in vacuo*. Chloroform (15 cm^3) and $MgSO_4$ (2 g) were added and the yellow solution filtered through a short Florisil column. The solvent was removed to yield the product in analytical purity (783 mg, 95%, 1.19 mmol) (Found: C, 49.5; H, 6.0; Cl, 10.5; N, 2.0. $C_{27}H_{39}Cl_2NOPt$ requires C, 49.2; H, 5.9; Cl, 10.8; N, 2.1%). NMR: ^{1}H, δ 0.88 [3 H, t, ^3J(HH) 7, H_m], 1.30 (18 H, m, H_l), 1.78 (2 H, m, H_k), 4.00 [2 H, t, ^3J(HH) 7, H_j], 4.88 [4 H, s, ^2J(PtH) 61, ethene], 6.88 [1 H, d, ^3J(HH) 16, H_e], 6.93 [2 H, AA′XX′, ^3J(HH) 8, H_g], 7.38 [1 H, d, ^3J(HH) 16, H_d], 7.48 [2 H, AA′XX′, ^3J(HH) 7, H_b], 7.50 [2 H, AA′XX′, ^3J(HH) 8, H_h], and 8.77 [2 H, AA′XX′, ^3J(HH) 7, ^3J(PtH) 34 Hz, H_a]; ^{13}C, δ 14.0 (s, C_m), 22–32 (C_l, C_k), 68.2 (s, C_j), 75.0 (s, ethene), 115.0 (s, C_h), 121.1 (s, $C_{d/e}$), 121.6 (s, C_b), 127.7 (s, C_f), 129.1 (s, C_g), 137.3 (s, $C_{d/e}$), 149.2 (s, C_c), 150.1 (s, C_a), and 160.8 (s, C_i). Far-IR: ν(Pt–Cl) 342s cm^{-1}.

(±)-trans-(η^2-*Alkene*)*dichloro*(*stilbazole*)*platinum*(II) *Complexes* $[PtCl_2(\eta^2\text{-}CH_2{=}CHC_mH_{2m+1})(C_nH_{2n+1}OC_6H_4CH{=}CHC_5H_4N)]$ **2**.—*trans*-Dichloro(4-decyloxy-4′-stilbazole)(ethene)platinum(II) (120 mg, 0.18 mmol) was suspended in diethyl ether (10 cm^3) and pent-1-ene (13 mg, 0.18 mmol) added. The mixture was stirred (15 min), then filtered; pentane (5 cm^3) was added and the solvents removed slowly to give the product as a yellow powder, of analytical purity. It is a racemic mixture of two optical isomers (123 mg, 97%, 0.176 mmol) (Found: C, 51.3; H, 6.2; Cl, 10.0; N, 1.9. $C_{30}H_{45}Cl_2NOPt$ requires C, 51.4; H, 6.4; Cl, 10.1; N, 2.0%). NMR: ^{1}H, δ 0.88 [3 H, t, ^3J(HH) 7, H_m], 1.05 [3 H, t, ^3J(HH) 7, H^5], 1.30 (18 H, m, H_l), 1.61 (2 H, m, H^4), 1.78 (2 H, m, H_k), 1.91 (1 H, m, H^3), 2.42 (1 H, m, $H^{3'}$), 4.00 [2 H, t, ^3J(HH) 7, H_j], 4.70 [1 H, dd, $^2J(H^1H^{1'})$ 2, $^3J(H^1H^2)$ 14, H^1], 4.74 [1 H, dd, $^2J(H^1H^{1'})$ 2, $^3J(H^{1'}H^2)$ 8, $H^{1'}$], 5.71 (1 H, m, H^2), 6.87 [1 H, d, ^3J(HH) 16, H_e], 6.93 [2 H, AA′XX′, ^3J(HH) 8, H_g], 7.36 [1 H, d, ^3J(HH) 16, H_d], 7.45 [2 H, AA′XX′, ^3J(HH) 7, H_b], 7.50 [2 H, AA′XX′, ^3J(HH) 8, H_h], and 8.73 [2 H, AA′XX′, ^3J(HH) 7, ^3J(PtH) 34 Hz, H_a]; ^{13}C, δ 10.3 (s, C^5), 14.0 (s, C_m), 22–32 (C_l, C_k, C^4, C^3), 68.2 (s, C_j), 69.9 (s, C^1), 103.1 (s, C^2), 114.9 (s, C_h), 120.4 (s, $C_{d/e}$), 121.5 (s, C_b), 127.6 (s, C_f), 129.0 (s, C_g), 136.8 (s, $C_{d/e}$), 148.7 (s, C_c), 150.7 (s, C_a), and 160.5 (s, C_i). Far-IR: ν(Pt–Cl) 341s cm^{-1}.

Low-angle X-Ray Scattering.—The experiments were carried out on beam line 8.2 (λ 1.54 Å) at the Daresbury SRS. No attempt was made to align the materials and data were collected on a flat-plate film at a distance of *ca.* 30 cm from the sample holder. For the exposure, compound **2** (n = 9, m = 5) was held in a Lindemann capillary (diameter 0.5 mm), while **2** (n = 12, m = 16) was sealed in a mica cell 0.01 in thick. Both exposures were for 12 min at 80 °C; temperature control (with a Eurotherm 825) was to ±0.1 °C.

Mixing Experiments.—Stock solutions of compounds A, **2** (n = 9, m = 5), and B, **2** (n = 12, m = 5) (0.01 mol in 25 cm^3 ether), were prepared. Measured aliquots (0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4 and 4.5 cm^3) of one of the solutions were mixed with measured aliquots of the other solution (4.5, 4, 3.5, 3, 2.5, 2, 1.5, 1 and 0.5 cm^3 respectively). The solvent was removed, leaving mixtures, by mole, of 10:90%, 20:80%, *etc.* of the two components A and B. The phase behaviour is described in Table 1 and Fig. 5. Compounds C, **2** (n = 12, m = 3), and D, **2** (n = 12, m = 6), were mixed in an identical manner; the phase behaviour is described in Table 2 and Fig. 6.

Decomposition of (±)-trans-(η^2-*Alkene*)*dichloro*(*stilbazole*)*platinum*(II) *Complexes*.—When compound **2** (n = 12, m = 6) was heated, at around 80 °C, on an open slide under the microscope, under an air, nitrogen or argon atmosphere, decomposition could be observed once the compound had passed into the mesophase. A cloudy precipitate separated; at higher temperatures the rate of this precipitation increased. When the sample was heated under an ethene atmosphere this decomposition did not start to occur until above 110 °C; it was deduced to involve a slow loss of the alkene, to give the dimer $[LClPt(\mu\text{-}Cl)_2PtLCl]$. A sample of compound **2** (n = 9, m = 3) which was subjected to prolonged heating (12 h, 100 °C) gave an insoluble amorphous powder (Found: C, 45.4; H, 5.0; Cl, 12.0; N, 2.2. $C_{44}H_{58}Cl_4N_2O_2Pt_2$ requires C, 44.9; H, 4.9; Cl, 12.0; N, 2.4%). Far-IR: ν(Pt–Cl) 340vs and 310s cm^{-1}.

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