Di-cyclopalladated Schiff's base liquid crystals: novel metallomesogens

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The double cyclopalladation of di-Schiff's bases and subsequent reaction with a β-diketone yields novel metallomesogens containing a dimetallated organometallic core: these compounds show nematic phases, and the use of simple alkyl substituted diketones has a very dramatic effect on both the melting and clearing points, bringing them down substantially.

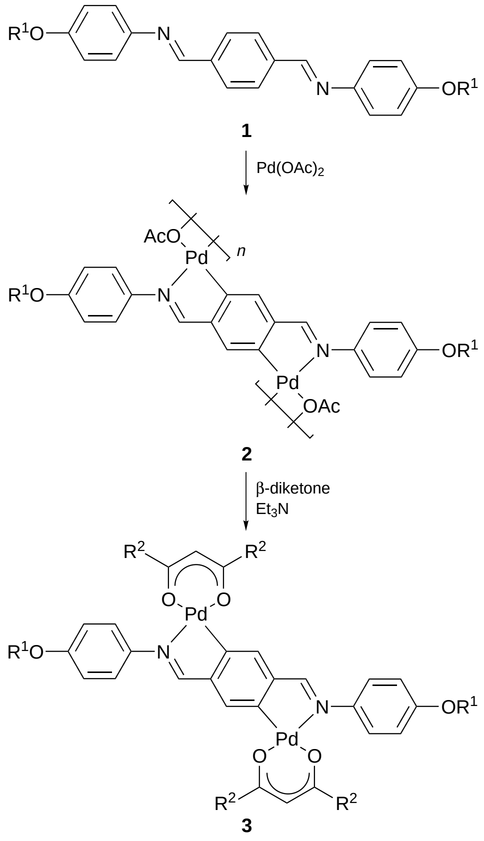
There is currently much interest in the synthesis of metal-containing liquid crystals (metallomesogens) due to the perceived advantages of combining the properties of liquid crystal systems with those of transition metals. The area has been well-reviewed recently,[1,2] with excellent new work appearing constantly.[3–7] Cyclopalladated compounds have proved to be a particularly fertile area of research, with many different examples from many different groups.[7–14]

Most recently, our own work has focused on the role of the co-ligand in a given mesogenic core.[14] Here we report the synthesis, characterisation and mesogenic behaviour of novel complexes that contain two metals cyclometallated to the central core. Although one co-ordination complex containing two metals has previously been reported[15] and two families of dimeric mesogens have been extensively investigated,[5,8,16–28] our new compounds represent the first examples of calamitic organometallic mesogens whose core contains two metals.

The synthesis of the new mesogens **3** is summarised in Scheme 1.† The complexes are based on a di-Schiff's base core[14] with two palladiums cyclometallated in a *trans* fashion to this core. The co-ligands on the palladium are diketonate derivatives. All the new compounds were analysed by ^{1}H NMR spectroscopy and microanalysis.‡ Thus, compounds with alkyl chains of between four and ten carbons on the di-Schiff's base core were synthesised with a simple acetylacetonate co-ligand. In addition, with one Schiff's base core (n = 8), the alkyl chain on the diketonate was systematically varied (R′ = Me, Bu, hexyl, octyl and Bu^t).

The thermal behaviour of the diketonate complexes **3** is detailed in Table 1 and summarised in Figs. 1 and 2. Thus nematic phases (identified on the basis of optical texture) were exhibited by all but three of the complexes. Confirmation of the mesomorphism was obtained by differential scanning calorimetry (DSC) measurements where possible (decomposition of some of the compounds obscured some of the transitions).

The simple acetylacetonate complexes (Fig. 1) exhibit nematic phases at relatively high temperatures (in most cases greater than 200 °C) and the transition from the nematic to the isotropic liquid was often accompanied by extensive decomposition. As one would expect, the melting and clearing points are brought down in temperature by the use of longer chains on the Schiff's base unit (*i.e.* increasing n). However, a more dramatic reduction in both the melting and clearing points (some 80 K) can be achieved by using short chain length alkyl diketones (Fig. 2). This effect is most marked for the m = 4 case, *i.e.* R′ = Bu, where the mesophase is observed well below the decomposition point of the compound. In contrast, when Bu^t groups are attached to the diketonate core, a high melting point is observed with no mesophase, even on rapid cooling. One way of viewing this behaviour is to consider the freely moving alkyl chains on the diketonate groups as disrupting the crystal



$R^1 = C_nH_{2n+1}$ (n = 4–8,10)
$R^2 = Bu^t, C_mH_{2m+1}$ (m = 1,4,6,8)

Scheme 1

Table 1 Mesogenic behaviour of compounds **3**

R^1	R^2	Transition	T/°C	ΔH/J g^{-1}
Bu	Me	K–D	285[a]	—
Pentyl	Me	K–D	280[a]	—
Hexyl	Me	K–N	261	—
		N–I	271[a]	—
Heptyl	Me	K–N	238	—
		N–I	253[a]	—
Octyl	Me	K–N	203	—
		N–I	255[a]	—
Decyl	Me	K–N	187	—
		N–I	246	—
Octyl	Bu	K–N	119	30.96
		N–I	148	0.69
Octyl	Hexyl	K–N	133	29.25
		N–I	142	0.46
Octyl	Octyl	K–I	140	25.59
		N–I	129[b]	0.53
Octyl	Bu^t	K–I	262	—

[a] With decomposition. [b] Monotropic.

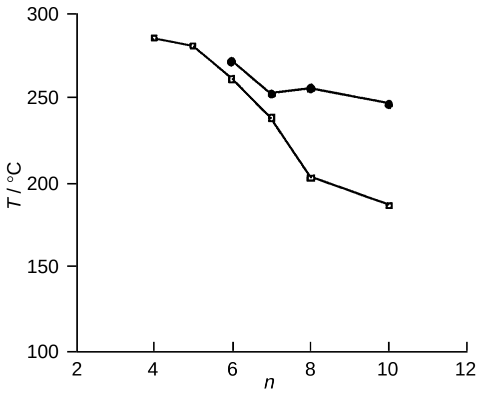


Fig. 1 Phase behaviour of compounds **3** as a function of *n*; (☐) K → N and (●) N → I

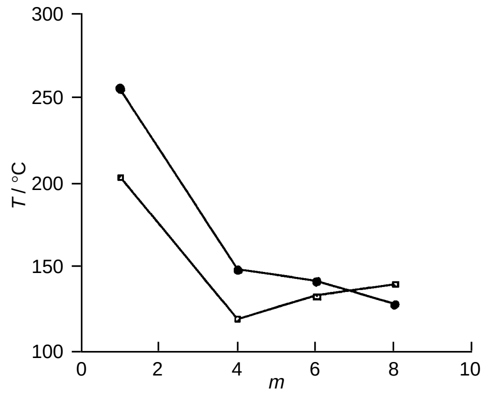


Fig. 2 Phase behaviour of compounds **3** as a function of *m*; (☐) K → N, I and (●) N → I

packing of the molecules and thus reducing the melting point. The Bu^t group is a compact group that cannot move freely, and will not disrupt the packing forces, hence its much higher melting point.

It is perhaps surprising that compounds **3** show any mesogenic behaviour at all: others have suggested that at least four aromatic rings would be necessary to promote mesogenic behaviour in molecules with large metal groups pendant to the central core.[30,31] Here we have only three aromatic rings, and two pendant metal groups. If, however, we consider the core of the molecule to be the central benzene ring, the two cyclometallated units and the two diketonate groups with the alkoxyphenyl groups being the pendant moieties, we encounter a similar problem. Thus it appears that it would be best to consider all of the central Schiff's base unit, with both the alkoxyphenyl and Pd–diketonate groups, as the mesogenic core of the molecule.

In conclusion, we have synthesised a totally new family of metallomesogens with two metal groups in a *trans* fashion about the central ring, and are now working on the *cis* compounds, where both cyclopalladated groups are on the same side of the ring.

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Footnotes and References

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† Palladium acetate (0.150 g, 6.70 × 10^{-4} mol) was added to a solution of **1** (n = 10) (0.200 g, 3.35 × 10^{-4} mol) in acetic acid (200 ml) at 60 °C and stirred (24 h). The solvent was removed, and the product **2** (n = 10) used without further purification.

Compound **2** (n = 10) (0.180 g, 2.00 × 10^{-4} mol) and sodium acetylacetonate (0.073 g, 6.00 × 10^{-4} mol, 1.5 equiv.) were suspended in acetone (200 ml) and stirred (24 h). The solvent was removed and the crude product extracted with $CHCl_3$. The product was further purified by chromatography on silica (eluent: $CHCl_3$): yield 0.154 g (77%).

‡ *Selected data* for **3** (n = 10, R′ = Me) (all others are similar): δ_H 8.13 (2 H, s, imine), 7.56 (2 H, s, central ring), 7.39 (4 H, AA′XX′, aromatic), 6.88 (4 H, AA′XX′, aromatic), 5.34 (2 H, s, central acac), 3.99 (4 H, t, ^3J 6.5, OCH_2), 2.07 (6 H, s, acac Me), 1.89 (6 H, s, acac Me), 1.40 (28 H, m, chain), 0.89 (6 H, t, ^3J 6.5 chain CH_3). Good elemental analysis data were obtained for all compounds. Evidence for the *trans* arrangement of the palladium atoms about the central ring comes from preliminary single crystal X-ray studies (ref. 29).

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