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Organometallic Liquid Crystals Based on Octahedral Rhodium(III)

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Reaction of mesomorphic alkynes with $[\text{RhMe}(\text{PMe}_3)_4]$ led to the Rh^{III} complexes *mer,trans*- $[\text{RhH}(\text{alkynyl})_2(\text{PMe}_3)_3]$ which are liquid crystalline; they are rare examples of rod-like liquid crystals based on an octahedral metal centre and represent a unique homologous series of mesomorphic metal complexes containing a hydrido function.

There is currently much interest in the synthesis of metal-containing liquid crystals 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,¹⁻⁶ and some excellent new work has been recently published.^{7,8} On reading such reviews, it is immediately apparent that the vast majority of mesomorphic complexes are derived from metals in d^8 - d^{10} electron configurations, usually with planar or linear geometries. While these complexes have proved both interesting and rewarding to study, many metals are excluded in concentrating on these systems. Planar and linear complexes are of course preferred as the shapes of the resulting complexes closely resemble the anisotropic rods or discs formed by organic systems and one can quickly imagine that the inclusion of an octahedral metal centre would act to modulate severely this anisotropy.⁹

However, it has been reasoned that if a sufficiently large liquid-crystalline ligand were employed, then the perturbation of the anisotropy due to the metal fragment could be minimised, and the first two examples of a calamitic thermotropic liquid crystal containing octahedrally co-ordinated manganese¹⁰ and rhenium¹¹ have recently been reported.

The complexes described herein are Rh^{III} complexes based on liquid-crystalline alkynes. Previously, Takahashi and co-workers¹² had reported some mesomorphic Pt^{II} acetylides containing trimethylphosphine ligands (**1**). Given the rather free rotation of these complexes about their long axis in the mesophase, we reasoned that liquid crystals should also be generated if a further two co-ordination sites were taken up by ligands no bulkier than trimethylphosphine. Thus, we elected to study, *mer,trans*- $[\text{RhH}(\text{C}\equiv\text{CR})_2(\text{PMe}_3)_3]$ **2** in which these criteria are met and which can be synthesised using a known route¹³ (Scheme 1).§ In order to enhance our chances of generating mesomorphic materials, we also chose to use more strongly mesomorphic alkynes (HL)¹⁴ which we have also

Table 1 Thermal data for the new complexes. Heating rates were 20 K min^{-1}

Compound	Transition	$T/^\circ\text{C}$
2a	Crys \longrightarrow Crys'	76
	Crys' \longrightarrow S	136
	S \longrightarrow N	174
	N \longrightarrow I	203 (decomp.)
2b	Crys \longrightarrow Crys'	83
	Crys' \longrightarrow S	146
	S \longrightarrow N	169
	N \longrightarrow I	198 (decomp.)
2c	Crys \longrightarrow Crys'	69
	Crys' \longrightarrow S	142
	S \longrightarrow N	172
	N \longrightarrow I	202 (decomp.)

shown to form mesomorphic complexes with Pt^{II} bound to PMe_3 .¹⁵ Compounds **2** were isolated as colourless powders in high yield: all were analysed by NMR spectroscopy (³¹P and ¹H) and by microanalysis.¶

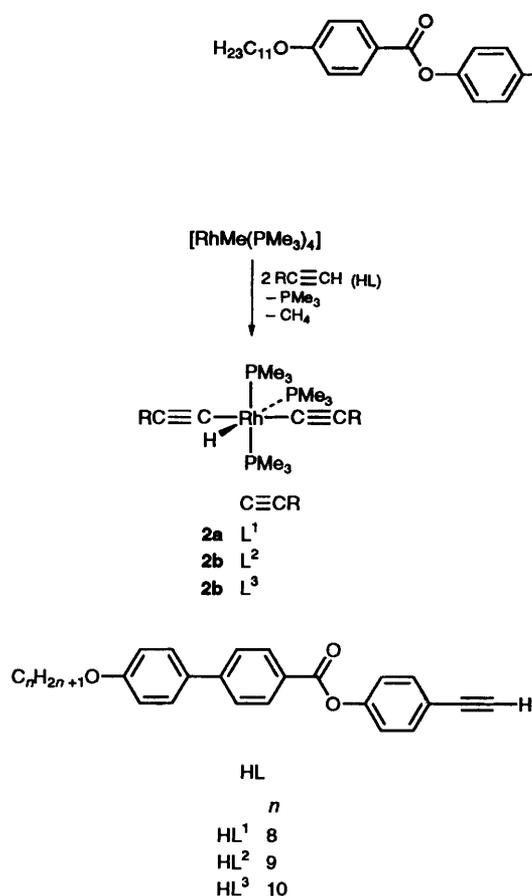
The thermal behaviour of compounds **2** is summarised in Table 1. Thus, all of the complexes studied showed a second crystal modification (crys'), a smectic phase (S) and a nematic phase (N), although decomposition set in during heating and was rather rapid in the nematic phase and (especially) the isotropic phase (I), even under an inert atmosphere. That the compounds decomposed in the nematic phase (identified by the presence of a schlieren texture) made identification of the smectic phase difficult (identification of smectic textures should always be attempted on cooling a higher-temperature phase)

¶ NMR data for compound **2a** (**2b** and **2c** are similar): ³¹P- $\{^1\text{H}\}$ (C_6D_6 , 81.02 MHz): δ -6.72 [2 P, dd, ¹J(Rh-P) 93, ²J(P-P) 26, P *trans* to P], -24.23 [1 P, dt, ¹J(Rh-P) 76, ²J(P-P) 26 Hz, P *trans* to H]; ¹H (C_6D_6 , 500.14 MHz): δ 8.33, (4 H, AA'XX', aromatic), 7.51, (4 H, AA'XX', aromatic), 7.47 (4 H, AA'XX', aromatic), 7.37 (4 H, AA'XX', aromatic), 7.19 (4 H, AA'XX', aromatic), 6.93 (4 H, AA'XX', aromatic), 3.72 [4 H, t, ²J(H-H) 7, OCH₂], 1.68 (4 H, m, OCH₂CH₂), 1.49 (18 H, t, J 3, PMe_3 *trans* to PMe_3), 1.4-1.25 (20 H, br m, CH₂ chain), 1.24 (9 H, d, J 8 Hz, PMe_3 *trans* to H), 0.93 [6 H, t, ³J(H-H) 7, CH₃], -9.09 [dq, ¹J(Rh-H) = ²J(P_{cis}-H)16, ²J(P_{trans}-H)196 Hz, hydride]. Microanalysis: **2a**, Found ($\text{C}_{67}\text{H}_{86}\text{O}_6\text{P}_3\text{Rh}$ requires): C, 67.6 (68.0); H, 7.4 (7.3); **2b**, Found ($\text{C}_{69}\text{H}_{90}\text{O}_6\text{P}_3\text{Rh}$ requires): C, 68.0 (68.4); H, 7.6 (7.5); **2c**, Found ($\text{C}_{71}\text{H}_{94}\text{O}_6\text{P}_3\text{Rh}$ requires): C, 68.7 (68.8); H, 7.8 (7.6%).

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§ A solution of HL¹ (121 mg, 2.84×10^{-4} mol) in tetrahydrofuran (thf) (15 cm³) was added to a solution of $[\text{RhMe}(\text{PMe}_3)_4]$ (60 mg, 1.42×10^{-4} mol) in thf (3 cm³) and the mixture stirred (16 h) under an inert atmosphere. The solvent was removed and the product crystallised from thf-hexane (50:50). Yield: 138 mg (82%, 1.16×10^{-4} mol).



Scheme 1 Synthesis of the new compounds

and we have not been able to arrive at a satisfactory conclusion about its identity. Differential scanning calorimetry studies indicated transitions corresponding to all the observed phases, but were complicated by the complex endothermic transition associated with the decomposition process.

We suspect that the susceptibility to thermal decomposition of these complexes may be attributed to the more labile nature of second-row transition-metal complexes, for while we¹⁵ and Takahashi and co-workers¹² have found that Pt^{II} complexed to alkynes are thermally rather stable, we found that the palladium congeners were much less thermally robust, decomposing at temperatures above 120 °C.¹⁵

It is of interest to compare the mesophase stability of these new complexes with those of the free ligand and of their Pt^{II} complexes, *trans*-[PtL(PMe₃)₂] (*i.e.* complexes of type 1, derived from the alkynes HL). Thus, the clearing point of the free alkyne ligands with an octyloxy or decyloxy chain is between 220 and 230 °C. According to a simple interpretation of the Maier-Saupe theory, coupling two together (*i.e.* by making a dialkyne) should lead to a compound with a very high clearing point [if the length is doubled, then the clearing point (in K) is roughly doubled], at least in excess of 500 °C. For the Pt^{II} complexes, it is difficult to estimate the clearing point as the complexes decompose above 320 °C, but by comparison with the related complexes with PEt₃ ligands,¹⁵ this temperature is probably quite close to the true clearing point. However, the Rh^{III} complexes described here clear with decomposition at around 200 °C, a much lower temperature. Thus, having the bulky trimethylphosphine groups in the middle of the molecule

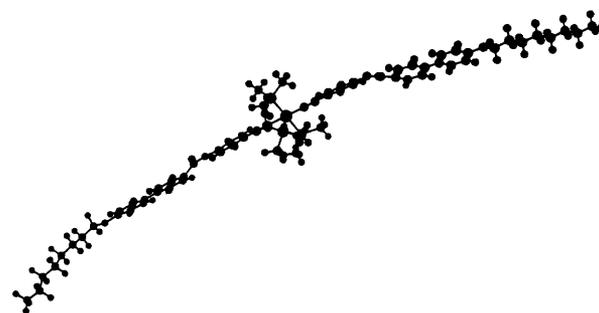


Fig. 1 Model of compound 2a

destabilises the nematic phase of the notional dialkyne dimer quite considerably, which is consistent with the reduction in structural anisotropy. Models of compounds 2 (Fig. 1) show well the bulky groups in the centre of a molecule and it is therefore slightly surprising that a smectic (*i.e.* layered) phase is observed, given the appreciable lateral interactions that its existence implies.

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