DALTON

Calamitic liquid crystals containing metal–metal bonds: design of mesomorphic materials based on the $Ru_2(CO)_4(\mu\text{-}\eta^2\text{-}O_2CR)_2L_2$ sawhorse unit †

Robert Deschenaux,* Bertrand Donnio, Gerd Rheinwald, Frédéric Stauffer, Georg Süss-Fink * and Jörg Velker

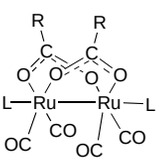
Institut de Chimie, Université de Neuchâtel, CH-2000 Neuchâtel, Switzerland

A series of complexes based on the stable $[Ru_2(CO)_4(\mu\text{-}\eta^2\text{-}O_2CR)_2L_2]$ sawhorse unit has been prepared and characterized. The derivatives $[Ru_2(CO)_4(\mu\text{-}\eta^2\text{-}O_2CR)_2\{NC_5H_4(CO_2C_6H_4OC_nH_{2n+1}\text{-}p)\text{-}p\}_2]$ (R = H, n = 10; R = C_6H_5, n = 6, 10, 12, 14 or 16; R = $C_6H_4CH_3$-*p*, n = 10; R = $C_6H_4OCH_3$-*p*, n = 6, 10 or 16) proved to be mesomorphic, giving rise to nematic phases.

A century after their discovery,[1] liquid crystals have made possible an unrivalled development in the technology of watch displays, calculators, mobile telephones and notebook computers.[2] With the rapidly growing interest in this field, special attention has been paid to metallomesogens which combine the physical characteristics of metal complexes (*e.g.* polarizability, colour, magnetism) with those of organic molecules which form liquid crystals.[3] Mesomorphic materials containing covalent metal–metal bonds are rare. The first examples of this type are the complexes $[Rh_2(\mu\text{-}\eta^2\text{-}O_2CC_nH_{2n+1})_4]$, reported by Marchon and co-workers,[4] which form columnar phases, the derivative with $n = 7$ showing an Rh–Rh distance of 2.38 Å. The air-sensitive $Ru^{II}Ru^{II}$ complexes $[Ru_2(\mu\text{-}\eta^2\text{-}O_2CC_nH_{2n+1})_4]$ formally contain an Ru=Ru double bond, whereas the mixed-valence $Ru^{II}Ru^{III}$ complexes $[Ru_2(\mu\text{-}\eta^2\text{-}O_2CC_nH_{2n+1})_5]$ are paramagnetic, both series also forming columnar phases.[5]

New mesomorphic dinuclear metal–metal bonded complexes have recently been published. Serrano and co-workers[6] reported a series of dirhodium(II) tetrabenzoate complexes containing a single metal–metal bond, which displayed columnar mesophases. Chisholm and co-workers[7] prepared liquid-crystalline compounds containing Mo–Mo or Cr–Cr quadrupole bonds, which exhibited hexagonal columnar phases. Finally, Serrano and co-workers[8a] described the thermal behaviour of a series of β-diketonatothallium(I) complexes. Some of the compounds displayed a monotropic hexagonal columnar phase. The authors suggested that the mesomorphic properties resulted from the dimeric nature of the complexes. This assumption was based on the single-crystal X-ray analysis of a non-mesomorphic homologue, which showed strong Tl–Tl bonding interactions.[8b]

In order to design diamagnetic, calamitic metallomesogens containing an Ru–Ru core with a covalent single metal–metal bond we have chosen the stable $[Ru_2(CO)_4(\mu\text{-}\eta^2\text{-}O_2CR)_2L_2]$ sawhorse unit. Complexes of this type were first discovered by Lewis and co-workers[9] who reported in 1969 the formation of the polymers $[\{Ru_2(CO)_4(\mu\text{-}\eta^2\text{-}O_2CR)_2\}_n]$ by refluxing $[Ru_3(CO)_{12}]$ in the corresponding carboxylic acid RCO_2H; these polymers dissolve in co-ordinating solvents [tetrahydrofuran (thf) or MeCN] to give the dinuclear complexes $[Ru_2(CO)_4(\mu\text{-}\eta^2\text{-}O_2CR)_2L_2]$. Both the polymers and the dinuclear species were shown later to contain an $Ru_2(CO)_4$ sawhorse moiety by a



single-crystal structure analysis of the derivatives $[\{Ru_2(CO)_4(\mu\text{-}\eta^2\text{-}O_2CC_6H_5)_2\}_n]$ (Ru–Ru 2.64 Å)[10] and $[Ru_2(CO)_4(\mu\text{-}\eta^2\text{-}O_2CBu^n)_2(PBu^t_3)_2]$ (Ru–Ru 2.73 Å).[11] Owing to the stability of the Ru–Ru backbone in this type of compound, a considerable number of representatives containing the $Ru_2(CO)_4(\mu\text{-}\eta^2\text{-}O_2CR)_2$ moiety has been prepared and characterized.[12]

Results and Discussion

Synthesis and characterization

Two possibilities have been considered to induce mesomorphic properties in the complex of type $[Ru_2(CO)_4(\mu\text{-}\eta^2\text{-}O_2CR)_2L_2]$ (above) since both L and R can be varied: (*a*) introduction of promesogenic ligands L in the axial positions (with small R), which leads to molecules of linear shape, and (*b*) introduction of large substituents R into the two bridging carboxylato ligands (the axial ligand L being small), which gives an orthogonal shape to the molecules.

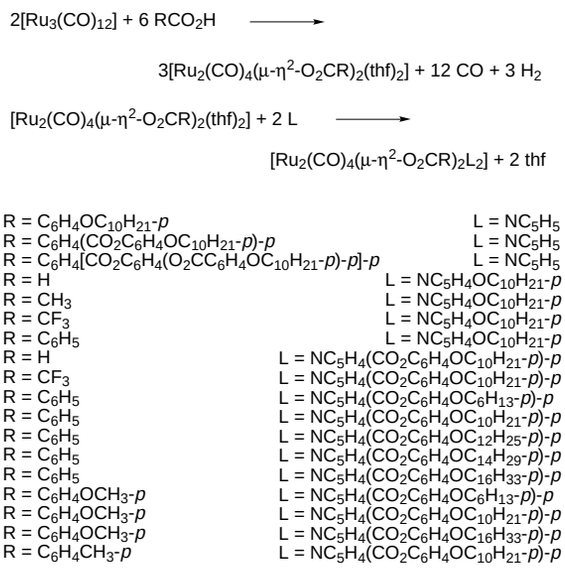
In a previous study[13] we have shown that diruthenium complexes with low melting points are accessible by using either phosphine ligands with long aliphatic chains in the axial positions L or carboxylato ligands containing long aliphatic substituents R. These compounds, however, did not show mesomorphic properties.[13] We therefore decided to synthesize diruthenium complexes containing pyridine ligands in the axial positions and to introduce not only aliphatic chains but also aromatic rings into the molecules. The variations of the ligands L and the substituents R are shown in Scheme 1.

All compounds **1**–**18** were prepared by treating $[Ru_3(CO)_{12}]$ with the corresponding carboxylic acid RCO_2H in tetrahydrofuran solution at 110–125 °C (using a pressure tube), followed by an exchange reaction at 25 °C with L. The yields, spectroscopic characteristics and microanalytical data are given in the Experimental section. The preparation and the spectroscopic data of the carboxylic acid and pyridine derivatives used for the synthesis of **1**–**18** are given in SUP 57291.

Thermal and mesomorphic properties

The thermal and liquid-crystalline behaviours of the complexes

† *Supplementary data available* (No. SUP 57291, 5 pp.): preparative and characterization details for reagents. See *J. Chem. Soc.*, *Dalton Trans.*, 1997, Issue 1.



Scheme 1 Synthesis of complexes **1**–**18**

prepared were examined by a combination of polarized optical microscopy (POM), differential scanning calorimetry (DSC) and thermogravimetry. The transition temperatures and enthalpy changes are listed in Table 1.

No mesomorphic properties were observed for complexes **1**–**7** and **9**. When heated they directly and clearly melted into the isotropic liquid. Upon cooling from the isotropic melt, crystallization was detected only for complexes **4**, **5**, **7** and **9**. The lack of liquid-crystalline behaviour of **1**–**7** and **9** could be explained in terms of their structures. In the case of **1**–**3** the complexes have two promesogenic carboxylato ligands lying in two perpendicular planes leading to an 'L'-shape structure. Such a structure does not have the appropriate molecular anisotropy responsible for generating mesomorphism. As for **4**–**7** and **9**, despite the presence of larger substituted pyridine ligands in the axial positions, which enhance the molecular anisotropy along the metal–metal bond (as compared to **1**–**3**), the lack of mesomorphism is, most likely, the consequence of too weak intermolecular interactions due to the bulky organometallic central core. Interestingly, compound **8**, functionalized by the smallest substituent (*i.e.* R = H) in the bridging positions gave an enantiotropic nematic phase. The latter was identified from its typical *schlieren* texture and from the formation of nematic droplets. Upon cooling, the observation of transition bars suggested the formation of a monotropic smectic C phase (which appeared when the sample crystallized). The nematic-to-smectic C phase transition was not detected by DSC, most likely because of its rather small temperature range. The occurrence of mesomorphism for **8** was not unexpected as, when compared with **4**–**7** and **9**, it has the highest length/width molecular anisotropic ratio. Since complex **8** showed limited thermal stability as detected by DSC, this substitution pattern was not investigated further.

All the mesomorphic complexes **10**–**18** displayed a nematic phase, which was found to be enantiotropic for **10**–**14**, **17** and **18**, and monotropic for **15** and **16**. The nematic phase was identified from the formation of typical marbled and threaded textures which developed on heating the sample (in the case of the enantiotropic compounds), and from the observation of the *schlieren* texture characterized by two and four brushes (for all the compounds) on cooling the sample from the isotropic melt.

In the series **10**–**14** the length of the terminal chains was varied from 6 to 16 carbon atoms. All compounds, with the exception of **12**, gave a crystal-to-crystal transition in the first heating run. In the case of the hexadecyloxy derivative **14**, besides the crystal-to-crystal transition, the following phase sequence was observed before entering into the isotropic liquid: crystal ⟶ nematic phase ⟶ crystal ⟶ nematic phase. This behaviour was reproducible for successive heating runs (on cooling the following sequence was observed: isotropic liquid ⟶ nematic phase ⟶ crystal). Such a melting–crystallization–melting process has been observed for other metallomesogens.[14]

Table 1 Phase-transition temperatures[a] and enthalpy changes of complexes **1**–**18**

Compound	Transition	T/°C	ΔH/kJ mol^{-1}
1	K–I	137	58.7
2	K–I	149	58.5
3	K–I	180	60.4
4	K–I	120	56.2
5	K–I	103	34.5
6	K–I	77	42.4
7	K–I	144	35.4
8[b]	K–N	147	41.3
	N–I	156	2.8
9	K–I	122	67.6
10	K–N	189	36.5
	N–I	225	2.5
11	K–N	163	34.7
	N–I	206	2.4
12	K–N	166	48.2
	N–I	195	2.8
13	K–N	156	49.2
	N–I	185	2.5
14	K–N	150	42.9
	N–K′	155	−2.0
	K′–N	161	4.1
	N–I	179	2.9
15	K–I	181	51.9
	I–N	176	2.7
	N–G	83	—
16	K–I	152	45.9
	I–N	151	2.0
17	K–N	137	—
	N–I	146	49.8[c]
18	K–N	163	—
	N–I	173	48.3[c]

[a] K, K′ = Crystalline states, N = nematic phase, I = isotropic liquid, G = frozen mesophase. [b] A monotropic smectic C phase formed near 135 °C during the crystallization process (see main text). [c] Cumulated enthalpies (peak overlap).

Substitution in the *para* position of the benzene ring by a methoxy group (series **15**–**17**) destabilized the nematic phase which resulted in the formation of a monotropic mesophase for **15** and **16** (compare **15** with **10** and **16** with **11**); enantiotropic behaviour was observed only for **17** which has the longest alkyloxy chains. It is likely that the incorporation of the methoxy group into the benzoato bridges led to a reduction of the intermolecular interactions and thus to a reduction of the clearing point (this effect being less pronounced in the case of the melting point; compare **10**, **11** and **14** with **15**, **16** and **17**, respectively). Upon cooling, the decyloxy derivative **16** did not crystallize but formed a glass (T_g = 46 °C). On heating, the frozen nematic state remained as such until 86 °C, at which temperature crystallization occurred. At 152 °C, **16** melted into the isotropic liquid. This behaviour was reproducible over several heating–cooling cycles. The formation of anisotropic glasses has been reported in the case of metallomesogens[15] and is of great interest in liquid-crystal display (LCD) technology, particularly for the manufacturing of optical information-storage devices.[15c,d]

The mesomorphic behaviour of complex **18** was found to be intermediate between those of **10**–**14** and of **15** and **16** in as much as it displayed an enantiotropic nematic phase, but with a

Table 2 Synthetic experimental conditions and analytical data for complexes **1**–**18**

Complex	RCO_2H *m*/mg	Reaction *T*/°C	Reaction *t*/h	Crystallization solvent	Yield (%)	Analysis (%)* C	H	N
1	130	120	24	CH_2Cl_2–pentane	66	56.1 (56.1)	5.8 (5.9)	2.7 (2.7)
2	187	120	25	CH_2Cl_2–pentane CH_2Cl_2–MeOH	39	58.7 (58.8)	5.5 (5.4)	2.2 (2.2)
3	243	125	25	CH_2Cl_2–MeOH–pentane	55	60.1 (60.0)	5.2 (5.0)	1.8 (1.9)
4	122	110	20	CH_2Cl_2–pentane CH_2Cl_2–MeOH	68	49.5 (49.4)	6.0 (6.0)	3.2 (3.2)
5	158	120	18	CH_2Cl_2–pentane CH_2Cl_2–MeOH	61	50.5 (50.5)	6.3 (6.25)	3.0 (3.1)
6	300	125	4	CH_2Cl_2–MeOH	34	45.1 (45.15)	4.85 (5.0)	2.6 (2.8)
7	57	120	27	CH_2Cl_2–MeOH	68	56.0 (56.1)	6.0 (5.9)	2.6 (2.7)
8	122	110	20	CH_2Cl_2–MeOH	59	53.8 (53.85)	5.4 (5.4)	2.4 (2.5)
9	300	125	4	CH_2Cl_2–MeOH–pentane	58	49.8 (49.9)	4.7 (4.7)	2.2 (2.2)
10	57	120	27	CH_2Cl_2–MeOH–pentane CH_2Cl_2–hexane	58	55.9 (56.15)	4.7 (4.5)	2.5 (2.4)
11	57	120	27	CH_2Cl_2–MeOH–pentane	81	58.75 (58.8)	5.5 (5.4)	2.1 (2.2)
12	57	120	27	CH_2Cl_2–MeOH–pentane	76	59.7 (59.9)	5.7 (5.8)	2.2 (2.1)
13	57	120	27	CH_2Cl_2–MeOH–pentane	91	60.7 (60.9)	6.2 (6.1)	2.1 (2.0)
14	57	120	27	CH_2Cl_2–MeOH–pentane	94	61.9 (61.9)	6.6 (6.5)	2.0 (1.95)
15	71	125	28	CH_2Cl_2–MeOH–pentane CH_2Cl_2–hexane	88	55.2 (55.35)	4.9 (4.6)	2.4 (2.3)
16	71	125	28	CH_2Cl_2–MeOH–pentane	74	57.9 (57.9)	5.55 (5.5)	2.2 (2.1)
17	71	125	28	CH_2Cl_2–MeOH–pentane	89	61.0 (61.0)	6.5 (6.5)	2.0 (1.9)
18	64	120	21	CH_2Cl_2–hexane	64	59.3 (59.3)	5.9 (5.6)	2.2 (2.2)

* Calculated values are given in parentheses.

narrower temperature range. The reduction of the liquid-crystalline domain was essentially due to the depression of the clearing temperature. This result was consistent with the data reported for **15**–**17**: reduction of the molecular anisotropy resulted in a decrease of the molecular interactions and thus in the destabilization of the nematic phase.

Finally, the complexes studied showed good thermal stability as confirmed by thermogravimetry analysis: for example, a mass loss of 1, 5 and 10% was detected at 257, 294 and 304 °C, respectively, for **13**.

Conclusion

Despite the bulky central cluster unit, we were able to obtain mesomorphic materials by a subtle combination of ligands L and substituents R. In order to generate mesomorphism, a minimum of two aromatic rings per ligand L was a necessary condition to thwart the large disruption of the molecular anisotropy. Similar conclusions were drawn for other calamitic metallomesogens containing bulky metallic fragments in the rigid core.[3]

It is important to note that the thermal behaviour shown by the complexes studied was dependent upon the type of carboxylato bridges. Accordingly, for the identical pyridine ligand $NC_5H_4(CO_2C_6H_4OC_{10}H_{21}$-*p*)-*p*, the mesophase was (*i*) suppressed for R = CF_3 (**9**), (*ii*) enantiotropic for R = H (**8**), C_6H_5 (**11**) and $C_6H_4CH_3$-*p* (**18**) and (*iii*) monotropic for R = $C_6H_4OCH_3$-*p* (**16**).

The case of complexes **10**–**18** suggests that the benzene rings of the carboxylato bridges interact with the aromatic rings of the neighbouring pyridine ligand, allowing the complexes to be organized along one direction, with a certain degree of freedom, giving rise to a nematic type of molecular organization. Substitution in the *para* position by a methyl (**18**) or a methoxy group (**15**–**17**) resulted in a dramatic decrease of the thermal stability of the nematic phase. This is consistent with a disruption of the π–π interactions between the benzene rings of R and those of L of adjacent complexes, when the benzoato bridges are substituted by methyl or methoxy substituents, essentially due to steric hindrance. As for **8**, the mesomorphism should be the consequence of the appropriate anisotropic structure giving rise to favourable lateral interactions (as also evidenced by the observation of the smectic C phase). Interestingly, the higher thermal stability of the nematic phase shown by **11** as compared to the one exhibited by **8** emphasizes the crucial role played by the π–π interactions (see above).

Finally, it is worth mentioning that this new family of metallomesogens represents rare examples of mesomorphic compounds containing covalent bonds between two metal atoms. They are of considerable interest in terms of their possible catalytic reactivity as shown recently for structurally related non-mesomorphic Ru–Ru complexes.[16]

Experimental

General comments

The high-temperature reactions were carried out under nitrogen using standard Schlenk techniques; all other manipulations

Table 3 Infrared and NMR data of complexes **1**–**18**

Complex	$\tilde{\nu}_{(CO)}$/cm^{-1} (thf)	δ_H($CDCl_3$) [a]	δ_C($CDCl_3$) [a]
1	2023s 1972m 1941s	[b] 0.87 [6 H, t, J(H_3C–H_2C) 6.9, H_3C], 1.25–1.45 (28 H, m, 7 H_2C), 1.83 [4 H, qnt, J(OH_2C–H_2CH_2C) 7, H_2C], 3.92 [4 H, t, J(OH_2C–H_2C) 6.6, H_2CO], AA′XX′ [6.74 (4 H, $HC^{4,6}$), 7.77 (4 H, $HC^{3,7}$)], AA′XX′M [7.51 (4 H, $HC^{2',4'}$), 7.90 (2 H, $HC^{3'}$), 8.92 (4 H, $HC^{1'5'}$)]	14.8 (CH_3), 23.4 (CH_2CH_3), 26.7 ($CH_2CH_2CH_2O$), 29.8 (CH_2CH_2O), 30.0, 30.0, 30.2, 30.2 (4 CH_2), 32.6 ($CH_2CH_2CH_3$), 68.8 (CH_2O), 114.1 ($C^{4,6}$), 125.5 ($C^{2',4'}$), 126.7 (C^2), 132.2 ($C^{3,7}$), 138.0 ($C^{3'}$), 152.8 ($C^{1',5'}$), 162.5 (C^5), 179.1 (RuCO), 205.0 (C^1)
2	2027s 1976m 1946s	[b] 0.88 [6 H, t, J(H_3C–H_2C) 6.9, H_3C], 1.25–1.50 (28 H, m, 7 H_2C), 1.78 [4 H, qnt, J(OH_2C–H_2CH_2C) 7, H_2C], 3.94 [4 H, t, J(OH_2C–H_2C) 6.6, H_2CO], AA′BB′ [6.90, 7.08 (4 H, $HC^{10,14}$), (4 H, $HC^{11,13}$)], AA′XX′M [7.57 (4 H, $HC^{2',4'}$), 7.96 (2 H, $HC^{3'}$), 8.94 (4 H, $HC^{1',5'}$)], AA′BB′ [7.97, 8.10 (4 H, $HC^{3,7}$), (4 H, $HC^{4,6}$)]	14.8 (CH_3), 23.4 (CH_2CH_3), 26.7 ($CH_2CH_2CH_2O$), 29.9 (CH_2CH_2O), 30.0, 30.1, 30.2, 30.3 (4 CH_2), 32.6 ($CH_2CH_2CH_3$), 69.1 (CH_2O), 115.8, 122.9 ($C^{10,14}$), ($C^{11,13}$), 125.8 ($C^{2',4'}$), 130.4, 130.4 ($C^{3,7}$), ($C^{4,6}$), 132.9 (C^5), 138.3 (C^2), 138.4 ($C^{3'}$), 144.8 (C^9), 152.6 ($C^{1',5'}$), 157.7 (C^{12}), 165.8 (C^8), 178.6 (RuCO), 204.6 (C^1)
3	2027s 1976m 1946s	[b] 0.89 [6 H, t, J(H_3C–H_2C) 6.9, H_3C], 1.25–1.50 (28 H, m, 7 H_2C), 1.82 [4 H, qnt, J(OH_2C–H_2CH_2C) 7, H_2C], 4.04 [4 H, t J(OH_2C–H_2C) 6.6, H_2CO], AA′XX′ [6.97 (4 H, $HC^{18,20}$), 8.13 (4 H, $HC^{17,21}$)], AA′BB′ [7.25 (8 H, $HC^{10,14}$, $HC^{11,13}$)], AA′XX′M [7.59 (4 H, $HC^{2',4'}$), 7.98 (2 H, $HC^{3'}$), 8.95 (4 H, $HC^{1',5'}$)], AA′BB′ [7.99, 8.12 (4 H, $HC^{3,7}$), (4 H, $HC^{4,6}$)]	14.8 (CH_3), 23.4 (CH_2CH_3), 26.8 ($CH_2CH_2CH_2O$), 29.8 (CH_2CH_2O), 30.0, 30.0, 30.2, 30.2 (4 CH_2), 32.6 ($CH_2CH_2CH_3$), 69.0 (CH_2O), 115.0 ($C^{18,20}$), 122.0 (C^{16}), 123.1, 123.5 ($C^{10,14}$), ($C^{11,13}$), 125.8 ($C^{2',4'}$), 130.5, 130.5 ($C^{3,7}$), ($C^{4,6}$), 132.6 (C^5), 133.0 ($C^{17,21}$), 138.4 ($C^{3'}$), 138.5 (C^2), 148.8, 149.3 (C^9), (C^{12}), 152.6 ($C^{1',5'}$), 164.3, 165.2, 165.5 (C^8), (C^{15}), (C^{19}), 178.5 (RuCO), 207.8 (C^1)
4	2025s 1973m 1943s	[c] 0.89 [6 H, t, J(H_3C–H_2C) 6.5, H_3C], 1.25–1.50 (28 H, m, 7 H_2C), 1.83 [4 H, qnt, J(OH_2C–H_2CH_2C) 7, H_2C], 4.06 [4 H, t, J(OH_2C–H_2C) 6.6, H_2CO], AA′XX′ [6.92 (4 H, $HC^{2,4}$), 8.55 (4 H, $HC^{1,5}$)], 8.34 (2 H, s, HCO_2)	14.2 (CH_3), 22.7 (CH_2CH_3), 25.9 ($CH_2CH_2CH_2O$), 28.8 (CH_2CH_2O), 29.3, 29.3, 29.6, 29.6 (4 CH_2), 31.9 ($CH_2CH_2CH_3$), 68.7 (CH_2O), 111.6 ($C^{2,4}$), 152.7 ($C^{1,5}$), 166.2 (C^3), 174.5 (RuCO), 203.9 ($C^{1'}$)
5	2021s 1969m 1938s	[c] 0.90 [6 H, t, J(H_3C–H_2C) 6.4, H_3C], 1.25–1.50 (28 H, m, 7 H_2C), 1.83 [4 H, qnt, J(OH_2C–H_2CH_2C) 7, H_2C], 2.05 (6 H, s, H_3CCO_2), 4.06 [4 H, t, J(OH_2C–H_2C) 6.4, H_2CO], AA′XX′ [6.90 (4 H, $HC^{2,4}$), 8.53 (4 H, $HC^{1,5}$)]	14.2 (CH_3), 22.7 (CH_2CH_3), 23.8 (CH_3CO_2), 25.9 ($CH_2CH_2CH_2O$), 28.8 (CH_2CH_2O), 29.3, 29.4, 29.6, 29.6 (4 CH_2), 31.9 ($CH_2CH_2CH_3$), 68.6 (CH_2O), 111.4 ($C^{2,4}$), 152.9 ($C^{1,5}$), 166.0 (C^3), 184.5 (RuCO), 204.5 ($C^{1'}$)
6 [d]	2037s 1986m 1958s	[c] 0.90 [6 H, t, J(H_3C–H_2C) 6.4, H_3C], 1.25–1.50 (28 H, m, 7 H_2C), 1.84 [4 H, qnt, J(OH_2C–H_2CH_2C) 7, H_2C], 4.08 [4 H, t, J(OH_2C–H_2C) 6.5, H_2CO], AA′XX′ [6.93 (4 H, $HC^{2,4}$), 8.43 (4 H, $HC^{1,5}$)]	14.2 (CH_3), 22.8 (CH_2CH_3), 25.9 ($CH_2CH_2CH_2O$), 28.8 (CH_2CH_2O), 29.3, 29.3, 29.6, 29.6 (4 CH_2), 31.9 (CH_2-CH_2CH_3), 68.7 (CH_2O), 111.7 ($C^{2,4}$), 114.9 [q, J(C–F) 290, CF_3], 152.6 ($C^{1,5}$), 166.4 (C^3), 169.5 [q, J(*F*CCOORu*C*O) 40, RuCO], 203.1 ($C^{1'}$)
7	2023s 1971m 1941s	[c] 0.90 [6 H, t, J(H_3C–H_2C) 6.5, H_3C], 1.25–1.55 (28 H, m, 7 H_2C), 1.88 [4 H, qnt, J(OH_2C–H_2CH_2C) 7, H_2C], 4.13 [4 H, t, J(OH_2C–H_2C) 6.6, H_2CO], AA′XX′ [7.00 (4 H, $HC^{2,4}$), 8.71 (4 H, $HC^{1,5}$)], AA′BMM′ [7.27 (4 H, $HC^{4',6'}$), 7.39 (2 H, $HC^{5'}$), 7.87 (4 H, $HC^{3',7'}$)]	14.2 (CH_3), 22.7 (CH_2CH_3), 26.0 ($CH_2CH_2CH_2O$), 28.9 (CH_2CH_2O), 29.4, 29.4, 29.6, 29.6 (4 CH_2), 32.0 (CH_2-CH_2CH_3), 68.6 (CH_2O), 111.3 ($C^{2,4}$), 127.8 ($C^{4',6'}$), 129.7 (4 H, $HC^{3',7'}$), 131.4, 133.7 ($C^{2'}$), ($C^{5'}$), 153.0 ($C^{1,5}$), 166.1 (C^3), 178.6 (RuCO), 203.4 ($C^{1'}$)
8	2030s 1979m 1950s	[c] 0.90 [6 H, t, J(H_3C–H_2C) 6.5, H_3C], 1.25–1.50 (28 H, m, 7 H_2C), 1.81 [4 H, qnt, J(OH_2C–H_2CH_2C) 7, H_2C], 3.98 [4 H, t, J(OH_2C–HC) 6.4, H_2CO], AA′BB′ [6.96 (4 H, $HC^{9,11}$), 7.15 (4 H, $HC^{8,12}$)], AA′XX′ [8.17 (4 H, $HC^{2,4}$), 9.00 (4 H, $HC^{1,5}$)], 8.36 (2 H, s, HCO_2)	14.2 (CH_3), 22.7 (CH_2CH_3), 26.1 ($CH_2CH_2CH_2O$), 29.3 (CH_2CH_2O), 29.4, 29.5, 29.6, 29.6 (4 CH_2), 32.0 (CH_2-CH_2CH_3), 68.5 (CH_2O), 115.3 ($C^{9,11}$), 122.1 ($C^{8,12}$), 124.9 ($C^{2,4}$), 138.4 (C^3), 143.7 (C^7), 152.7 ($C^{1,5}$), 157.4 (C^{10}), 163.2 (C^6), 174.6 (RuCO), 203.0 ($C^{1'}$)
9 [d]	2041s 1992m 1964s	[c] 0.90 [6 H, t, J(H_3C–H_2C) 6.5, H_3C], 1.25–1.55 (28 H, m, 7 H_2C), 1.81 [4 H, qnt, J(OH_2C–H_2CH_2C) 7, H_2C], 3.98 [4 H, t, J(OH_2C–H_2C) 6.4, H_2CO], AA′BB′ [6.97 (4 H, $HC^{9,11}$), 7.15 (4 H, $HC^{8,12}$)], AA′XX′ [8.22 (4 H, $HC^{2,4}$), 8.88 (4 H, $HC^{1,5}$)]	14.2 (CH_3), 22.8 (CH_2CH_3), 26.1 ($CH_2CH_2CH_2O$), 29.3 (CH_2CH_2O), 29.4, 29.5, 29.6, 29.6 (4 CH_2), 32.0 ($CH_2CH_2CH_3$), 68.5 (CH_2O), 115.0 [q, J(C–F) 286, CF_3], 115.3 ($C^{9,11}$), 122.0 ($C^{8,12}$), 125.2 ($C^{2,4}$), 138.8 (C^3), 143.7 (C^7), 152.5 ($C^{1,5}$), 157.5 (C^{10}), 163.0 (C^6), 169.7 [q, J(*F*C-COORu*C*O) 39, RuCO], 202.1 ($C^{1'}$)
10–**14** [e]	2027s 1977m 1947s	[b] 0.91 [6 H, t, J(H_3C–H_2C) 6.5, H_3C], 1.25–1.55 ([f]28 H, m, 7 H_2C), 1.82 [4 H, qnt, J(OH_2C–H_2CH_2C) 7, H_2C], 4.00 [4 H, t, J(OH_2C–H_2C) 6.4, H_2CO], AA′BB′ [6.99 (4 H, $HC^{9,11}$), 7.20 (4 H, $HC^{8,12}$)], AA′BMM′ [7.31 (4 H, $HC^{4',6'}$), 7.43 (2 H, $HC^{5'}$), 7.87 (4 H, $HC^{3',7'}$)], AA′XX′ [8.26 (4 H, $HC^{2,4}$), 9.16 (4 H, $HC^{1,5}$)]	14.8 (CH_3), 23.4 (CH_2CH_3), 26.7 ($CH_2CH_2CH_2O$), 29.9 (CH_2CH_2O), 30.0, 30.1, 30.3, 30.3 ([g]4 CH_2), 32.6 (CH_2-CH_2CH_3), 69.2 (CH_2O), 116.0 ($C^{9,11}$), 122.7 ($C^{8,12}$), 125.4 ($C^{2,4}$), 128.6 ($C^{4',6'}$), 130.3 ($C^{3',7'}$), 132.4 ($C^{5'}$), 133.9 ($C^{2'}$), 138.9 (C^3), 144.4 (C^7), 153.5 ($C^{1,5}$), 158.1 (C^{10}), 164.1 (C^6), 179.5 (RuCO), 204.3 ($C^{1'}$)
15–**17** [e]	2025s 1975m 1945s	[b] 0.90 [6 H, t, J(H_3C–H_2C) 6.9, H_3C], 1.30–1.52 ([f]28 H, m, 7 H_2C), 1.82 [4 H, qnt, J(OH_2C–H_2CH_2C) 7, H_2C], 3.79 (6 H, s, $H_3C^{8'}$), 4.00 [4 H, t, J(OH_2C–H_2C) 6.6, H_2CO], AA′XX′ [6.79 (4 H, $HC^{4',6'}$), 7.81 (4 H, $HC^{3',7'}$)], AA′BB′ [6.99 (4 H, $HC^{9,11}$), 7.19 (4 H, $HC^{8,12}$)], AA′XX′ [8.24 (4 H, $HC^{2,4}$), 9.15 (4 H, $HC^{1,5}$)]	14.8 (CH_3), 23.4 (CH_2CH_3), 26.7 ($CH_2CH_2CH_2O$), 29.9 (CH_2CH_2O), 30.0, 30.1, 30.3, 30.3 ([g] 4 CH_2), 32.6 (CH_2-CH_2CH_3), 56.0 (C^8), 69.2 (CH_2O), 113.7 ($C^{4',6'}$), 116.0 ($C^{9,11}$), 122.7 ($C^{8,12}$), 125.3 ($C^{2,4}$), 126.6 ($C^{2'}$), 132.2 ($C^{3',7'}$), 138.8 (C^3), 144.4 (C^7), 153.5 ($C^{1,5}$), 158.1 (C^{10}), 163.1 ($C^{5'}$), 164.1 (C^6), 179.1 (RuCO), 204.4 ($C^{1'}$)
18	2026s 1976m 1946s	[b] 0.92 [6 H, t, J(H_3C–H_2C) 6.8, H_3C], 1.28–1.52 (28 H, m, 7 H_2C), 1.83 [4 H, qnt, J(OH_2C–H_2CH_2C) 7, H_2C], 2.34 (6 H, s, $H_3C^{8'}$), 4.01 [4 H, t, J(OH_2C–H_2C) 6.6, H_2CO], AA′BB′ [7.00 (4 H, $HC^{9,11}$), 7.21 (4 H, $HC^{8,12}$)], AA′XX′ [7.10 (4 H, $HC^{4',6'}$), 7.75 (4 H, $HC^{3',7'}$)], AA′XX′ [8.25 (4 H, $HC^{2,4}$), 9.15 (4 H, $HC^{1,5}$)]	14.1 (CH_3), 21.5 ($C^{8'}$), 22.7 (CH_2CH_3), 26.0 (CH_2CH_2-CH_2O), 29.2 (CH_2CH_2O), 30.0, 30.1, 30.3, 30.3 (4 CH_2), 32.6 ($CH_2CH_2CH_3$), 68.5 (CH_2O), 115.3 ($C^{9,11}$), 122.0 ($C^{8,12}$), 124.6 ($C^{2,4}$), 128.6 ($C^{4',6'}$), 129.6 ($C^{3',7'}$), 130.6 ($C^{2'}$), 138.1 (C^3), 142.1 ($C^{5'}$), 143.7 (C^7), 152.8 ($C^{1,5}$), 157.4 (C^{10}), 163.4 (C ^{6}), 178.8 (RuCO), 203.6 ($C^{1'}$)

[a] Numbering of carbon atoms of the ligands follows the description of the free carboxylic acids and pyridines given in SUP 57291; numbering of the second ligand is given with primed numbers and starts from the carbon atom closest to the ruthenium atom; *J*/Hz. [b] At 400 (^{1}H) and 100 MHz (^{13}C). [c] At 200 (^{1}H) and 50 MHz (^{13}C). [d] δ_F(188.15 MHz) 31.3 (CF_3). [e] Spectroscopic data given for complex with decyloxy chain. [f] Integral different for the other complexes. [g] Number of signals different for the other complexes.

were carried out in air. The solvents were distilled over drying agents and N_2-saturated prior to use. The compound $[Ru_3(CO)_{12}]$ was synthesized following a published procedure.[17] Acetic acid, benzoic acid, formic acid, *p*-methoxybenzoic acid (purum), *p*-methylbenzoic acid (purum), trifluoroacetic acid (purum) and pyridine (purum) were puriss. p.a. quality from Fluka, unless stated otherwise, and used without further purification.

Instrumentation

The NMR spectra were recorded using a Varian Gemini 200 BB (200 MHz) or a Bruker AMX-400 (400 MHz) spectrometer. For the IR spectra a Perkin-Elmer 1720 FT-IR spectrometer was used. Transition temperatures (onset point) and enthalpies were determined with a Mettler DSC 30 differential scanning calorimeter connected to a Mettler TA 4000 processor, under N_2, at a rate of 10 °C min^{-1}. Data treatment used Mettler TA72.2/.5 GRAPHWARE: for complexes **1**–**10**, first heating run; for **11**–**18**, second heating run. Thermogravimetry analyses were performed with a Mettler TG 50 thermobalance connected to a Mettler TA 4000 processor, at a rate of 20 °C min^{-1}. Optical studies were conducted using a Zeiss-Axioscop polarizing microscope equipped with a Linkam-THMS-600 variable-temperature stage, under N_2.

The elemental analyses were carried out by the Mikroelementaranalytisches Laboratorium der ETH Zürich.

Synthesis of the complexes 1–18

A solution of $[Ru_3(CO)_{12}]$ (100 mg, 0.16 mmol) and the appropriate amount of the organic acid RCO_2H (see Table 2) in tetrahydrofuran was heated in a pressure Schlenk tube (300 cm^3) according to the conditions indicated in Table 2. After cooling, the appropriate pyridine L (0.46 mmol) was added to the orange thf solution, resulting in an immediate colour change to yellow and in a shift of the characteristic three-band ν_{CO} pattern of the IR spectrum to lower wavenumbers. The solution was stirred at room temperature for 1 h, then the solvent was evaporated and the complex isolated from the residue by crystallization using the solvent mixture given in Table 2. For the purpose of the analytical and thermal characterization, the complexes were crystallized once again and dried *in vacuo*. The IR and NMR data for complexes **1**–**18** are given in Table 3.

Acknowledgements

We are grateful to the Swiss National Science Foundation for financial support, to Ciba-Geigy-Jubiläums-Stiftung for a fellowship to B. D., and to the Johnson Matthey Technology Centre for a generous loan of ruthenium trichloride hydrate.

References

1 F. Reinitzer, *Monatsh. Chem.*, 1888, **9**, 421.
2 D. Pauluth and T. Geelhaar, *Nachr. Chem. Techn. Lab.*, 1997, **45**, 9.
3 D. W. Bruce, in *Inorganic Materials*, 2nd edn., eds. D. W. Bruce and D. O'Hare, Wiley, Chichester, 1996, ch. 8; *Metallomesogens: Synthesis, Properties and Applications*, ed. J. L. Serrano, VCH, Weinheim, 1996; R. Deschenaux and J. W. Goodby, in *Ferrocenes: Homogeneous Catalysis, Organic Synthesis and Materials Science*, eds. A. Togni and T. Hayashi, VCH, Weinheim, 1995, ch. 9.
4 A.-M. Giroud-Godquin, J.-C. Marchon, D. Guillon and A. Skoulios, *J. Phys. Chem.*, 1986, **90**, 5502; O. Poizat, D. P. Strommen, P. Maldivi, A.-M. Giroud-Godquin and J.-C. Marchon, *Inorg. Chem.*, 1990, **29**, 4851.
5 P. Maldivi, A.-M. Giroud-Godquin, J.-C. Marchon, D. Guillon and A. Skoulios, *Chem. Phys. Lett.*, 1989, **157**, 552; J.-C. Marchon, P. Maldivi, A.-M. Giroud-Godquin, D. Guillon, A. Skoulios and D. P. Strommen, *Philos. Trans. R. Soc. London*, *Ser. A*, 1990, **330**, 109; L. Bonnet, F. D. Cukiernik, P. Maldivi, A.-M. Giroud-Godquin, J.-C. Marchon, M. Ibn-Elhaj, D. Guillon and A. Skoulios, *Chem. Mater.*, 1994, **6**, 31.
6 J. Barbera, M. A. Esteruelas, A.-M. Levelut, L. A. Oro, J. L. Serrano and E. Sola, *Inorg. Chem.*, 1992, **31**, 732.
7 R. H. Cayton, M. H. Chisholm and F. D. Darrington, *Angew. Chem.*, *Int. Ed. Engl.*, 1990, **29**, 1481; D. V. Baxter, R. H. Cayton, M. H. Chisholm, J. C. Huffman, E. F. Putilina, S. L. Tagg, J. L. Wesemann, J. W. Zwanziger and F. D. Darrington, *J. Am. Chem. Soc.*, 1994, **116**, 4551.
8 (*a*) J. Barbera, C. Cativiela, J. L. Serrano and M. M. Zurbano, *Adv. Mater.*, 1991, **3**, 602; (*b*) R. Atencio, J. Barbera, C. Cativiela, F. J. Lahoz, J. L. Serrano and M. M. Zurbano, *J. Am. Chem. Soc.*, 1994, **116**, 11 558.
9 G. R. Crooks, B. F. G. Johnson, J. Lewis, I. G. Williams and G. Gamlen, *J. Chem. Soc. A*, 1969, 2761.
10 M. Spohn, T. Vogt and J. Strähle, *Z. Naturforsch.*, *Teil B*, 1986, **14**, 1373.
11 H. Schumann, J. Opitz and J. Pickardt, *J. Organomet. Chem.*, 1977, **128**, 253.
12 M. Bianchi, P. Frediani, U. Matteoli, G. Menchi, F. Piacenti and G. Petrucci, *J. Organomet. Chem.*, 1983, **259**, 207; S. J. Sherlock, M. Cowie, E. Singleton and M. M. de V. Steyn, *Organometallics*, 1988, **7**, 1663; G. Süss-Fink, G. Herrmann, P. Morys, J. Ellermann and A. Veit, *J. Organomet. Chem.*, 1985, **284**, 263; G. F. Schmidt and G. Süss-Fink, *J. Organomet. Chem.*, 1989, **362**, 179; G. Süss-Fink, J. L. Wolfender, F. Neumann and H. Stœckli-Evans, *Angew. Chem.*, *Int. Ed. Engl.*, 1990, **29**, 429; M. Rotem, Y. Shvo, I. Goldberg and U. Shmueli, *Organometallics*, 1984, **3**, 1758; M. Rotem, I. Goldberg, U. Shmueli and Y. Shvo, *J. Organomet. Chem.*, 1986, **314**, 185; D. S. Bohle and H. Vahrenkamp, *Inorg. Chem.*, 1990, **29**, 1097.
13 J. Velker, G. Rheinwald and G. Süss-Fink, unpublished work; G. Rheinwald, Thèse de doctorat, Université de Neuchâtel, 1994.
14 R. Deschenaux, J.-L. Marendaz and J. Santiago, *Helv. Chim. Acta*, 1993, **76**, 865; D. W. Bruce and S. A. Hudson, *J. Mater. Chem.*, 1994, **4**, 479.
15 (*a*) D. W. Bruce, B. Donnio, D. Guillon, B. Heinrich and M. Ibn-Elhaj, *Liq. Cryst.*, 1995, **19**, 537; (*b*) F. Neve, *Adv. Mater.*, 1996, **8**, 277; (*c*) J. Buey, L. Diez, P. Espinet, H.-S. Kitzerow and J. A. Miguel, *Chem. Mater.*, 1996, **8**, 2375; (*d*) S. Tantrawong and P. Styring, *Liq. Cryst.*, 1997, **22**, 17.
16 C. Bruneau and P. H. Dixneuf, *Chem. Commun.*, 1997, 507.
17 M. I. Bruce, C. M. Jensen and N. L. Jones, *Inorg. Synth.*, 1989, **26**, 259.

Received 3*rd July* 1997; *Paper* 7/04712F