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Mesomorphic Metallo-Dendrimers Based on the Metal–Metal Bonded $\text{Ru}_2(\text{CO})_4$ Sawhorse Unit

Stéphane Frein,[†] Mathieu Auzias,[†] Aline Sondenecker,[†] Ludovic Vieille-Petit,[†] Boris Guintchin,[†] Natacha Maringa,[†] Georg Süss-Fink,[†] Joaquín Barberá,[‡] and Robert Deschenaux^{*,†}

Institut de Chimie, Université de Neuchâtel, Avenue de Bellevaux 51, Case postale 158, 2009 Neuchâtel, Switzerland, and Química Orgánica, Facultad de Ciencias-Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain

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Dinuclear ruthenium complexes containing the stable metal–metal bonded $\text{Ru}_2(\text{CO})_4$ sawhorse unit with two dendritic carboxylato bridges have been synthesized and characterized. All complexes $\text{Ru}_2(\text{CO})_4(\text{O}_2\text{CR})_2\text{L}_2$ ($\text{R} = \text{R}^1, \text{R}^2, \text{R}^3$) containing cyanobiphenyl-based poly(arylester) dendrons of first (R^1), second (R^2), and third (R^3) generation and triphenylphosphine, pyridine, or 4-picoline ligands L proved to be mesomorphic, giving rise to smectic A or smectic A and nematic phases. The supramolecular organization within the smectic A phase is governed by the nature and structure of the mesogenic units and dendritic core. Such materials are of interest for the design of catalytically active anisotropic fluids.

Introduction

For almost twenty years, the synthesis of mesomorphic metallo-complexes has found a steadily growing interest in view of combining the physical characteristics of transition metal complexes (optical, magnetic, and electronic properties) with those of anisotropic fluids.¹ Mesomorphic materials containing metal–metal bonds are rare. The first example of these kinds of chemicals are the $\text{Rh}_2(\text{O}_2\text{CC}_n\text{H}_{2n+1})_4$ compounds, described by Marchon and co-workers,² which develop columnar phases. Similarly, ruthenium–ruthenium bonded complexes $\text{Ru}_2(\text{O}_2\text{CC}_n\text{H}_{2n+1})_5$ have been shown to develop columnar phases.³ During the 1990s, new mesomorphic dinuclear metal–metal bonded complexes have been published by Serrano and co-workers using dirhodium tetrabenzoato complexes which develop rectangular or hexagonal columnar phases⁴ as well as thallium β -diketonate complexes which display a hexagonal columnar phase;⁵ moreover, there was the hypothesis that the mesomorphic

properties in the latter case are due to the dimeric nature of the thallium complexes by comparison with a non-mesomorphic homologue.⁶ Chisholm and co-workers⁷ obtained mesomorphic complexes with Mo–Mo or Cr–Cr quadrupole bonds, which exhibit hexagonal columnar phases.

To obtain metallomesogens containing a Ru–Ru core with a single metal–metal bond, we focused on the stable sawhorse unit $\text{Ru}_2(\text{CO})_4(\text{O}_2\text{CR})_2\text{L}_2$. Sawhorse-type ruthenium complexes have been known since 1969, when Lewis and co-workers reported the formation of $[\text{Ru}_2(\text{CO})_4(\text{O}_2\text{CR})_2]_n$ polymers by refluxing $\text{Ru}_3(\text{CO})_{12}$ in the corresponding carboxylic acid and the depolymerization of these materials in coordinating solvents to give dinuclear complexes of the type $\text{Ru}_2(\text{CO})_4(\text{O}_2\text{CR})_2\text{L}_2$, L being acetonitrile, pyridine, or other two-electron donor ligands.⁸ These dinuclear complexes have been shown later, by single-crystal X-ray structure analysis of $\text{Ru}_2(\text{CO})_4(\text{O}_2\text{CBu}^n)_2(\text{PBu}^t)_2$, to have a $\text{Ru}_2(\text{CO})_4$ backbone in a sawhorse-type arrangement with two $\mu_2\text{-}\eta^2$ -carboxylato bridges and two axial phosphine ligands.⁹

In a previous study, we observed the formation of nematic phases for the complexes $\text{Ru}_2(\text{CO})_4(\text{O}_2\text{CR})_2\text{L}_2$ [$\text{R} = \text{C}_6\text{H}_5$, $\text{C}_6\text{H}_4\text{-OCH}_3$; $\text{L} = \text{NC}_5\text{H}_4(\text{CO}_2\text{C}_6\text{H}_4\text{OC}_n\text{H}_{2n+1})$].¹⁰ In these complexes, the mesomorphic units were in the axial pyridine ligands. We now decided to study $\text{Ru}_2(\text{CO})_4$ sawhorse

* Corresponding author. E-mail: robert.deschenaux@unine.ch.

[†] Université de Neuchâtel.

[‡] Universidad de Zaragoza-CSIC.

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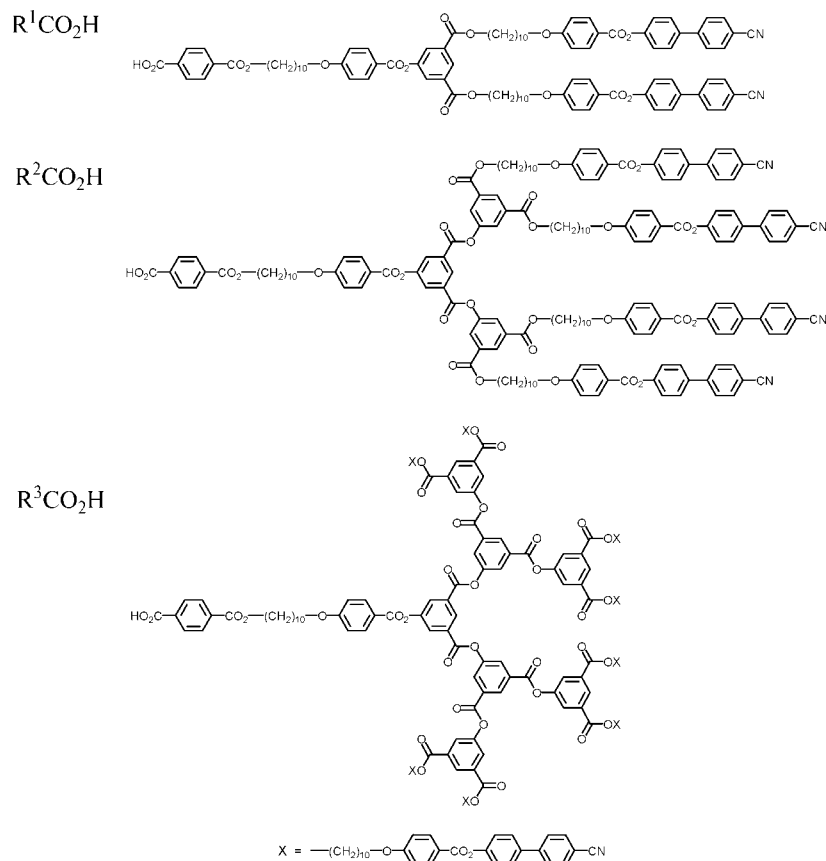
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Chart 1



complexes containing the mesogenic units in the equatorial carboxylato bridging ligands.

An elegant strategy to obtain mesomorphic materials from the $Ru_2(CO)_4$ sawhorse unit would be to use liquid-crystalline dendrimers for its functionalization. Liquid-crystalline dendrimers have reached a high degree of sophistication, and the type and nature of the mesophases can be controlled through structural engineering (dendrimer generation, stiffness or flexibility of the dendritic core, number, nature, and location of the mesogenic units) at the molecular level.¹¹ Furthermore, the use of liquid-crystalline dendrimers could thwart the possible negative influence (for the formation of mesophases) of the bulky $Ru_2(CO)_4$ framework. Indeed, liquid-crystalline dendrimers have been successfully employed for the preparation of liquid-crystalline materials from three-dimensional units such as ferrocene,¹² lanthanide complexes,¹³ and [60]fullerene.¹⁴

From the point of view of applications, the incorporation of metal–metal bonded organometallics within an anisotropic environment could lead to materials with novel properties, such as magnetic, redox, or catalytic properties. To exploit

such properties in complex media, the supramolecular organization has to be known and should be controllable to tune the desired properties. Liquid-crystalline dendrimers are materials of choice to create such an environment.

We describe, herein, the synthesis, characterization, liquid-crystalline properties, and supramolecular organization of the title compounds **1–7**, in which the dendrimer generation (from first to third generation) and the axial ligands (triphenylphosphine, pyridine, and 4-picoline) were varied. Cyano-biphenyl-based dendrimers were selected as the liquid-crystalline promoter. The dendrimers were synthesized by applying a convergent synthetic methodology.¹⁵

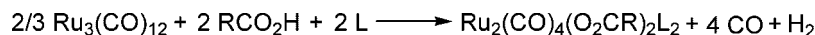
Results and Discussion

Materials and Syntheses. The dendritic poly(arylester) carboxylic acids R^1CO_2H (first generation), R^2CO_2H (second generation), and R^3CO_2H (third generation, Chart 1) used in this study are obtained in good yields by the oxidation of the corresponding aldehydes¹⁶ with sodium chlorite and sulfamic acid in aqueous tetrahydrofuran (THF). The syn-

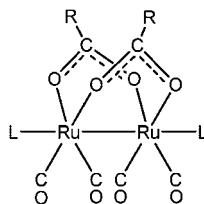
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Chart 2



	1	2	3	4	5	6	7
R	R ¹	R ¹	R ¹	R ²	R ²	R ²	R ³
L	PPh ₃	NC ₅ H ₅	NC ₅ H ₄ -4-Me	PPh ₃	NC ₅ H ₅	NC ₅ H ₄ -4-Me	PPh ₃



theses of R¹CO₂H¹³ and R²CO₂H¹⁷ have already been described by our group elsewhere. The preparation of R³CO₂H is reported in the Supporting Information.

The thermal reaction of Ru₃(CO)₁₂ with an excess of the dendritic acids RCO₂H (R = R¹, R², R³) in refluxing THF yields a yellow solution containing the corresponding THF complex Ru₂(CO)₄(O₂CR)₂(THF)₂, which reacts easily with two-electron ligands to give the stable triphenylphosphine, pyridine, or 4-picoline analogues (Chart 2). The complexes Ru₂(CO)₄(O₂CR¹)₂L₂ (**1**, L = PPh₃; **2**, L = NC₅H₅; **3**, L = NC₅H₄-4-Me), Ru₂(CO)₄(O₂CR²)₂L₂ (**4**, L = PPh₃; **5**, L = NC₅H₅; **6**, L = NC₅H₄-4-Me), and Ru₂(CO)₄(O₂CR³)₂(PPh₃)₂ (**7**) have been isolated by chromatographic methods and characterized by IR and NMR spectroscopies as well as elemental analysis. The analytical data are reported in the Supporting Information.

Liquid-Crystalline Properties. The thermal and liquid-crystalline properties of the ruthenium complexes **1–7** and dendrons R¹CO₂H and R³CO₂H were investigated by polarized optical microscopy (POM) and differential scanning calorimetry (DSC). The mesomorphic properties of R²CO₂H have already been described elsewhere.¹⁷ The phase transition temperatures and thermodynamic data are reported in Table 1. As an illustrative example, the DSC thermogram of **7** is shown in Supporting Information (Figure S1).

Compounds **1–7** lead to the formation of a smectic A phase. An additional nematic phase is observed for **2**, **3**, **5**, and **6**. The mesophases were identified by POM from the formation of typical textures (smectic A phase, focal-conic fan and homeotropic textures; nematic phase, schlieren texture). The textures of the nematic and smectic A phases displayed by **2** and **7** are shown in Figures 1 and 2, respectively, as illustrative examples. The fact that **1** shows a smectic A phase, whereas its mesomorphic precursor R¹CO₂H gives a nematic phase, is due to the increase of cyanobiphenyl units upon complexation. Indeed, two and four cyanobiphenyl units are located on R¹CO₂H and **1**, respectively. Therefore, **1** has the same number of cyanobiphenyl groups as the second generation dendrimer R²CO₂H, which gives a smectic A phase. Finally, the clearing point increases with the dendrimer generation as a consequence of stronger intermolecular interactions.

Table 1. Phase-Transition Temperatures^a with Enthalpy and Entropy Changes for the Diruthenium Complexes **1–7** and the Dendrimer Precursors RCO₂H (R = R¹, R², R³)

compound	T _g (°C)	transition	T (°C)	ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)
R ¹ CO ₂ H		Cr → N	39	1.9	6
		N → I	194	6.2	13
1	38	SmA → I	150	18.3	43
2	62	SmA → N	145	3.5	8
		N → I	156	5.7	13
3	55	SmA → N	143	6.6	16
		N → I	155	4.2	10
R ² CO ₂ H ¹⁷	45	SmA → I	203	18.6	39
4	43	SmA → I	175	23.3	52
5	57	SmA → N	168	13.3	30
		N → I	171	6.5	15
6	58	SmA → N	170	13.6	31
		N → I	173	5.2	12
R ³ CO ₂ H	55	SmA → I	227	4.9	10
7	39	SmA → I	204	28.2	59

^a T_g = glass transition temperature determined during the second heating; Cr = semicrystalline solid, SmA = smectic A phase, N = nematic phase, I = isotropic liquid. Temperatures are given as the onset of the peaks obtained during the second heating run.

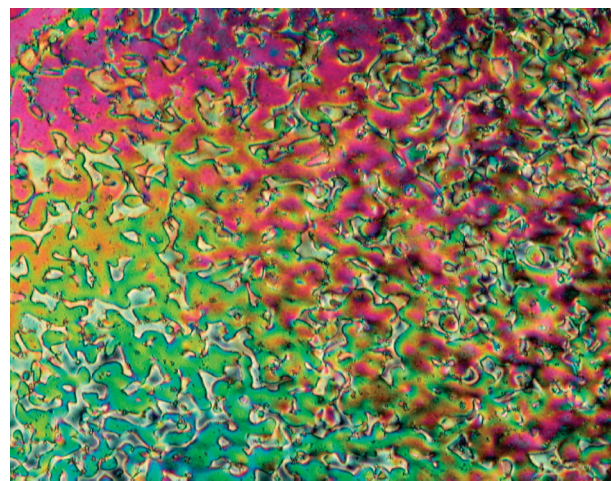


Figure 1. Thermal optical micrograph of the schlieren texture displayed by **2** in the nematic phase at 155 °C.

The formation of smectic A phases observed for **1–7** is in agreement with the nature of the dendromesogens, which have a strong tendency to align parallel one to each other and so give rise to the formation of layers.^{11,14} The fact that the triphenylphosphine derivatives **1**, **4**, and **7** do not exhibit nematic phases is most likely due to the presence of the bulky

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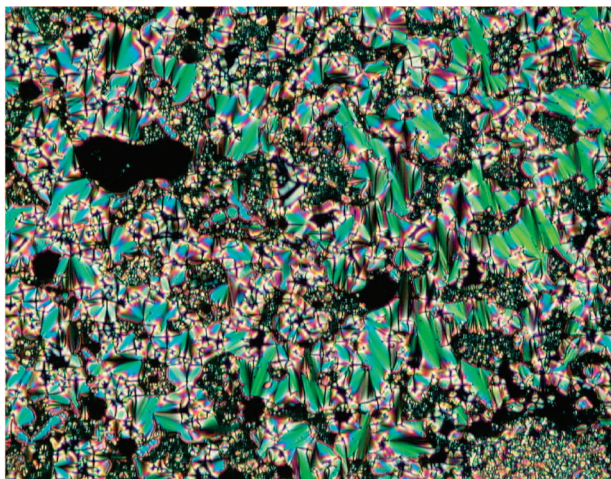


Figure 2. Thermal optical micrograph of the focal-conic fan texture displayed by **7** in the smectic A phase at 147 °C.

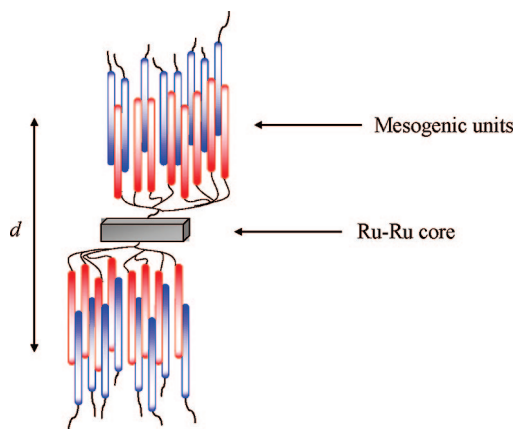


Figure 3. Postulated supramolecular organization of **7** within the smectic A layers. The interdigitation is illustrated by the red and blue cyanobiphenyl units: the red units belong to the dendrimer which is displayed on the drawing, and the blue units belong to dendrimers of adjacent layers.

PPh₃ groups in the axial positions that disrupt the nematogenic organization.

Supramolecular Organization. The structure of the smectic A phase displayed by compound **7** was analyzed by X-ray diffraction. A *d*-layer spacing of 52 Å was determined at 100 °C. By analogy to a methanofullerene (see compound **5** in ref 18) functionalized with the same third generation dendron, for which an alike *d*-layer spacing was obtained (i.e., 55 Å at 140 °C; *T_g*, not detected; SmA → I, 212 °C), we can conclude that within the smectic A phase both **7** and

the above-mentioned methanofullerene lead to a similar supramolecular organization: for **7**, the organometallic unit, including the CO, carboxylato, and PPh₃ ligands, is embedded in the dendritic core which is oriented parallel to the layer planes, and the cyanobiphenyl mesogenic units orient above and below the dendritic core. Interdigitation of the mesogens occurs from one layer to the adjacent one (Figure 3). Thus, this study strengthens previous results, that is, the liquid-crystalline properties and the supramolecular organization depend on the dendrimer and mesogenic unit, whereas the internal core [Ru₂(CO)₄ sawhorse unit (this work) or [60]fullerene^{16–18}] has little influence because it is camouflaged within the dendritic matrix. In the case of the lower-generation complexes **1–6**, the supramolecular organization can be deduced from results obtained for methanofullerenes¹⁸ in which the [60]fullerene sphere is derivatized by similar dendrons: for all molecules, the mesogenic units point to the same direction giving rise to cylinder-like structures, which then organize into layers.

Conclusion

Grafting cyano-based poly(arylester) dendrimers, from the first to the third generation, onto dinuclear ruthenium clusters leads to a new family of mesomorphic materials. Those compounds give rise to smectic A or nematic and smectic A phases in agreement with the structural features of the dendrimers, mesogens, and axial ligands. As for liquid-crystalline fullerodendrimers, the supramolecular organization of the high-generation ruthenium clusters depends on the dendritic core and mesogenic units. Therefore, fine-tuning of the mesomorphic properties could be achieved by structural engineering at the molecular level. The strategy developed in this paper can be applied to other polynuclear metal–metal bonded clusters and is of interest for the development of anisotropic catalysts.

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Supporting Information Available: Techniques, instruments, synthetic procedures, and analytical data of all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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