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REVIEW

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# The Contribution of Ruthenium in the Development of Metallomesogens

Bruno Therrien*[a]

[a] Institute of Chemistry, University of Neuchatel, Avenue de Bellevaux 51, CH-2000 Neuchatel, Switzerland,
e-mail: bruno.therrien@unine.ch

To *Robert Deschenaux* on the occasion of his 65th birthday

Ruthenium remains one of the most popular metals in inorganic and organometallic chemistry. The multiple oxidation state that it possesses and the versatility in its coordination mode have contributed to this success. However, despite the facility to synthesize all kind of ruthenium-based complexes, the insertion of ruthenium in metallomesogens remains scarce. This review presents all metallomesogens incorporating ruthenium over the last 35 years, suggesting that the contribution of ruthenium in the development of metallomesogens has just begun.

**Keywords:** liquid crystals, lyotropy, mesomorphism, metallomesogens, thermotropy, ruthenium.

## 1. Introduction

Metallomesogens represent a particular family of liquid crystalline materials.[1] Insertion of metals in the design and structure of liquid crystalline mesogens, when compared to purely organic systems, provides an opportunity to achieve new molecular geometries as well as to introduce new electronic and physical properties to liquid crystals.[2–6] However, despite having a broad spectrum of metals and multiple synthetic strategies to prepare metallomesogens, the number of publications dealing with metallomesogens represents less than 0.3 % of all liquid crystal studies.[7] Indeed, less than a thousand of publications contain the keyword metallomesogen, while over 360 thousand studies associated to liquid crystals have been published. This is surprising considering the huge potential of metallomesogens, and the fact that the word metallomesogen was first coined in the late 1980s,[1,8] about 35 years ago.

Among metals, ruthenium occupies a central position in the periodic table of the elements, having various oxidation states, and accordingly a rich chemistry.[9] Therefore, ruthenium is often a transition metal of choice in the laboratory, offering not only electronic but also structural diversity.[10–12] The most common oxidation states found in the different structural families of ruthenium-based complexes are +1, +2, +3 and +4. In ruthenocene, half-sandwich (arene-ruthenium), sandwich and polypyridyl complexes, the ruthenium is generally in a +2 oxidation state, while in diruthenium paddlewheel derivatives Ru(II) and Ru(III) or a mixture of both oxidation states are observed. In the case of sawhorse diruthenium complexes the metals are +1, while in polyhalides and polyoxides, higher oxidation states are observed (+4 to +8). Such diversity has prompted chemists to incorporate ruthenium in mesogens, in view to modify liquid-crystalline properties of materials.

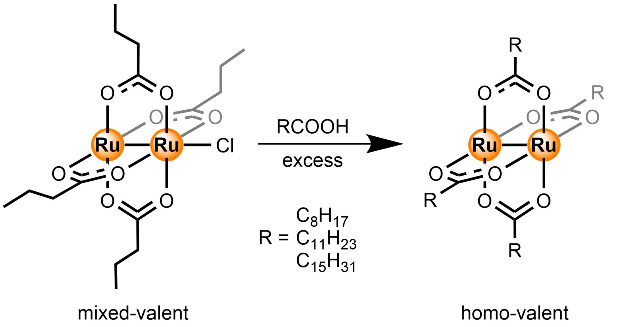
As anticipated, this review will only focus on metallomesogens built around ruthenium metal centers, using primarily a structural approach. The family of ruthenium-based complexes will be discussed separately, describing the nature of the metallomesogens obtained and discussing their properties according to the structure. Therefore, this review will give an overview of what has been done so far in the field of ruthenium-based metallomesogens. This should provide to the readers not only state-of-the-art examples, but also new research avenues, as the chemistry of ruthenium is well established, extremely rich and quite versatile.

## 2. Ruthenium-Based Metallomesogens

For non-specialists, the chemistry of ruthenium is commonly associated to applications such as catalysis,[13] bio-inorganic chemistry[14] or light harvesting materials,[15] while for those working with ruthenium, the family in which the ruthenium complex belong is often more revealing. The versatility and facility of ruthenium to bind to different ligands, in different oxidation states, have allowed inorganic and organometallic chemists to prepare a plethora of ruthenium-based complexes, from mononuclear (ruthenocene, polypyridyl, arene, sandwich, carbene), to dinuclear (paddlewheel, sawhorse, bridged), to trinuclear (carbonyl, cluster), to multinuclear species (polyoxo, nanoparticle, MOF). Therefore, this classification by family has been followed in this review, presenting in a chronological order ruthenium-based metallomesogens according to their family.

### *2.1. Paddlewheel Complexes*

Dinuclear tetracarboxylate complexes, also called paddlewheels, are popular systems for the preparation of metallomesogens.[16] Among them, diruthenium tetracarboxylates have attracted a particular attention.[17–19] Such complexes are easily synthesized, and the ruthenium atoms can be either in a +2 or +3 oxidation state, thus offering electronic tunability. Therefore, it is not surprising that the first metallomesogen incorporating ruthenium was developed in 1989 using such scaffold.[20] Paddlewheel diruthenium complexes with palmitate ($C_9H_{17}O_2$), laurate ($C_{12}H_{23}O_2$) and pelargonate ($C_{16}H_{31}O_2$) side-chains were obtained in good yields from chlorodiruthenium(II,III) tetrabutyrate (*Scheme 1*). In this early report, the chlorodiruthenium(II,III) tetrabutyrate was first reduced with chromium(II) before exchange of butyrates with the corresponding fatty acid (RCOOH = nonanoic acid $C_9H_{18}O_2$, dodecanoic acid $C_{12}H_{24}O_2$, hexadecanoic acid $C_{16}H_{32}O_2$).In these liquid crystalline systems, the transition temperatures were not perfectly correlated to the length of the alkyl chains, the highest being the one with 16-carbons at 99.5 °C, followed by the nonanoic derivative at 96 °C and the dodecanoic at 91 °C. These Ru(II)–Ru(II) tetracarboxylate complexes are extremely air sensitive, and therefore limiting their utility, which can also explain the phase transition behavior, which was not linked to the length of the alkyl chain.[21]



**Scheme 1.** Synthesis of paddlewheel diruthenium(II,II) complexes from chlorodiruthenium(II,III) tetrabutyrate.[20]

Bruno Therrien is an associate professor within the Institute of Chemistry at the University of Neuchatel, and since 2005, he has developed an independent career. During his PhD thesis in the late 1990s, he already started to play with ruthenium, and still today, his research focusses on ruthenium-based complexes. His main research interests are the use of water soluble arene-ruthenium metalla-assemblies as carriers or sensors and the synthesis of hybrid ruthenium-porphyrin compounds to treat cancer by photodynamic therapy.

Similar systems, with analogous carboxylates ($C_8H_{16}O_2$, $C_{12}H_{24}O_2$, $C_{18}H_{36}O_2$) have been studied and their liquid crystalline properties compared to paddlewheel complexes incorporating not only ruthenium but also other metal centers (Mo, W, Cr and Rh).[22] In the case of the ruthenium derivatives, the crystalline materials were stable at temperatures up to 250 °C in an inert atmosphere, and they all showed a discotic mesophase above 100 °C. However, these compounds did not melt before decomposition, again limiting their potential as liquid crystalline materials.

A year later, the first ruthenium-based mixed-valent paddlewheel metallomesogens were studied. The liquid crystalline properties of the pentacarboxylates (mixed-valent) and tetracarboxylates (homo-valent) were compared, showing that despite the polymeric nature of the pentacarboxylate derivatives (*Figure 1*), where the carboxylate anion bridged multiple dinuclear complexes, the mesomorphic phases of homo- and mixed-valent complexes were very similar.[23] At the time, it was unclear why comparable phase transitions were taking place despite the anticipated

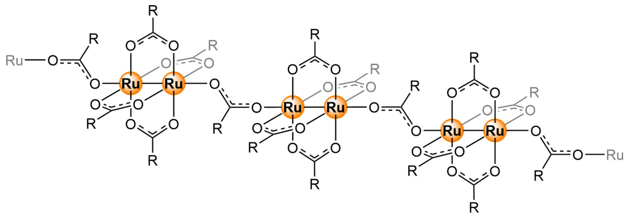


**Figure 1.** Polymeric structure of mixed-valent diruthenium(II,III) pentacarboxylate paddlewheel complexes.[23]

structural differences, from polymeric (mixed-valent) to discrete (homo-valent).

Replacing the carboxylate bridging ligands with di(hexadecyl) phosphate anions is another strategy to modify the liquid crystalline properties of paddlewheel complexes (*Figure 2*).[24] A lamellar phase prior to the columnar hexagonal mesophase was observed upon addition of a second alkyl chain on the bridging anion (di(hexadecyl)phosphate) within mixed-valent diruthenium complexes. This simple modification, by rational design, shows how the numbers and position of mesogenic groups are key for tuning the liquid crystalline properties.

Insertion of C=C bonds in the side chains of the paddlewheel dinuclear complexes (*Figure 3*) has significantly decreased the transition temperature of the thermotropic columnar mesophases.[25] The series was further extended to longer alkyl chains, as well as to fluorinated derivatives, showing similar columnar organization,[26] except for the fluorinated derivatives which were not mesomorphic. In these systems, the columnar mesophases were explained by intermolecular axial interactions between the metal centers and oxygen atoms, thus forming a compact polymeric structure from weak interactions (*Figure 4*). Such interactions can explain the similar liquid crystalline behavior observed for the tetra- and penta-carboxylate analogues.[23] Despite the polymeric nature of the liquid crystalline arrangement and the close proximity of the metal centers, no magnetic properties were observed for these systems, probably due to the non-alignment of the metal centers.

Similar unsaturated systems in which the C=C double bond was located in the middle of the side-chains of the carboxylate ligands (*Figure 5*) have showed a hexagonal discotic mesophase at room temperature.[27] The position of the double bond seems to be crucial, and when compared to those having the unsaturation at the end of the side-chain,

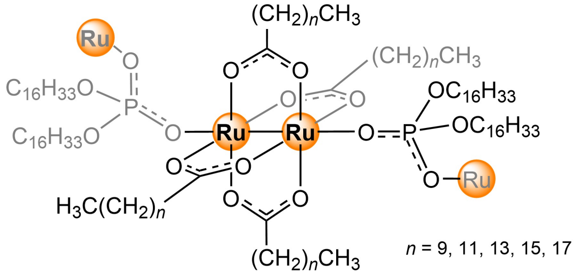


**Figure 2.** Polymeric structure of mixed-valent diruthenium(II,III) paddlewheel complexes bridged by di(hexadecyl) phosphate anions.[24]

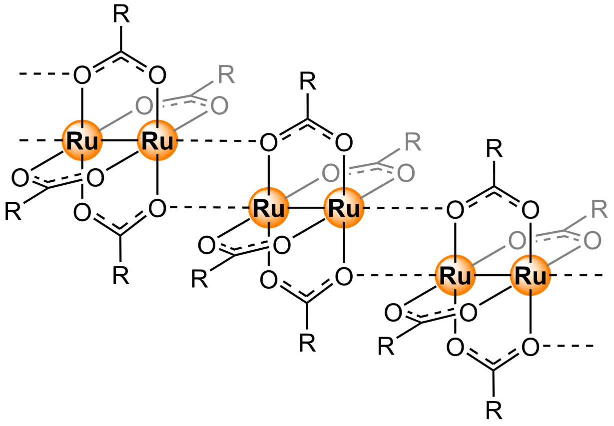


**Figure 4.** Polymeric chains of paddlewheel diruthenium (II,II) complexes through metal-oxygen interactions.[26]

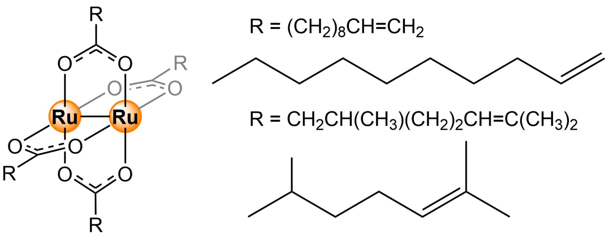


**Figure 3.** Ruthenium-based paddlewheel complexes with C=C double-bond at the end of the alkyl groups.[25]

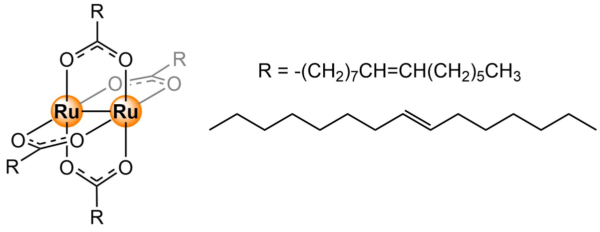


**Figure 5.** Ruthenium-based paddlewheel complexes with C=C double-bond in the middle of the alkyl groups.[27]

the transition temperature decreases as well, but also the flexibility and adaptability of the side-chain are reduced, which overall increased the stability of the liquid crystalline phase.

When dealing with cationic diruthenium(II,III) complexes, the nature of the anion can influence greatly the liquid crystalline arrangement. Indeed, when moving from the chloro salts, which are not mesomorphic, to the dodecyl sulfate ($DOS^-$) or carboxylate derivatives, a columnar hexagonal mesophase above 150 °C was observed for a series of paddlewheel complexes incorporating linear aliphatic carboxylates.[28] It was suggested that the presence of a small anion forces the cations and anions to organize perpendicularly to each other, which is not the case for bulkier anions. In the presence of larger or bridging anions, parallel polymeric chains with alternance of cations and anions (*Figure 1*) are formed, thus leading to a lamellar arrangement in which the separation is dictated by the length of the alkyl chains and the ability for the chains to intercalate. Therefore, to regain liquid crystalline properties of the chloro salts (*Figure 6*), bulkier carboxylates were needed, such as 3,4-dialkylbutyrate derivatives ($RCO_2 = 3{,}4\text{-}(CH_3(CH_2)_nO)_2PhCO_2$: $n = 11$, 14, 15). The presence of two alkyl chains per carboxylate increases the filling efficiency between the cations and anions, thus generating stable columnar mesophases, even for the chloro salts.

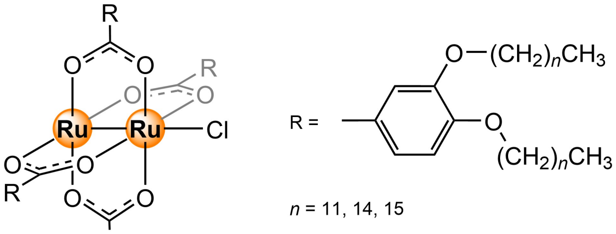


**Figure 6.** Molecular structure of di-substituted chlorodiruthenium(II,III) tetracarboxylates.[28]

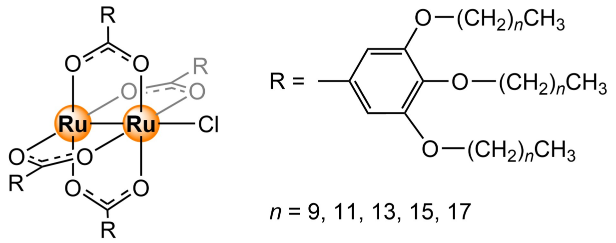


**Figure 7.** Molecular structure of tri-substituted chlorodiruthenium(II,III) tetracarboxylates.[29]

To further increase the size of the carboxylate ligand, 3,4,5-trialkyloxybenzoate derivatives were synthesized and after complexation to ruthenium, the paddlewheel complexes were tested as liquid crystalline materials (*Figure 7*).[29] All complexes show a columnar hexagonal mesophase at room temperature. The transition temperatures increase with the length of the alkyl chain, for $n = 9$ it starts at room temperature, while for $n = 17$ the mesophase begins at 58 °C. However, for all complexes decomposition occurs before isotropy (> 220 °C).

The lyotropic behavior of analogous tri-substituted derivatives (*Figure 8*) was studied in dodecane mixtures at three temperatures (40, 70 and 100 °C), and at solvent concentrations ranging from 0 to 70 wt-%.[30] It was demonstrated that at low temperature, the addition of dodecane (40–60 wt-%) did not alter the mesophase, while at higher temperatures and with similar dodecane concentrations, the viscosity is significantly reduced. Nevertheless, even under these conditions, a nematic columnar mesophase like the one of the pure compounds was observed. The addition of dodecane appears to increase the intercolumnar distance up to a point where the hexagonal order is lost, and under extreme conditions, the mesophase is eventually dissolved into the solvent.

The supramolecular structure of such di- and tri-substituted derivatives was studied by polarized optical microscopy (POM), differential scanning calorimetry (DSC) and X-ray diffraction (XRD) experiments.[31] In the columnar hexagonal arrangement, the $Ru_2(O_2CR)_4Cl$ polymeric chains are not linear,

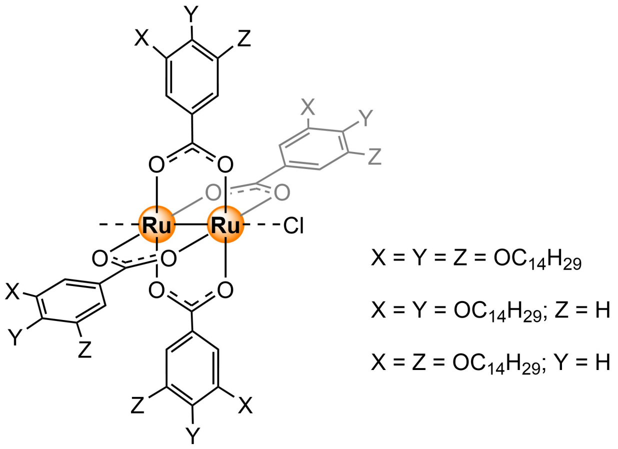


**Figure 8.** Molecular structure of lyotropic tri-substituted chlorodiruthenium(II,III) tetracarboxylates.[30]

the Ru···Cl···Ru angle is 117°, thus adopting instead a zig-zag conformation. Then, these non-linear polymeric chains, with the paddlewheel units acting as the flat central cores of discoid mesogens, are surrounded by poorly ordered interdigitated aliphatic chains, which overall explain the limited electronic communication observed in most systems.

The magnetic and liquid crystalline properties of analogous mixed-valent complexes bridged by cyanato anions have been recently studied.[32] The cyanato and chloro derivatives were compared, showing that the antiferromagnetic interactions between the dinuclear units was strong. X-ray powder diffraction (XRPD) suggest that the Ru-chloro-Ru angle is smaller than that of the Ru-cyanato-Ru angle, thus increasing the electronic communication between adjacent paddlewheel complexes.

As previously mentioned, the mixed-valent dinuclear paddlewheel complexes are air and water sensitive. The decomposition process was studied by Cukiernik in 1999 on carboxylate salts similar to those presented in *Scheme 1*.[33] The decomposition proceeds through a two-step mechanism, first forming at *ca.* 200 °C the homo-valent system (*Eqn. 1*): This first step involves the loss of the anion and a one electron reduction at the diruthenium unit. Then, at higher temperature (>275 °C), a full decomposition of the paddlewheel complex takes place, producing black materials (Ru), carbon dioxide and other unidentified organic products of small molecular weights {H, C, O} (*Eqn. 2*).

$$\begin{aligned}&[\mathrm{Ru_2(O_2CR)_4}](\mathrm{O_2CR}) \rightarrow \\ &[\mathrm{Ru_2(O_2CR)_4}] + \mathrm{CO_2} + \{\mathrm{H, C, O}\}\end{aligned} \qquad (1)$$

$$[\mathrm{Ru_2(O_2CR)_4}] \rightarrow 2\,\mathrm{Ru} + x\mathrm{C} + y\mathrm{CO_2} + \{\mathrm{H, C, O}\} \qquad (2)$$

Probably the prime reason for incorporating paddlewheel complexes to metallomesogens is to add electronic properties to mesogenic materials. However, so far, despite the polymeric nature of diruthenium paddlewheel complexes, poor or no electronic communication along the metallic chain has been observed. This drawback was finally overcome recently, by introducing rigid and linear tetrazine spacers between diruthenium(II,II) units (*Figure 9*).[34] An extruded fiber (5 mm) exhibited an electrical conductivity of 0.4 S·m$^{-1}$ with a resistance of 1.8·10$^{5}$ Ω, which suggest that such materials can be used as molecular wires.

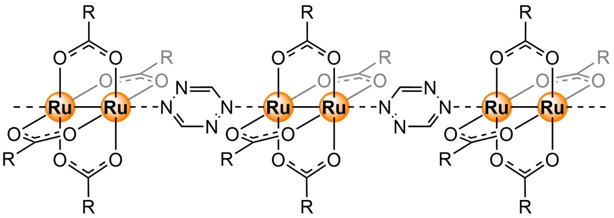


**Figure 9.** Molecular structure of polymeric tetrazine paddlewheel derivatives, R=Ph{O($C_nH_{2n+1}$)}$_3$ with $n$=2, 10.[34]

The chemistry of paddlewheel complexes is not limited to ruthenium, and therefore the same chemistry can be performed with all kinds of transition metals, thus offering unlimited possibilities to develop metallomesogens with paddlewheel structure. Unfortunately, the stability of the dinuclear ruthenium complexes appears to be limited, but as we will see, other ruthenium-based systems are highly stable and can be used as well to generate metallomesogens.

### 2.2. Polypyridyl Complexes

Ruthenium tris-bipyridyl complexes have been first used to prepare lyotropic metallomesogens. A micelle-like structure was obtained in water, the ruthenium complex playing the role of the polar head group. Interestingly, for complexes with two bipyridine (bipy) and an alkylated bipy (bipy-R) ligand (*Figure 10*), the nature of the counter anion was crucial on the liquid crystalline properties.[35] Indeed, when the hexafluorophosphate salts do not display any lyotropic mesomorphism, the chloro parent complexes show a cubic phase at room temperature, and for $n$=30, the longest alkyl chain, the liquid crystalline phase is stable from 0 to 100 °C in water.

Following a similar strategy, bis-terpyridine derivatives with one or two alkyl chains as hydrophobic tails (*Figure 11*) have been prepared and their lyotropic

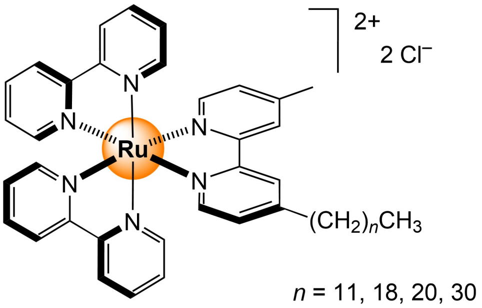


**Figure 10.** Molecular structure of the chloro salt of [Ru(bipy)$_2$(bipy-R)]$^{2+}$.[35]

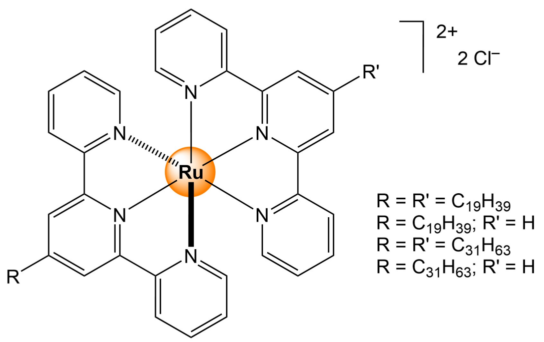


**Figure 11.** Molecular structure of bis-terpyridine complexes $[Ru(terpy\text{-}R)_2]^{2+}$ and $[Ru(terpy)(terpy\text{-}R)]^{2+}$.[36]

mesomorphism studied in water, as well as in ethylene glycol.[36] The difunctionalized derivatives do not show any lyotropic behavior, being insoluble and unable to form micelle-like structure in solution. However, the mono-functionalized $C_{19}H_{39}$ derivatives show cubic phases above 70 °C in water, while the one with the longest alkyl chain ($C_{31}H_{63}$) only shows a cubic phase in ethylene glycol (*ca.* 96 °C), but remains stable up to 150 °C.

Monosubstituted and disubstituted phenanthroline (phen-R) and bipyridyl (bipy-R) derivatives have been coupled to $Ru(phen)_2$ and $Ru(bipy)_2$ moiety to generate the cationic complexes $[Ru(phen)_2(phen\text{-}R)]^{2+}$ and $[Ru(bipy)_2(bipy\text{-}R)]^{2+}$, respectively. All complexes were isolated as their chloro salts (*Figure 12*).[37–44] Such complexes have been incorporated in mesoporous silica by true liquid crystal templating method.[37] Then, upon calcination, the ruthenium particles that have been loaded in the mesoporous materials act as heterogenous catalysts. Despite the position, number and length of the alkyl chains attached to the substituted ligand, the complexes show in water a hexagonal lyotropic mesophase, with variation in the transition temperature being linked to the nature of the ligands. Interestingly, the liquid crystalline structures of racemic mixtures of disubstituted complexes appear to be more closely packed than those of the corresponding enantiomerically pure (Δ, Λ) systems.[44]

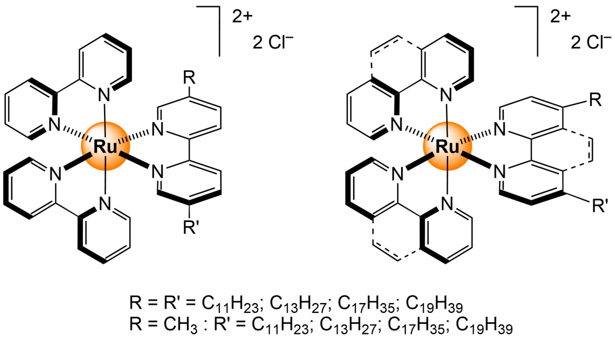


**Figure 12.** Molecular structures of monosubstituted and disubstituted systems.[37–44]

Polymeric systems in which $Ru(bipy)_2$ units were inserted on bipyridyl monomers have been synthesized (*Figure 13*).[45] The metal-containing polymers show lyotropic mesophase in a hexamethylphosphoramide (HMPA) 4 % LiCl solution. The mesophases are better observed at low ruthenium content (20–35 %), otherwise when the Ru-content exceeds 50 %, no liquid crystalline phases are observed. The ruthenium derivatives emit red light *ca.* 700 nm due to metal-ligand-charge-transfer processes, thus showing great potential for photosensitization, charge transport, and light-emitting applications.

In view to develop light-emitting electrochemical or photovoltaic cells, a series of phosphorescent ionic $[Ru(bipy)_2(bipy\text{-}R)]^{2+}$ complexes have been prepared (*Figure 14*).[46] The presence of two 3,4,5-trialkyloxybenzoyloxymethyl groups at the 4,4′ positions of a functionalized bipy-R ligand induces liquid crystalline properties at room temperature. Hexagonal columnar and columnar rectangular mesophases have been observed. The emission quantum yields of liquid crystalline films of these complexes remain excellent despite the functionalization, thus suggesting that

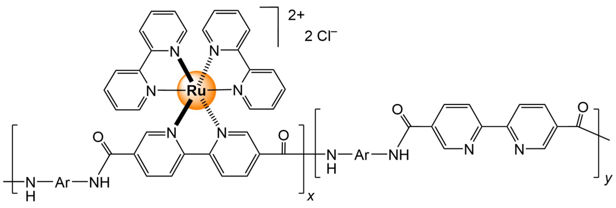


**Figure 13.** Molecular structure of polymeric tris-bipyridyl systems.[45]

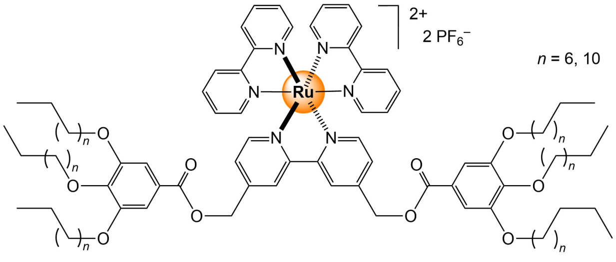


**Figure 14.** Molecular structure of tris-bipyridyl complexes.[46]

such materials can be exploited as photo-chemical devices.

As previously discussed, counter ions can play an important role on the liquid crystalline behavior of ionic metallomesogens. This has been nicely illustrated by a series of mixed $[Ru(bipy)_2(phen\text{-}R)]X_2$ salts ($X{=}PF_6^-$, $Cl^-$, $NTf_2^-$; $NTf_2^-$ = bis(trifluoromethylsulfonyl)imide) (*Figure 15*).[47] A smectic A phase was observed for all salts, the highest transition temperature being assigned to the chloro salts (*ca.* 200 °C) and the lowest to the $NTf_2^-$ salts (< 100 °C). Such a difference in the liquid crystalline properties is remarkable, and surprisingly, the luminescence of the cationic complexes was also controlled, to some extent, by the anions, showing a maximum shift from 630 nm for $[Ru(bipy)_2(phen\text{-}R)]NTf_2$ to 740 nm for $[Ru(bipy)_2(phen\text{-}R)]Cl_2$.

Ruthenium polypyridyl complexes have attracted a lot of attention in multiple fields, in particular because of their photochemical and photophysical characteristics. Therefore, one can expect more polypyridyl ruthenium-based metallomesogens in the future, especially in view to introduce luminescence or other photochemical processes to liquid crystalline materials.

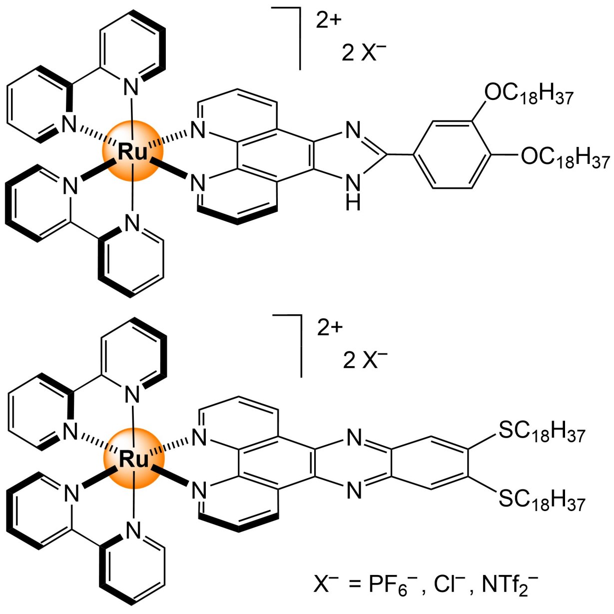


**Figure 15.** Molecular structure of mixed $[Ru(bipy)_2(phen\text{-}R)]X_2$ salts.[47]

### *2.3. Ruthenocene, Sandwich and Half-Sandwich Complexes*

Like ferrocene,[48] ruthenocene is an interesting platform for the preparation of metallomesogens. The functionalization of ruthenocene is relatively easy and several isomers of various symmetry can be synthesized and isolated in a pure form. In 1993, Deschenaux and Santiago have published the first and only ruthenocene metallomesogens with thermotropic liquid crystalline properties.[49] A series of 1,1′-functionalized ruthenocenes incorporating different alkyl chains at their periphery was synthesized from an esterification reaction between 1,1′-ruthenocene diacid chloride and the corresponding phenol derivatives (*Figure 16*). All derivatives showed a monotropic smectic A phase between 160 and 175 °C, with a narrow liquid crystalline domain (13 °C for $n = 14$), which slightly increases with the length of the alkyl chain.

A few years later, a sandwich-type complex with biphenyl rod-coil ligand was synthesized and characterized (*Figure 17*).[50] The liquid crystalline behaviors of the ligand alone and the arene ruthenium complex were compared. In both cases, a smectic B phase was observed, but the phase transition temperature of the ruthenium complex appeared 20 °C lowered than that of the organic ligand, thus to some extent, offering a possibility to adjust the transition temperature of phenyl-based organic mesogens by metal-complexation on aromatic rings.

More recently, 1,3,5- and 1,2,3-trisubstituted sandwich-type complexes were prepared in view to make liquid crystalline materials (*Figure 18*). Unfortunately, no liquid crystalline mesophase was observed for these multi-functionalized systems.[51] Similarly, a ser-

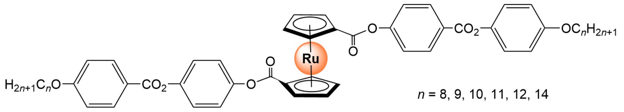


**Figure 16.** Ruthenocene derivatives.[49]

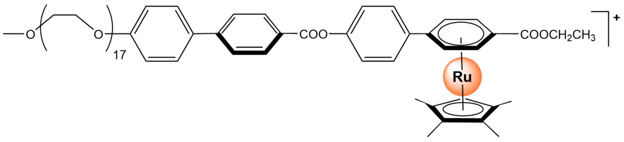


**Figure 17.** Molecular structure of the cationic sandwich-type metallomesogen.[50]

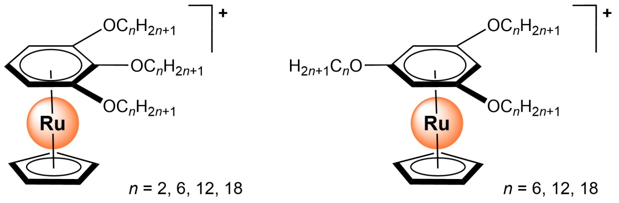


**Figure 18.** Molecular structure of the trisubstituted cationic sandwich-type complexes.[51]

ies of arene ruthenium complexes with functionalized arene ligands have showed no liquid crystalline behavior.[52] In both cases, these systems have showed in the solid state an arrangement reminiscent to liquid crystals, and therefore mesophases were expected for these arene ruthenium complexes.

Arene ruthenium complexes are popular building blocks in supramolecular chemistry.[53] Addition of 1,4-di(4-pyridinyl)benzene poly(arylester) derivative to the dinuclear arene-ruthenium complex [$Ru_2$(*p*-cymene)$_2$(donq)][DOS]$_2$ (donq = dihydroxynaphthoquinonato, DOS = dodecyl sulfate) has generated a tetranuclear metallacycle, which was isolated as its DOS salt (*Figure 19*).[54] The presence of four dendritic arms bearing cyano-biphenyl end-groups ensures mesomorphic properties above 50 °C. Both compounds, the bis-pyridyl linker and the arene ruthenium metallacycle, show a smectic phase with an intricate multilayered organization.

Ruthenocene, sandwich-type and arene ruthenium complexes are among the most studied ruthenium-based complexes, especially in catalysis and bio-organometallic chemistry. Therefore, this is quite surprising that only a few examples of liquid crystalline studies have been published so far. However, considering the high stability of most of these complexes and the synthetic facility to functionalize such complexes, more metallomesogens from these families should be expected in the upcoming years.

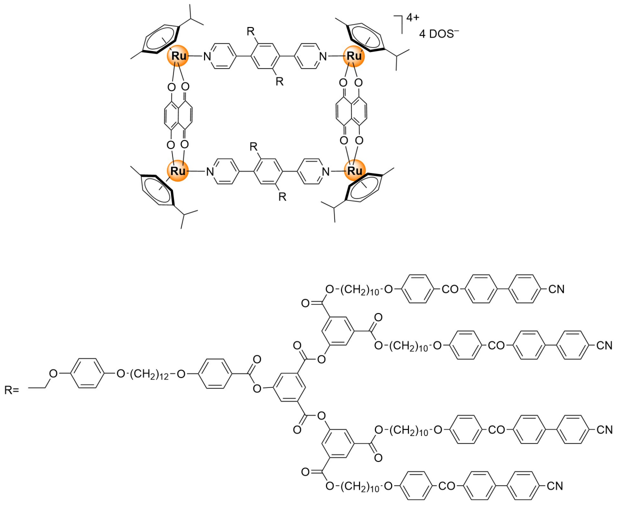


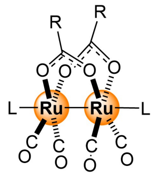
**Figure 19.** Molecular structure of liquid-crystalline metallacycle.[54]

### *2.4. Sawhorse Complexes*

Dinuclear Ru–Ru bonded complexes with four carbonyls, two carboxylates ($O_2CR$) and two axial ligands (L), of the general formula [$Ru_2(CO)_4(\mu\text{-}\eta^2\text{-}O_2CR)_2L_2$], are known for more than 50 years,[55] and they are often called sawhorse complexes. These complexes offer two possibilities to introduce mesomorphic properties through coordination chemistry, from the carboxylate bridges or the axial ligands. When introduced on the two carboxylates, an orthogonal orientation is obtained between the mesogenic groups, while positioning the mesogens on the two axial ligands gives a linear shape arrangement.

Using both coordination possibilities, a first series of eighteen stable sawhorse complexes were prepared with relatively small mesogenic groups (*Figure 20*).[56] The nature of the carboxylate derivatives was crucial for the thermal behavior of the dinuclear complexes. The presence of a phenyl group in both, the carboxylato and axial ligands, gives rise to $\pi-\pi$ interactions between neighboring complexes, thus facilitating intermolecular interactions and accordingly increasing the stability of the nematic liquid crystalline phase.

A second series, involving cyanobiphenyl-based poly(arylester) dendrons, was prepared ten years later.[57] Three generations of dendrons ($HO_2CR$, R′, R″, R‴) were coordinated to the sawhorse unit through the carboxylate ligands (*Figure 21*). All complexes show smectic A phase, while those with pyridine and 4-picoline axial ligands show smectic A and nematic phases. The more bulky triphenylphosphine axial ligand appears to force the lamellar structure to form



R = H, $CH_3$, $CF_3$, $C_6H_5$, $C_6H_4CH_3$, $C_6H_4OCH_3$, $C_6H_4OC_{10}H_{21}$, $C_6H_4CO_2C_6H_4OC_{10}H_{21}$, $C_6H_4CO_2C_6H_4O_2CC_6H_4OC_{10}H_{21}$

L = $NC_5H_5$, $NC_5H_4OC_{10}H_{21}$, $NC_5H_4CO_2C_6H_4OC_{10}H_{21}$

**Figure 20.** Sawhorse complexes with various carboxylates and axial ligands.[56]

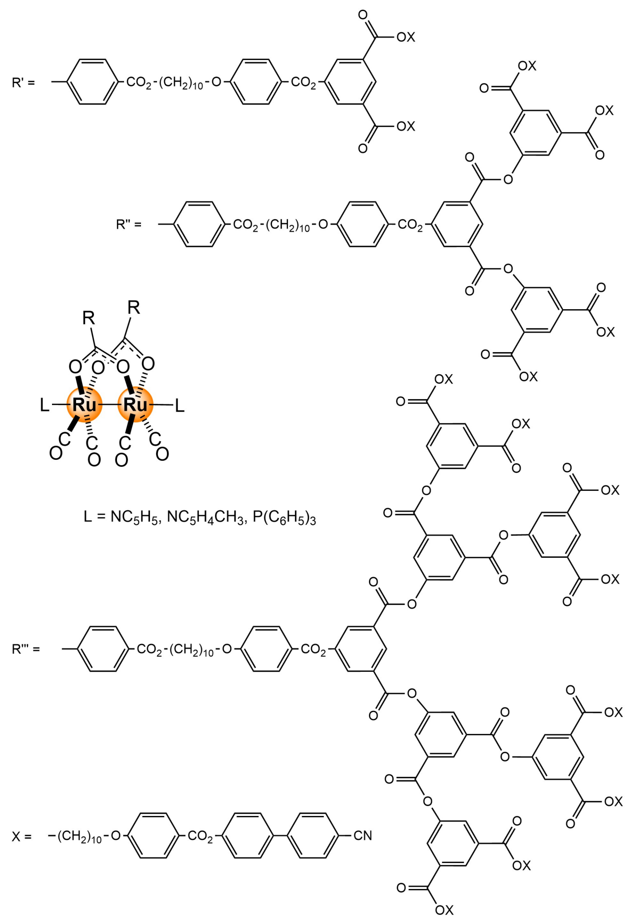


**Figure 21.** Sawhorse complexes containing cyanobiphenyl-based poly(arylester) dendrons of first (R′), second (R′′) and third (R′′′) generation.[57]

planes parallel to each other with limited interdigitation.

Like paddlewheel derivatives, sawhorse complexes are offering an ideal platform to develop metallomesogens.[58] Functionalization of carboxylate derivatives is synthetically easy, and having a second coordination site (axial ligands) increases the complexity of the systems without adding particular synthetic challenges. In addition, such systems are extremely stable in air, and can resist to high temperatures, thus being an ideal scaffold for the synthesis of mixed (axial, orthogonal) metallomesogens.

### *2.5. Other Ruthenium Complexes*

We have found only two other studies dealing with liquid crystalline materials including ruthenium-based moieties. The first one is an inorganic complex of the general formula $[Ru(CO)(PPh_3)_2(O_2CC_6H_4\text{-}p\text{-}O_2CC_6H_4\text{-}p\text{-}OBu)Cl]$.[59] According to the Authors, the neutral complex shows a smectic C phase transition at 225 °C, just before sublimation of the compound. However, the characterization of the mesophase is inconclusive, and it is unclear if the mesophase observed was due to the complex or only the carboxylato ligand after decomplexation. Nevertheless, this study proposed another strategy to synthesize metallomesogens from ruthenium-based complexes.

The second type of ruthenium complexes is not directly introduced in the mesogens. They were used to induce chirality in nematic phases by doping.[60] For example, the $\Lambda$ and $\Delta$ isomers of the $[Ru(acac)_2L]$ complex (L = dibenzoylmethanate ligand functionalized with octyloxy chains) was added to liquid crystalline MBBA (MBBA = *N*-(4-methoxybenzylidene)-4-*n*-butylaniline), to induce enantiotropic mesophases (*Figure 22*).[61] The best results were obtained with the complexes showing two octyloxy chains, having a helical twisting power of $+176\ \mu m^{-1}$ for the $\Lambda$ isomer and $-175\ \mu m^{-1}$ for the $\Delta$ isomer. To further modify the liquid crystalline property of MBBA and other organic mesogens, a similar $[Ru(acac)_2L]$ complex was synthesized, in which an azo group was inserted in the functionalized dibenzoylmethanate ligand. Upon light (400 nm), the azo group changes conformation, and accordingly the structure of the mesophase, while conserving the induced helicity.[62]

For similar purposes, mixed O∩O and N∩N complexes were synthesized (*Figure 23*).[63] The bis-acetylacetato bipyridyl ruthenium complex was also used as dopant for nematic liquid crystals. Like the tris-diketonato ruthenium complexes, a large helical twisting power was observed, confirming the versatility of these ruthenium complexes in the field of liquid crystalline materials.

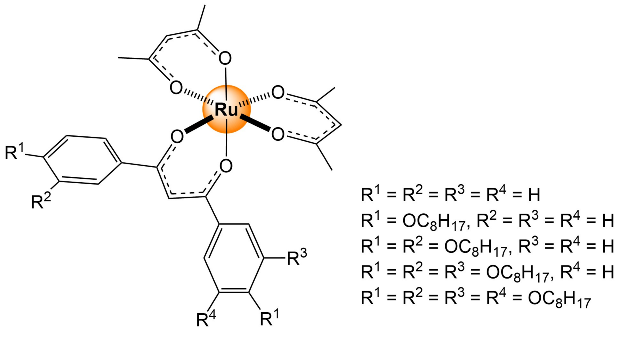


**Figure 22.** Molecular structures of chiral ($\Delta$, $\Lambda$) tris-diketonato-ruthenium complexes.[61]

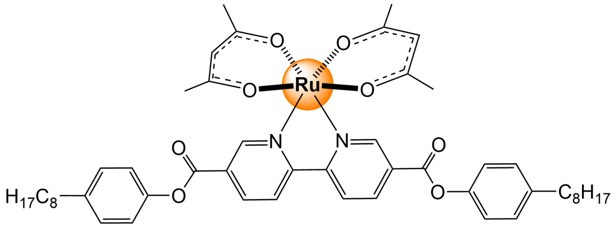


**Figure 23.** Molecular structure of a chiral (Δ, Λ) bis-diketonato bipyridine ruthenium complex.[63]

## 3. Conclusion

Ruthenium is at the forefront of several research projects and involved in many industrial processes. Known for nearly two centuries, ruthenium is relatively cheap compared to other platinum group metals (Os, Rh, Ir, Pd and Pt), thus providing a positive argument for developing new materials based on that metal.[9] Nevertheless, when looking at liquid crystalline materials, the use of metal-based units to generate mesogenic compounds remains scarce, as illustrated by the number of publications dealing with metallomesogens since 1988 (*Figure 24*).[7] And among these metallomesogen-based publications ($<1000$), only a fraction has been developed around ruthenium.

The limited number of studies dealing with ruthenium-based metallomesogens might be due to the fact that most ruthenium complexes adopt an octahedral geometry, thus complicating the design of metallomesogens. For rational design, controlling the orientation of the mesogens is crucial, and accordingly, linear and square-planar systems are certainly the most common geometries used so far for the development of metallomesogens.[1–3] Nevertheless, the higher coordination number of ruthenium is in my opinion an opportunity for those ready to take a challenge and for those looking for highly complexed mesogenic organizations. As illustrated in this review, different strategies can be used to control the position and orientation of the mesogenic groups. Moreover, most systems offer multiple coordination sites, thus adding structural diversity and tunability. Therefore, we can expect in the future not only a growth in metallomesogen research, but as well an increasing contribution to the field from ruthenium-based metallomesogens.

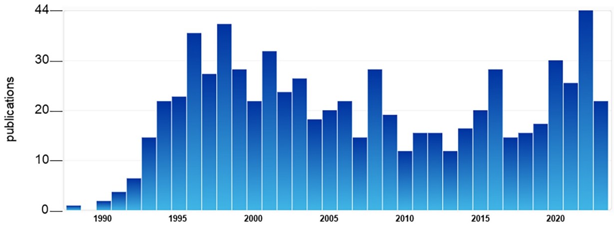


**Figure 24.** Publications per year on metallomesogens since 1988.[7]

## Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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